PHOTOCATALYTIC DEGRADATION OF CONGO RED Over 1wt% CuO-ZnO COMPOSITE CATALYST

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Abstract: **In this paper, the photocatalytic removal efficiency of this dye by a 1wt % CuO-ZnO nanocomposite was studied. The synthesized CuO-ZnO catalyst was characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-Visible spectroscopy.The degradation of Congo red was monitored using UV-Visible spectrophotometer. The XRD analysis of the catalyst revealed a hexagonal wurtzite structure. The effect of operating variables such as initial Congo red concentration, catalyst dosage and pH of the solution were studie.**

Keywords: **Photosynthetic, pH, Variable, Wurtzite, Degradation, Nano composite.**

1. INTRODUCTION

With increasing population and global industrialization, potential risks associated with contaminating potable water streams have increased tremendously. Different coloring industries discharge various kinds of organic dyes into the freshwater streams, consequently generating wastewaters. With the increasing demand of potable water, these organic coloring substances must be treated in order to make water safe to drink. Congo red (CR) is a sodium salt of benzidinediazo-bis1-naphthylamine-4-sulfonic acid.1 In this study, CR has been selected because of its anionic structure and severe environmental issues.

A large number of industries such as textiles, printing, dyeing, paper, and plastic produce CR effluents which can contaminate the freshwater supply. If metabolized, CR can turn into benzide, a well-known human carcinogen. The treatment of CR-contaminated wastewater may also be complicated because of the complex aromatic structure, which resists degradation. Several physical, chemical, and biological methods qualify for the treatment of colored waters. These methods include adsorption, reverse osmosis, coagulation, biological, and photochemical degradation of organic dyes in water.

Photocatalysis (photochemical degradation) is a low-cost treatment method that uses catalysts in order to accelerate degradation of organic dyes using sunlight. A class of photocatalysts called semiconductor photocatalysts have also been reported for effective degradation of organic compounds in water. Over the years, several semiconductor particles such as TiO_2 and ZnO_2 were reported for photocatalysis. However, these materials exhibited lower photocatalytic activity attributed to wide band gaps ($\sim$3.2 eV for TiO_2 under visible light). Many heterogeneous and hierarchical photocatalysts were reported previously for degradation of different dyes such as CR, methyl orange (MO), cyanide, rhodamine B (RhB), p-chlorophenol, norfloxacin, and phenol. As the UV and visible lights constitute and 43% of the solar light spectrum, respectively, developing new catalysts for visible light photocatalysis are of great interests. In semiconducting materials, bismuth ferrites, $BiFeO_3$ (called BFO hereafter), have shown promising results for photocatalysis using visible light irradiation attributed to their narrow band gap ($\sim$2.2 eV). The band gap in BFOs can be further improved by doping with other ions, which alternatively improves its photocatalytic activity under the visible light irradiation. (Abdullah *et al.,* 2019)

Approximately 15% of the total world manufacture of dyes is lost during the dyeing process and is released in the textile sewerages. The release of those coloured wastewaters in the ecosystem is a demonstrative source of non-aesthetic pollution, eutrophication and perturbations in the aquatic life. As international environmental standards are becoming more stringent (ISO 14001, October 1996), technological systems for the removal of organic pollutants, such as dyes have been recently expanded. Between them, physical methods, such as biological methods (biodegradation), adsorption, and chemical methods (chlorination, ozonation) are the most frequently used. Photocatalysis is considered as one of the important and efficient approaches to dismiss the dyes in wastewater. Different methods have been provided for the synthesis of nanoparticles such as chemical, physical and green methods. Lately, researchers focus on green chemistry methods to provide metal nanoparticles with favourable size and morphology and the results of this method are significant and important. In the last decade, preparing the nanocatalyst via photocatalytic capability by using green synthesis methods has been an idea for researchers. Plant extracts for the biological synthesis of nanoparticles have received more attention because it is inexpensive, simple, environmentally safe and non-toxic. Further, most of the plant extracts are fortified by the variety of biomolecules like alkaloids, phenols, terpenoids, flavonoids and so on. In this work, we report the synthesis of spinel $ZnMn_2O_4$ NPs via novel biological way and use the tragacanth gel to provide sol–gel. We have studied the photocatalytic activity of $ZnMn_2O_4$ using followed degradation of Congo red as the industrial dye in aqueous solution under visible irradiation. X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), diffuse reflectance spectroscopy (DRS) and field emission scanning electron microscopy (FESEM) are the techniques that we used for the characterisation of biosynthesised $ZnMn_2O_4$ (Saeid *et al.,* 2019)

