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Synthesis and Characterization of semiconductor nano metal oxide photo catalyst: Photo degradation studies on hydroquinone under UV slurry photo reactor

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Abstract—**The effluents from pharmaceutical and cosmetic industries serves as a serious source of pollutant in the water bodies. Phenolic compounds like hydroquinone are most widely used in the preparation of skin creams, sunscreen lotions etc. These toxic effluents can cause adverse effects to the environment and human health. Advanced oxidation processes are used for the complete destruction of organic contaminants in water. Extensive research has been carried out for the removal of contaminants from the water streams by semiconductor metal oxide photo catalysis employing UV light irradiation. The semiconductor of interest must posses a suitable band gap of around 3.0 - 3.2 eV. In recent trend many researchers have reported many metal oxides in the form of film nanostructure, nanorods, nanofibers, and particulate coatings for oxidation of organic effluents. In this study we report the photo catalytic degradation of a phenolic compound using nano crystalline metal oxide photo catalyst under UV irradiation. Nano crystalline metal oxide photo catalyst was prepared by a modified sol-gel method employing the respective acetates as precursors and characterized by FT-IR, XRD, UV-DRS, FESEM and EDAX analysis. The results proved that the prepared photo catalyst were highly crystalline, nanosized and possesses absorption in the UV region. The UV-DRS results suggested that the band gap was 3.1 eV for the prepared photo catalyst. The photodegradation efficiency of hydroquinone was analyzed by the prepared photo catalyst employing various experimental parameters namely pH, catalyst dosage, variation of concentration and effect of electrolyte addition on the degradation of the phenolic compound. Neutral pH was found to be optimum for the effective degradation of the phenolic compound. A catalyst dosage of 70mg/10ml resulted in higher percentage of degradation and the addition of sodium bicarbonate electrolyte showed a maximum interference in the photo degradation process. The photo degradation process followed a pseudo first order kinetics and was continuously monitored by UV-Visible absorbance measurement and COD. The degradation of hydroquinone was above 90% under UV light irradiation employing Nano crystalline metal oxide as photo catalyst.**

Keywords-Semiconductor, Metal oxide, Nanoparticle, Hydroquinone, UV irradiation.

I. INTRODUCTION

Phenol and its derivatives are a major component of industrial waste that are highly toxic and recalcitrant in nature. These compounds, present in wastewater from various industry outlets, may result in extensive contamination of the aquatic ecosystem due to their hazardous and carcinogenic properties [1]. Toxic effluents can cause adverse effects to the environment as well as to the human health. Traditional methods such as solvent extraction, activated carbon adsorption, and common chemical oxidation often suffer from serious limitations and disadvantages [2,3]. Advanced oxidation process which employs photo catalysis, is an extensively researched area for the removal of contaminants from the water stream. Photo catalytic process makes use of large band gap semiconductors as a UV light activated photo catalyst for the removal of organic contaminants from the various media. In recent years, TiO2, ZnO, WO3 have been employed as UV active semiconductor photocatalysts. This has emerged as a promising route for the degradation of persistent organic pollutants, which result in by-products of lower toxicity. [4,5]. Metal oxide is a well known n-type semiconductor with a wide band gap of 3.3eV, high activity, low cost and environmentally friendly nature [6–9]. Metal oxide offers great potential as an industrial technology for detoxification or remediation of waste water due to several factors. (i) The process occurs under ambitent conditions very slowly;direct UV light exposure increase the rate of reaction. (ii) The formation of photocyclized intermediate products,unlike direct photolysis techniques,is avoided. (iii) Oxidation of the substrate to CO2 is complete.(iv) The photocatalyst is inexpensive and has a high turnover. (v) Metal oxide can be supported on suitable reactor substrates [10-11].