The removal of organic pollutants from wastewater is a significant measure of environmental protection. Several types of hazardous dyes, extra marketable pigments, and bleaches have developed the attention of environmental remediation efforts (Zhu *et al.* 2009; Bilal *et al.* 2019; Rasheed *et al.* 2019A; Liu *et al.* 2019). Nowadays, the world is facing the main difficulties of environmental contamination. Organic chemicals are present in effluents from domestic and industrial sources. These pollutants must be destroyed or removed before these are discharged to the near aquatic resources. The discharging of a large amount of wastewater from textile, pharmaceutical, dying, cosmetic, food, printing, and photographic industries produces environmental pollution. These effluents are dangerous in nature because they normally contain considerable amount of different poisonous materials, which are not decomposable (Bilal *et al.* 2017; Bilal *et al.* 2018a; Bilal *et al.* 2018b; Ali *et al.* 2019). Dye constituents are one of the main categories of organic compounds, which may find many beneficial uses in everyday life. For example, leather, paper, plastic, and textile industries accumulate up to 80% of the total dyes. Synthetic dye materials with some other dyestuff are comprised of the main group of world water pollutants. In the end, about 1 to 15% of the synthetic fabric dyes used in different industries are disposed to the wastewater channels and in the last reached the main water streams (Bilal and Asgher 2015; Salazar-López *et al.* 2017). The dying process also produced effluent which contains more than 10–15% dyestuff. The serious problem is to decrease the harmfulness levels and to allowed limits of the effluents before releasing the dye to water channels (Bilal *et al.* 2017; Rasheed *et al.* 2019B; Rasheed *et al.* 2019C). Some traditional or conventional physicochemical methods are used for the handling and treatment of dying polluted wastewater, which comprises adsorption, coagulation, filtration, and advanced oxidation processes such as photochemical oxidation, ozonation, and Fenton's reagent (Bilal *et al.,* 2018a). Different degradation procedures can be used for wastewater treatment and clarification, like catalysis, adsorption, degradation, electrochemical degradation, biological degradation, sonocatalytic degradation, and photo catalytic degradation (Bilal *et al.* 2017; Salazar-López *et al.,* 2017; Bilal *et al.* 2017). Photocatalysis has emerged as a desirable technology for the treatment of wastewater and considered an efficient, eco-friendly, and cost-effective method to resolve problems of environmental pollution (Soylak *et al.* 2004; Bedoui *et al.* 2009; Samiey *et al.* 2014). The organic pollutants can be decreases using the technique of photo catalysis because it is one of the growing destructive technique and it is oxidation reduction reaction by using the energy of the photon, and in this process, electron gain energy and get excited and jump to the conduction band from valance shell, which as a result generate photo-generated hole (h+) and enhance catalytic performance (Bedoui *et al.* 2009; Casbeer *et al.* 2012; Iqbal *et al.* 2017).

1.1 DYES

Dye can generally be described as a coloured substance that has an affinity to the substrate to which it is being applied. The dye is usually used as an aqueous solution and may require a mordant to improve the fastness of the dyes on the fiber. Dyes are used for coloring a fabric. Dyes are molecules which absorb and reflect light at specific wavelength to give human eyes the sense of colour (del-Rio *et al.,2009*).

1.2 CLASSIFICATION OF DYES

There are two major types of dye, these are

a. Natural dyes

b. Synthetic dyes

a. Natural dyes: are obtained from animal, vegetable or animal origin with no or very little processing. The greatest source of dyes has been the plant kingdom notable roots, berries, bark leaves and wood, but only a few have ever been used on a commercial scale.

b. Synthetic dyes: the man-made organic dye marveling was discovered by will ion Henry parking in 1886. Many thousands of dyes have been prepared and because of vastly improved properties imparted upon the dyed material widely replaced the traditional natural dyes.

1.3 METHODS FOR TREATMENT OF DYE EFFLUENTS

Generally, the release of dye colors waste water from industrial influent into water bodies such as lakes, oceans, and rivers has created severe environmental problems, most of the coloured effluents are toxic and potentially carcinogenic hence considered as a threat for human survival.

Although various chemical and physical processes have been employed in the removal of colour effluents, however, this method do lead to complete destruction of the dye.

Moreover, further treatments are needed since the method employed just transfer the contaminant from one phase to another. This will indirectly enhance the operational cost. Some advantages and drawbacks on current technology for the removal pollutant in last decoded. Advance oxidation process (AOP) have been growing since there able to deal with the problem of dye destruction in aqueous system (Konstantinous and Albans, 2004) the generation of hydroxyl radical (OH) that oxidize various pollutant quickly and non-selectively have improve the degradation of organic compound compared to conventional method. Among advance oxidation process (AOP) semiconductor photocatalysis appear as the emerging destruction technology.

1.4   CONGO RED

Congo red (1-Napthalenesulfonic acid, 3,3-(4,4–Biphenylenebis (azo) bis 4–amino) disodium salt) is an organic compound that is water-soluble yielding a red colloidal solution, it's solubility greater in organic solvents. Congo red is an unsafe dyes which not only possess extremely toxic properties affecting the cells of mammals but also possesses the power to cause anaphylactic shocks in humans and is potentially carcinogenic (Rohan, 2015). It has a maximum wave length of 497nm and colour index is 22120.

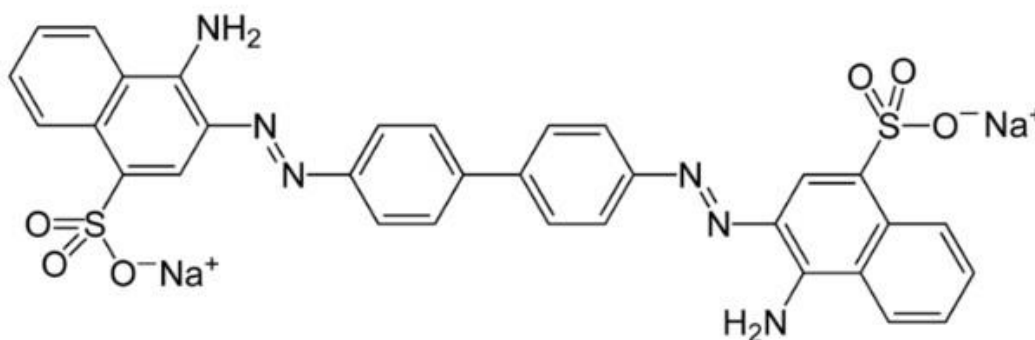### 1.4.1 STRUCTURE AND PROPERTIES OF CONGO RED

Fig 1 .1 Structure of Congo Red

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Some of the properties of Congo red dye include;

Molecular Formula: $C_{32}H_{22}N_6Na_2O_6S_2$

Molecular Weight: 696.7g/mol

Melting Point: >360ºC

Solubility: Soluble in ethanol and very slightly soluble in acetone and practically insoluble in ether.

Boiling Point: 100ºC

Density: 1g/L

1.5 PHOTOCATALYSIS

Photocatalysis is a type of catalyst that results in the modification of the rate of a photo reaction.Chemical reaction that involves the absorption of light by one or more reacting species,by adding substances (catalysis) that participate in the reaction without being involved (Garcia, 2003).

Photocatalytic reaction may occur homogenously or heterogeneously, but heterogeneous catalysis is by far more intensively studied in recent years because of its potential use in a variety of environmental and energy related application as well as in organic synthesis (Dimitris, 2010)

In catalyzed photolysis, the light is absorbed by an adsorbed substrate. While in photogenerated catalysis the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron-hole pairs, which generate free radicals (e.g Hydroxyl radicals; OH^- which is able to undergo secondary reactions. It is generally conceded that the semiconductor photo-catalysts can act as sensitizers for light induced redox processes, due to the electronic of this photo-catalyst that are characterized by filled valence band and an empty conduction band. Some of the most prominent semiconductors used in photo-catalysis include TiO_2, ZnO, CdS, Fe_2O_3. (Debjani, 2011).

1.5.1 TYPES OF PHOTOCATALYSIS

Homogenous photocatalysis

In homogenous photocatalysis, the reactants and the photocatalysis exist in the same phase, the most commonly used homogenous photocatalysis include ozone and photo fenton system (Fe and Fe/ H_2O_2)The reactive species is the OH which is used for various purposes. The photo-fenton reactions have been proven highly efficient than the other photocatalysts but the disadvantages of this process are the low pH values which are required, since iron precipitates at higher pH values and the fact that iron has to be removed after treatment (Wu *et al.,*2006).

Heterogeneous photocatalysis

The heterogeneous photocatalysts has the catalyst in a different phase from the reactants. Heterogeneous photocatalysis is a principle which requires a very large variety of reactions, mild or total oxidations dehydrogenation, hydrogen transfer and deuterium, alkane isotopic exchange, metal deposition water detoxification gaseous pollutant removal etc.(Wu *et al.,*2006).

1.5.2 MECHANISM OF PHOTOCATALYSIS

Photocatalytic reaction is initiated when a photo excited electron is promoted from the filled valance band of a semiconductor photocatalysts (Abou- Helal, *et al.* 2002) to the empty conduction band as the absorbed photon energy,hv equals or exceeds the band gap of the photocatalysts. The hole pair (e^- -h^+) is generated at the surface of the photo excited photo excited photocatalysts as shown below (Gaya, *et al.,* 2008)

Photo excitation: Sc$SC{\rightarrow}e^- + h^+$…………………………………………………………………1

Adsorbed oxygen: (O_2) ad + $e^- \rightarrow O_2$ ………………………………………………………..2

Ionization of water :$H_2O \rightarrow OH^- +H^+$ ……………………………………………………….3

Protonation of superoxides $O_2^- + H^+ \rightarrow HOO$ …………………………………………………4

$HOO + e^- \rightarrow HO_2^-$ ………………………………………………………………………….5

$HOO^- + H^+ \rightarrow H_2O_2$ ………………………………………………………………………….6

$H_2O_2 + e^- \rightarrow OH + OH^- + OH$ …………………………………………………………...7

$H_2O + h^+ \rightarrow H^+ + OH^-$ ………………………………………………………………………..8

The hydroxyl (OH) radical is a powerful oxidant for degrading non selective organic compound Glaze, 1987, *et al.,* 2001)

1.6 ZINC OXIDE SEMICONDUCTOR

Is an inorganic compound with the formula ZnO.ZnO is a white powder that is insoluble in water, and it is widely used as an additive in numerous materials and products including rubbers, plastics, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, foods, batteries, ferrites, fire retardants, and first-aid tapes (Modirshahla, 2006).

It occurs naturally as the mineral zincates, but most zinc oxide is produced synthetically.

ZnO has a molecular mass 81.38g/mol. Appearance while solid, colourless, density 5.606g/cm^3, melting point 1.975degrees C. Boiling point (3,587 degrees F, 2,248 degrees K) decomposes solubility in water 0.0004% (17.8 degrees C) band gap 3.3 ev (direct), Refractive index (no). The native doping of the semiconductor due to oxygen vacancies or zinc interstitials in n-type. This semiconductor has several favorableproperties including good transparency, high electron mobility, wide band-gap, and strong room temperature luminescence. Those properties are used in emerging applications for transparent electrodes in liquid crystal displays, in energy-saving or heat-protecting windows, and in electronics as thin-film transistors and light-emitting diodes (Modirshahla, 2006).

1.7 COPPER OXIDE SEMICONDUCTOR

Copper oxides are semiconductors that have been studied for several reasons such as the natural abundance of starting material copper (Cu); the easiness of production by Cu oxidation, their nontoxic nature and the reasonably good electrical and optical properties.

Copper forms two well-known oxides: tenorite (CuO) and cuprite (CuO). Both the tenorite and cuprite were p-type semiconductors having band gap energy of 1.21 to 1.51 eV and 2.10 to 2.60 eV respectively. As a p-type semiconductor, conduction arises from the presence of holes in the valence band (VB). CuO is attractive as a selective solar absorber since it has high solar absorbency and a low thermal emittance (Johan *et al.,* 2011).

The p-type semi-conductor of copper oxide (CuO) is an important functional material used for gas sensors, magnetic storage media, solar energy transformation, electronics, semi-conductors, resistors, and catalysis. It has therefore been studied together with other copper oxides, especially with respect to its applications as a photo-thermally active and photoconductive compound. Thus, great efforts have been made to study the preparation of nano sized CuO in the past two decades. Conventional methods for the preparation of CuO powder include one-step solid-state reaction at room temperature, thermal decomposition of copper salts and mechanical milling of commercial powders. It is well known that the unique functions of semiconductors nano-particles have led to the development of novel photovoltaic and light emitting devices. Thus, there is a renewed interest in understanding the fundamental physical properties of CuO, as well as for upgrading its performance in applications (Vidayasagar*et al*., 2011).