Our study deals with the synthesis and characterization of zinc oxide nanorod photocatalyst. The photocatalytic activity of the prepared material was evaluated by the degradation of hydroquinone in aqueous solution under UV light irradiation. The extent of degradation was evaluated using UV–Vis spectroscopy (Shimadzu UV 2101PC), GC-Mass and also in terms of reduction in chemical oxygen demand (COD).

II. MATERIALS AND METHODS

The chemicals used for the study are Zinc acetate (AR, SD Fine Chemicals Ltd.,), hydroquinone (SRL), Sodium hydroxide, Hydrochloric acid, Sulphuric acid (Merck), Potassium dichromate (Extrapure AR, SRL), Ferroin solution (AR, SD Fine Chemicals ltd), Ferrous ammonium sulphate (Extrapure AR, SRL), Magnesium sulfate (Qualigens Fine chemicals), Silver sulfate (Merck). All solutions were made using deionised water.

The photo catalyst nano particles were synthesized from its precursor through a simple sol-gel method. Prepared photo catalyst was characterized by XRD, FT-IR, UV-DRS and FESEM techniques. The efficacy of the photo catalyst was tested using hydroquinone as a model organic pollutant. In order to optimize the degradation of hydroquinone, the following experimental parameters were studied viz. the effects of pH, dye concentrations, mass of catalyst and kinetics. The extent of degradation was evaluated using UV–Visible spectroscopy (Shimadzu UV 2101PC), GC-Mass and also in terms of reduction in chemical oxygen demand (COD).

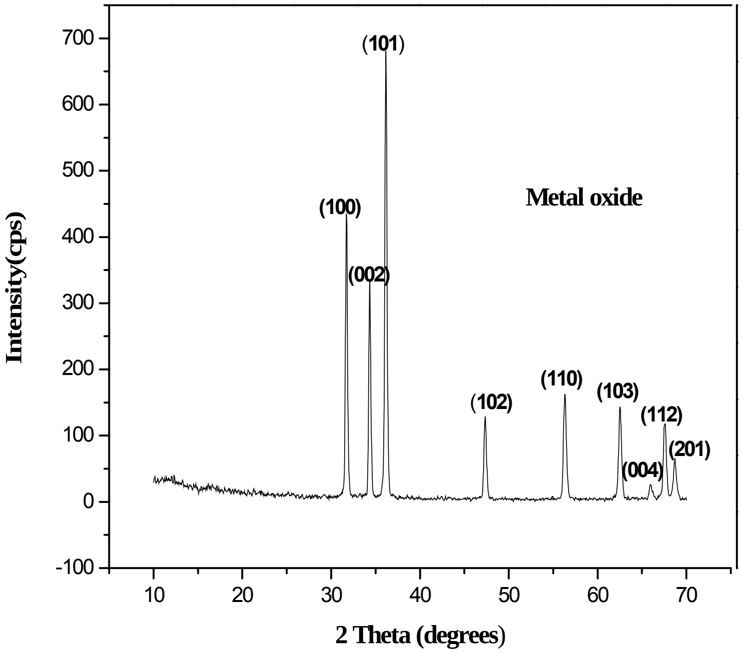
III. RESULTS & DISCUSSION

A. Phase Analysis

The XRD patterns of the metal oxide nanorods (NRMO) are shown in Fig.1. The NRMO exhibited strong XRD peaks due to the hexagonal phase of metal oxide. No other impurity phases were observed. The average size of the metal oxide was calculated using Scherer equation:

$$d=0.94\lambda/\beta COS\theta$$

The results proved that the prepared photocatalyst was nanosized.



B. Band gap Analysis (UV-DRS)

The band gap of the NRMO was determined using UV-DRS measurements (Fig.2).The results showed high absorbance in the UV light region, which suggests that they will be photocatalytically active under UV irradiation. The increased band gap energy of NRMO resists the recombination of the separated electron-holes thereby enhancing its photocatalytic efficiency.