CuO is a semiconducting compound with a narrow band gap and used for photoconductive and photo-thermal applications. However, up till now, the reports on the preparation and characterization of nano-crystalline CuO are relatively few compared to some other transition metal oxides such as zinc oxide, titanium oxide, tin oxide and iron oxide (Wang *et al*., 2002).

1.8 AIM AND OBJECTIVE OF THE SUDY

As a student of Physical Chemistry, my aim is to study the photocatalytic removal of Congo red using composite CuO-ZnO catalyst.

Some of the objectives for this research work are listed below:

1. To synthesize CuO-ZnO composite catalyst for the removal of Congo red.

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2. To characterize the synthesized CuO-ZnO catalyst using X-Ray Diffractormeter (XRD) and Scanning Electron Microscope (SEM).

3. To investigate the photocatalytic degradation of Congo red.

1.9 LITERATURE REVIEW

The synthesized nanoparticles were absorbed by UV light, electrons were stimulated from the valence band to the conduction band. The light energy caused holes and reacted with water and hydroxyl radical was created. The hydroxyl radical was forceful, non-selective oxidant and oxidizing agent thereby resulting in the degradation of dyes.The light energy on reaction with electrons and in turn with molecular oxygen resulting in the generation of superoxide radical anions, which was responsible for the degradation of dye solution.Photodegradation efficiency of nano materials was calculated using the formula,

$$D (\%) = (A0 - At) / (A0) \times 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots. (3)$$

Where, D is the degradation efficiency (in %). A0 is the UV absorption of dye with sunlight irradiation time (0 min) and at is the UV absorption of dye after UV-light irradiation (t-min). Figure-8 (i) and (ii) shows the photodegradation efficiency of Undoped ZnO and Mg, Ti-doped ZnOnanocomposites with UV irradiation in various time stretch (30, 60, 90, 120, 150 and 180 mins). The photodegradation efficiency values calculated were 55% for UndopedZnO and 91.5% for Mg and Ti codoped ZnO nanoparticles. The results of Photodegradation analysis of congo red dye with Undoped and doped ZnOphotocatalyst clearly presented a higher dye removal efficiency of the Mg and Ti codoped ZnO nanoparticles. Therefore, the experimental results concluded that the Mg and Ti codoped ZnO nanoparticles were a respectable dye removal catalyst comparing UndopedZnO nanoparticles. This route could be suitable for sewage and industrial water treatment. (Arul and Senthilnathan, 2019).

The influence of initial concentration of the dye solution on the photocatalytic degradation is a significant aspect of the study. The initial concentrations of Congo red were selected in the range of 5-30 ppm and it was revealed that the percentage of photodegradation decreased as initial concentration of the dye solution increased.One possible explanation of such circumatances is that as initial concentration increases, more and more organicsubstances are adsorbed on the surface of ZnO; therefore, the generation of hydroxyl radicals is reduced, since there are only fewer active sites in the system causing little adsorption of hydroxyl ions, which in turn leads to the decrease in the generation of hydroxyl radicals. Further, as the concentration of a dye solution increases, the photons get intercepted before they could reach the catalyst surface, hence the absorption of photons by the catalyst decreases, and consequently, the degradation percentage is reduced. (Movahedi*et al.,* 2008).

The effect of initial pH on the degradation efficiency of ZnO catalyst on photodecomposition of both dyes, experiments were carried out at various pH, ranging from 2 to10, except for CR, where tests were done from 6 to 10 for avoiding dye aggregation. The results showed that the pH significantly affected the degradation efficiency for both dyes.Photocatalytic activity of anionic dyes (mainly sulfonated groups) such as CR and BP$_4$B reaches a maximum value in lower pH zpc (i.e. pH =8). At alkaline mediums, excess of hydroxyl anions facilitate photogeneration of •OH radicals which is accepted as primary oxidizing species responsible for photocatalytic degradation, resulting in enhancement of the efficiency of the process. Furthermore we found that, where the adsorption of dyes was weak, degradation scarcely occurred. The adsorption affects strongly the accessibility of the surface reducing species to the CR and BP$_4$B reduction kinetics. However, adsorption is not the only factor that controls the photocatalytic degradation of dyes. Although the adsorption extents of both dyes were lower, the degradation rates were in the reverse order. The drastic decrease in the degradation activity with dyes concentration is ascribed to the increase in the local concentration of CR as well as BP$_4$B on the ZnO surface, while the UV light irradiation time and photocatalyst amount are kept constant, leading to the formation of dimer and higher order aggregates owing to hydrophobic interactions between aromatic rings and hence the rate formation of hydroxylic and superoxide anion radicals are dramatically reduced thereby decreasing rate of degradation. The maximum concentration of both dyes that could be degraded by 0.5 and 1g/L of ZnO for CR and BP$_4$B respectively is found to be 20mg/L. Similar trend was observed in the photocatalytic degradation of Reactive Black 5 and Reactive Orange 4 dyes using ZnO and TiO$_2$ as photocatalysts.(Elaziouti*et al.,*2011).

The codoped nanohybrids were tested for their photocatalytic dye degradation application. The apparatus detailed as Hitachi (UV-3310) UV−vis spectrophotometer is used to test the photocatalytic property of the nanohybrids. An amount of 100 mg of nanohybrids was used to be tested in the prepared solution of 100 mL of CR so that the concentration of the dye solution is taken as 100 mg L−1 and the solution is put into stirring in dark condition for about 120 min. As to ignore the thermal degradation activity, the solution is put in the ice bath under constant stirring. Visible light is taken from the xenon lamp (300 W), a 5W light-emitting diode was used for UV (ultraviolet) source. Every 30 min, an amount of 3 mL of the solution is taken out from the main solution during the complete process; the taken amount was centrifuged at 7000 rpm to get the supernatant. The supernatant is then used to check the concentration of CR using the Hitachi UV-3310 UV−vis spectroscope, and the curve is measured at a specific wavelength of 496 nm. (Abdullah *et al.,* 2019).

Characterisation of $ZnMn_2O_4$ nanoparticles: FTIR spectra were registered in solid phase using the KBr pellet technique in the range of 400–4000 cm−1 . This technique was exploited to stabilise the formation of metal–metal (M–M) bonds and metal–oxygen (M–O) in the spinel structure of the sample. FTIR absorption spectra of $ZnMn_2O_4$ NPs calcined at 600°C for 4 h. The FTIR spectrum analysis demonstrates two ranges of the absorption bands: in the range of 400–1000 cm−1 , two absorption bands for the spinel structure of the $ZnMn_2O_4$ v1 at 621 cm−1 and v2 at 507 cm−1 were observed. The band, v1, suggests the stretching vibrations of the metal (Mn ↔ O) and the v2 is attributed to stretching vibrations of the metal (Zn ↔ O) Zhang *et al.,* 2011). These are the first evidence of $ZnMn_2O_4$ formation. The phase and structural determination of the spinel $ZnMn_2O_4$ nanoparticles was confirmed by XRD technique. The XRD pattern of the $ZnMn_2O_4$ nanoparticles is shown, the diffraction peaks at 2θ of 18.31°, 29.45°, 31.27°, 33.02°, 36.44°, 38.96°, 44.81°, 50.90°, 52.12°, 54.66°, 56.85°, 59.08°, 60.88°, 65.36°, 71.17°, 75.15° and 77.57° are corresponded to (101), (112), (200), (103), (211), (004), (220), (204), (105), (312), (303), (321), (224), (400), (305), (413) and (422) planes of the tetragonal spinel ZnMn2O4 NPs, respectively. All the diffraction peaks were readily indexed to a pure phase tetragonal spinel structure (JCPDS Card No. 77-0470). No diffraction peaks of other impurities were detected. The average crystallite size of ZnMn2O4 nanoparticles was distinguished from the full width at half maximum (FWHM) of the (211) diffraction peak using the Scherrer formula. (Taghavi *et al.*, 2018)

2. MATERIALS AND METHODS

In this study, the dye usedwas (Congo Red) and the catalyst was a composite catalyst CuO-ZnO.

2.1 APPARATUS

Magnetic stirrer,

100watt Bulb

Mortar and Pestle,

Weighing balance,

Magnetic Stirrer bar,

Muffle furnace.

2.2 REAGENTS

All the reagents listed below were of analytical grade and were used without further purification.

Copper Nitrate $Cu(NO_3)_2$

Sodium hydroxide NaOH

Congo red Dye

Zinc oxide ZnO

Sulfuric Acid H_2SO_4

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2.3 METHODS

2.3.1 CATALYST SYNTHESIS

The catalyst CuO-ZnO was synthesized by a wet impregnation method. A suspension of 0.99mol ZnO (80.57g) in 100ml of water containing $0.01molCu(NO_3)_2$ (1.876g) allowed to stand for 24hrs. The remaining water content was evaporated in an oven overnight at 110°C. The dried solid were ground in an agate mortar and calcined at 400°C for 6h in a muffle furnace.

2.3.2 PREPARATION OF STOCK SOLUTION

0.1g of Congo red was dissolved in $30cm^3$ of distilled water in a 100ml of volumetric flask and then made to the mark with distilled water. To determine the maximum absorbance of the dye, it was measured using UV spectrophotometry and was found to be 497nm another standard solution was prepared from the stock solution using the dilution formula, and a solution of 7ppm, 12ppm, 17ppm, 22ppm and 32ppm) were prepared and was taken for absorbance by validated UV-spectrometer. However; 7ppm was found to have the highest absorbance and was used for the photoexperiments.

2.3.3 DETERMINATION OF WAVELENGTH AT MAXIMUM ABSORPTION AND CALIBERATION CURVE FOR CONGO RED.

The Congo red concentrations were determined spectrophotometically at maximum absorption wavelength (497nm) which shows an intense peak in the visible region of 497nm wavelength which corresponds to the maximum absorption peak of Congo Red. A calibration curve for quantitative analysis was obtained at the Congo red concentration range of 7ppm, 12ppm, 17ppm, 22ppm, 32ppm and the correlation coefficient was determined to be 0.9929 and the calculated factor(slope) was found to be 0.0327.

2.3.4 PHOTOEXPERIMENTS

The batch experiments were carried out and studies was done on three factors. The three operating factors were the effect of pH, effect of catalyst dosage and effect of initial concentration.

Photocatalysis was carried out in a batch reactor equipped with a lamp of 100watts positioned perpendicularly above the beaker, whose distance from the lamp was about 10cm.

2.3.5 EFFECT OF pH

CuO-ZnOphotocatalyst sample was weighed (0.6g) separately and were added to five samples of dye keeping all the parameters constant only the pH varied, either by addition of H_2SO_4 to make it acidic or by addition of NaOH to make it basic, the pH of 3,5,7 ,11 and 13 were used in the experiment to study the effect of pH.

2.3.6 EFFECT OF CATALYST DOSAGE

On the effect of catalyst loading, all other parameters were kept constant only the catalyst varies in dose from 0.2g to 1g and was then placed under same UV light for 30mins. The resulting solution was taken for absorbance to determine the effect of catalyst dosage on the degradation of Congo red dye.

2.3.7 EFFECT OF INITIAL CONCENTRATION

Different concentration of the dye was prepared from 7ppm to 32ppm and the same quantity of the CuO-ZnO photocatalyst was weighed (0.5g) and was added to the separate dye concentrations, each of the mixture of the dye and catalyst was placed on a magnetic stirrer, under UV light and each of the concentrations were stirred continuously for thirty minutes and the absorbance was dertermined.

3. RESULT AND DISCUSSION

3.1 THE X-RAY POWDER DIFFRACTION

Powder X-ray diffraction, which is the most useful techniques for phase identification, was employed to investigate the crystallinity and structure of the prepared samples. The XRD patterns of CuO-ZnO nanoparticles are shown in the figure below. It is clear, without any observable peaks of impurity phases.The diffraction angle 47.8°is characteristics of CuO. The extreme sharpness of the diffraction peaks in Fig. 3.1 are evidences of high crystallinity of the nanocomposite particles.
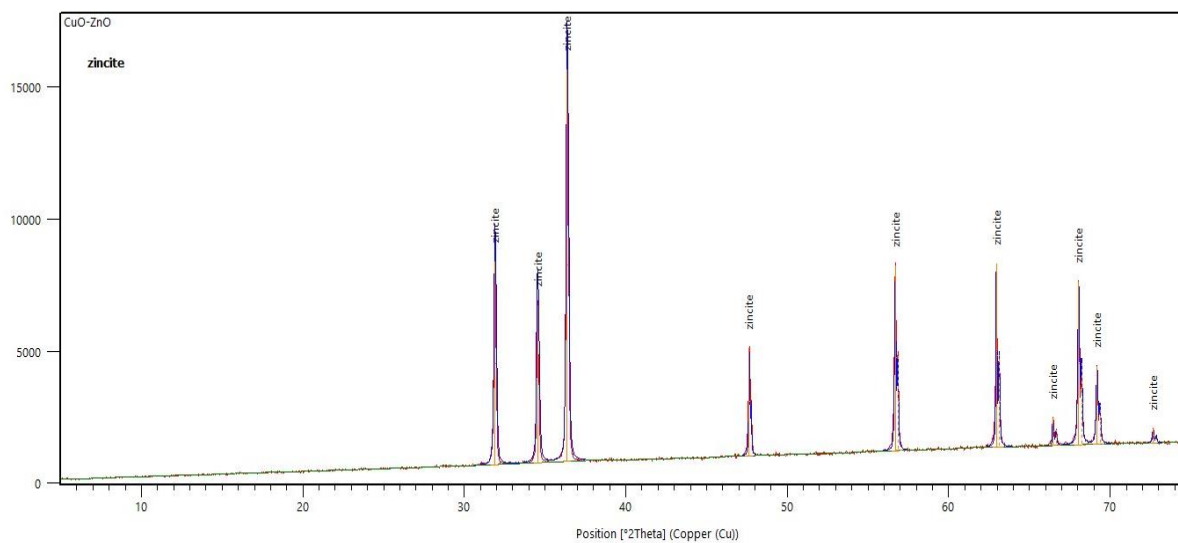
Fig. 3.1: XRD patterns of the synthesized 1wt% CuO/ZnO catalyst.

3.2 SCANNING ELECTRON MICROSCOPE (SEM)

The surface morphology of the CuO doped ZnO catalyst was examine using scanning electron microscope with CuO, at accelerating voltage of 15 KV and scale of 200micrometer. The image is shown in the figure below.

Fig. 3.2 SCANNING ELECTRON MICROSCOPE (SEM) IMAGE OF CuO/ZnO

3.3 EFFECT OF INITIAL CONCENTRATION

The effect of initial dye concentration of Congo Red dye on the photocatalytic degradation was studied by varying the Congo red dye concentration from (7ppm to 32ppm) and 0.5g CuO-ZnO was added to each. This shows that percentage degradation of Congo red decreases with increase in concentration, it was observed from the graph that, at 32ppm the percentage degradation of Congo red decreases. Initial concentration of the dye increase the colour of the dye solution which becomes deeper and results in the reduction of penetration of light to the surface of the catalyst decreasing the number of excited dye molecules.
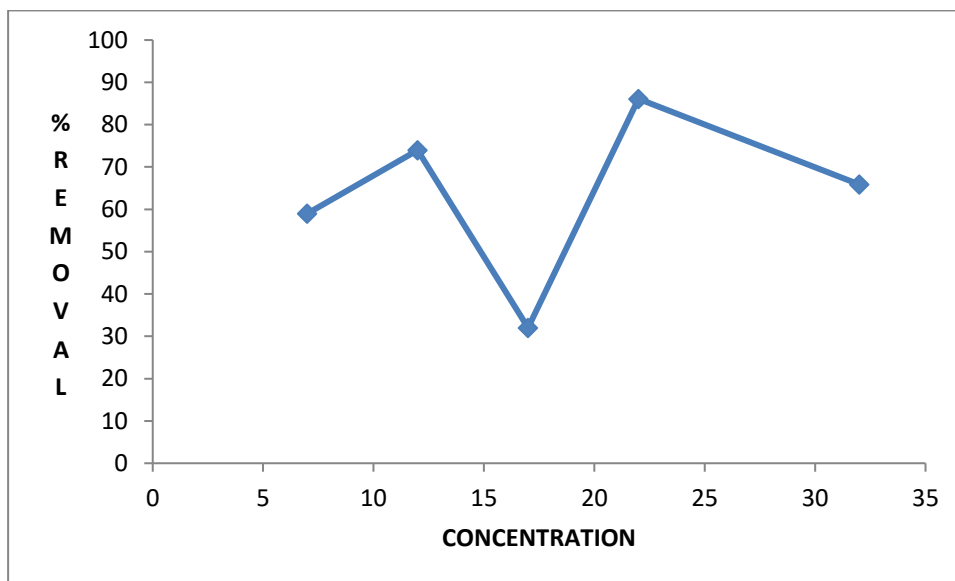

Fig. 3.3: Effect of Concentration on photocatalytic Degradation of CR

3.4 EFFECT OF CATALYST DOSAGE

A series of experiment were carried out by varying the amount of CuO-ZnO catalyst from 0.2g to 1.0g, while keeping all other operating factors constant to establish the effect of the photocatalysts dosage and to avoid unnecessary excess of the photocatalyst, and can be noticed from the graph that at 0.8 there was no further increase in degradation with additional quatity of the catalyst due to the kinetic factors like surface area of catalyst exposed to UV light, and temperature. If the catalyst surface exposed for excitation to UV light is limited, then the hydroxyl radical generated will be limited, which as well affect the percentage degradation.
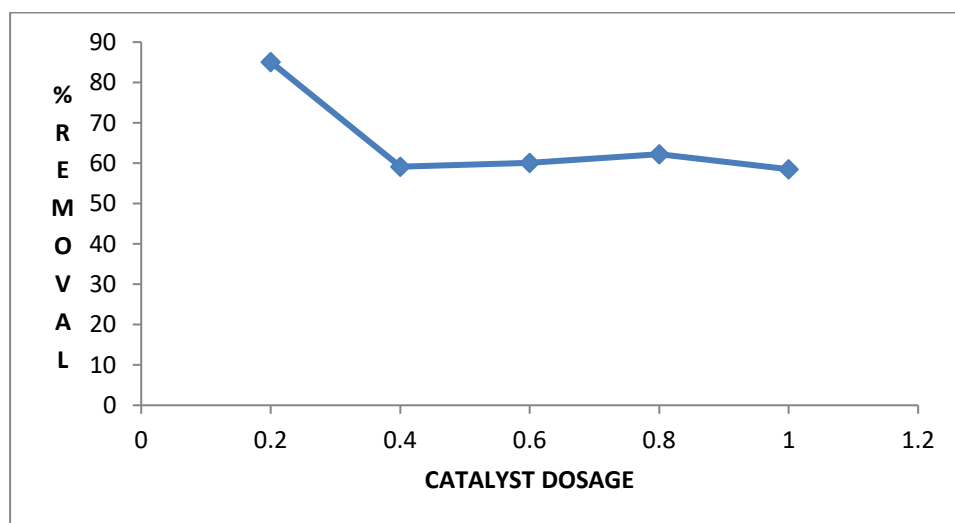

Figure 3.4: Effect of catalyst dosage on photocatalytic degradation of CR

3.5 EFFECT OF pH

The importance of studying the effect of pH in the photodegradation of Congo Red dye is that, the change of CuO-ZnO surface and Congo Red dye vary with shift in pH primarily, ZnO in CuO-ZnO will be hydroxylated in the presence of water to form hydroxide layers (Zn-OH) the zinc hydroxide surface can be can be charged by reacting H^+ (acidic environment) or OH^- (basic environment) ions due to the surface amphoteric reactions.

$Zn-OH + H^+ \rightarrow Zn-OH_2^+$ (acidic environment).

$Zn-OH + OH^- \rightarrow ZnO^- + H_2O$ (basic medium).
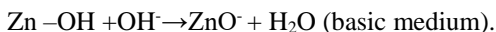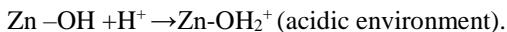
The amount of Congo redphotodegraded gradually decreased with increasing pH, decreasing photodegradation percentage is due to decline of the electrostatic repulsive forces and increased interaction between photocatalyst surface and Congo red because of increasing pH.
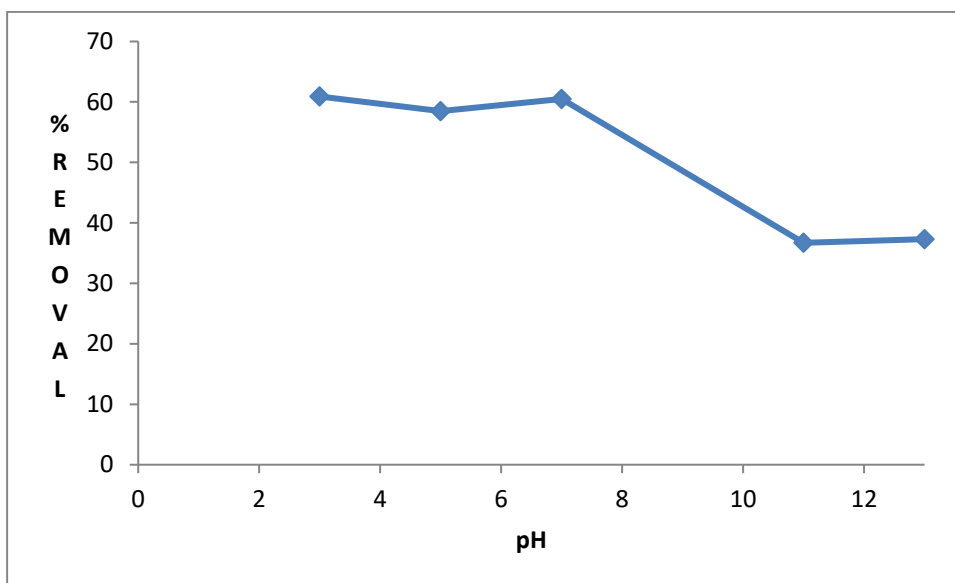

Figure 3.5: Effect of pH on the photocatalytic degradation of CR

3.6 KINETICS OF PHOTOCATALYTIC DEGRADATION OF CONGO RED

The initial concentration influence of compounds in thephotocatalytic degradation rate of most organic compounds isalso described by pseudo-first-order kinetics.Photodegradation rates of chemical compounds onsemiconductor surfaces follow the Langmuir-HinshelWood model(Movahedi*et al.*, 2009)

$R = dC/dt = kr\theta = kr\ KC/\ (1 + KC)$…………………………………………………………….. (1)

Where Kr is the reaction rate constant, K is the adsorptioncoefficient of the reaction, and C is the reactant concentration. The values of Kr and K are used to explain the coefficientsdefining the rate determining reaction events, and pre-equilibriumadsorption within an adsorbed monolayer at theoxide surface and the aqueous solution interface, respectively.The effect of light intensity is also incorporated in Kr, and Kespecially expresses the equilibrium constant for fastadsorption-desorption processes between surface monolayerand bulk solution. (Movahedi*et al.*, 2009).

Integration of (Eq. 1) yields thefollowing (Eq. 2):

$\ln(Co/C) + K'\ (Co - C) = KrKt$………………………………………………………………….. (2)

When the initial concentration Co is small, (Eq. 2) changes into (Eq. 3), which expresses a pseudo-first order reactionkinetic regime.

$\ln(C0/C) = KrKt = Kt$………………………………………………………………………. (3)

Which yields half-life t½ (in min) that is t½ = 0.693/k, where K is the pseudo-first-order reaction rate constant, K = Kr K inmin-1. (Movahedi*et al.*, 2009).

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Pseudo First Order Kinetics

Pseudo first order kinetic model (Lagergren, 1898) has been most widely used to describe the kinetic process of ligand solid phase adsorption, i.e for the adsorption of an adsorbate from an aqueous solution, the linear form of the model is $Log(qe - qt) = \log qe \frac{K1}{2.303} t$

Where qe is the amount of catalyst adsorbed at equilibrium per unit mass (mg/g), qt is the amount of catalyst absorbed at time t per unit mass (mg/g). The rate constant of pseudo first order adsorption model ($mg.g^{-1}$, min^{-1}). K_1 can be evaluated from the graph of log (qe-qt) versus t such plot will give a straight line for the pseudo first –order adsorption with (log qe) as intercept and ($-k_1/2.303$) as the slope of the graph.

Pseudo Second Order Kinetics

The adsorption kinetics can also be described by pseudo second order model. The linear form of this model is given by this equation;

$$\frac{1}{qt} = \frac{1}{k2qe2} + \frac{1}{qe}t$$

Where K_2 is the rate constant of pseudo second order adsorption. If experimental data fits this model, a linear relationship is produced when plotting t/q_t against t, from which K_2 and qe can be determined from the slope and intercept from the graph. The calculated correlation coefficient (R^2) is also close to unity for pseudo second order kinetics models than the other tested kinetics model Where k_2 is the rate constant of pseudo second order adsorption.

The Langmuir-Hinshelwood rate expression has been used to describe the relationship between the heterogeneous photocatalytic degradation rate and the initial pollutant concentration. Basically, the rate of removal of CR may be given by equation (Eq. 4).

$r = -d [CR]/dt = K_rK_e[CR]/ 1+ K_e[CR]$……………………………………………………... (4)

Where K_r is the reaction rate constant (mg/L.min) and K_e is the adsorption coefficient of the CR onto the photocatalyst particle (L/mg). At low CR concentration, the rate of photo-reaction can be simplified to an apparent first-order equation (Eq. 5),

$r = -d [CR]/dt= K_rK_e [CR]$………………………………………………………………….. (5)

Let $K_{app}=K_rK_e$, so that Eq. 5 yields the differential rate of CR degradation (Eq. 6).

$r = -d[CR]/dt= K_{app}[CR]$……………………………………………………………………. (6)

Where the K_{app} is the apparent pseudo-first-order constant Eq. 7 is an integrated version of Eq. 6.

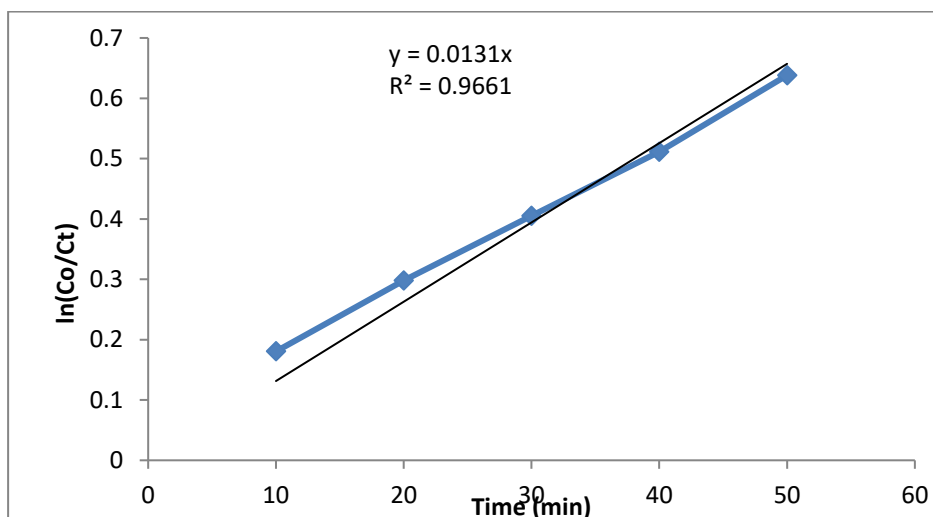$\ln(C_o/C_t) = K_{app}t$………………………………………………………………………….. (7)

Fig. 3.6 Langmuir-Hinshelwood plot of CR degradation in 1wt% CuO-ZnO.

Experimental results at optimum conditions (Fig. 3.6) indicated a reasonable agreement of the photodegradation rate of CR in presence of UV/1% CuO-ZnO (R^2 = 0.966) with the linear form of the Langmuir-Hinshelwood (L-H) kinetics. The K_{app} realized (0.013 min-1).(Gaya *et al.* 2019).,

4. CONCLUSION

The photocatalytic degradation of Congo Red dye was carried out under UV-light irradiation, photoexperiments were carried out based on different variables. Some of the parameters studied include catalysts dosage, effect of pH, and effect of dye concentration. Result shows that at high pH, the percentage removal of Congo red decreases, catalyst dosage 0.8g indicates the high percentage degradation of Congo red. This study indicates the potential of CuO-ZnO composite catalyst to remove aqueous Congo red dye under UV light.Kinetic study shows that the degradation process follows the pseudo first order kinetics. And the results demonstrates that CuO-ZnO catalyst could be a very effective for the removal of dyes from aqueous solutions.

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