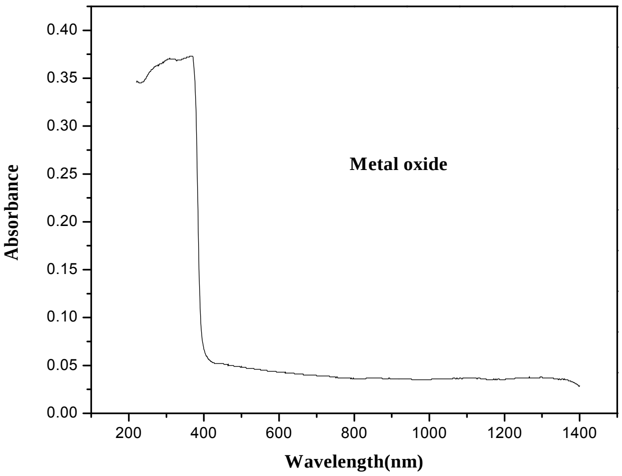


Fig. 2 shows the UV-DRS spectrum of NRMO.

C. FT-IR spectroscopy

FT-IR spectrum of NRMO was recorded in the range of 500 to 4000 cm-1 as shown in Fig.3. The FT-IR spectrum of before and after irradiation of NRMO produced similar peaks. The band located near 600 cm-1 can be attributed to the M-O stretching mode. The band at 3200 to 3600 cm-1 corresponds to the stretching vibration of–OH bond. These stretching vibrations correspond to the water molecule bound on the surface of sample.

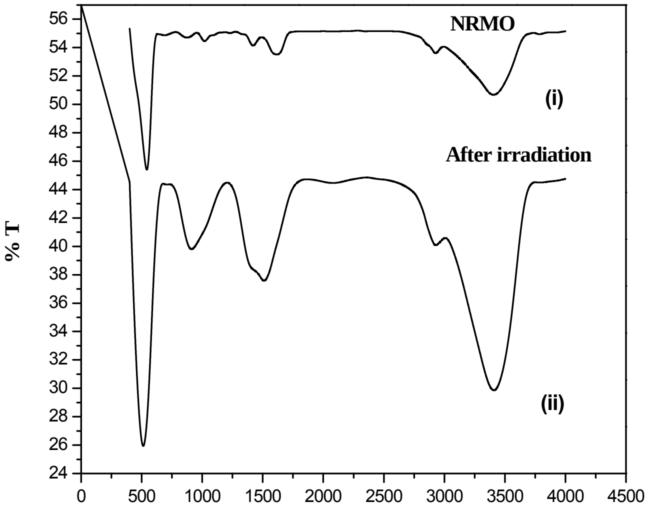
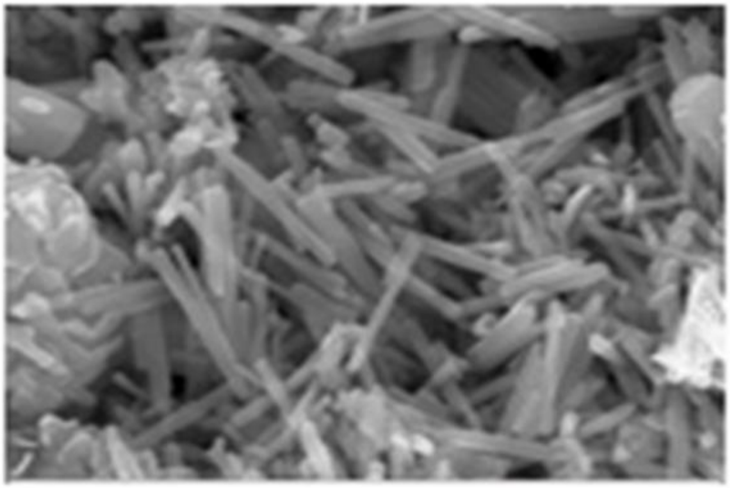


Fig.3 shows the FT-IR patterns of the prepared NRMO before and after irradiation

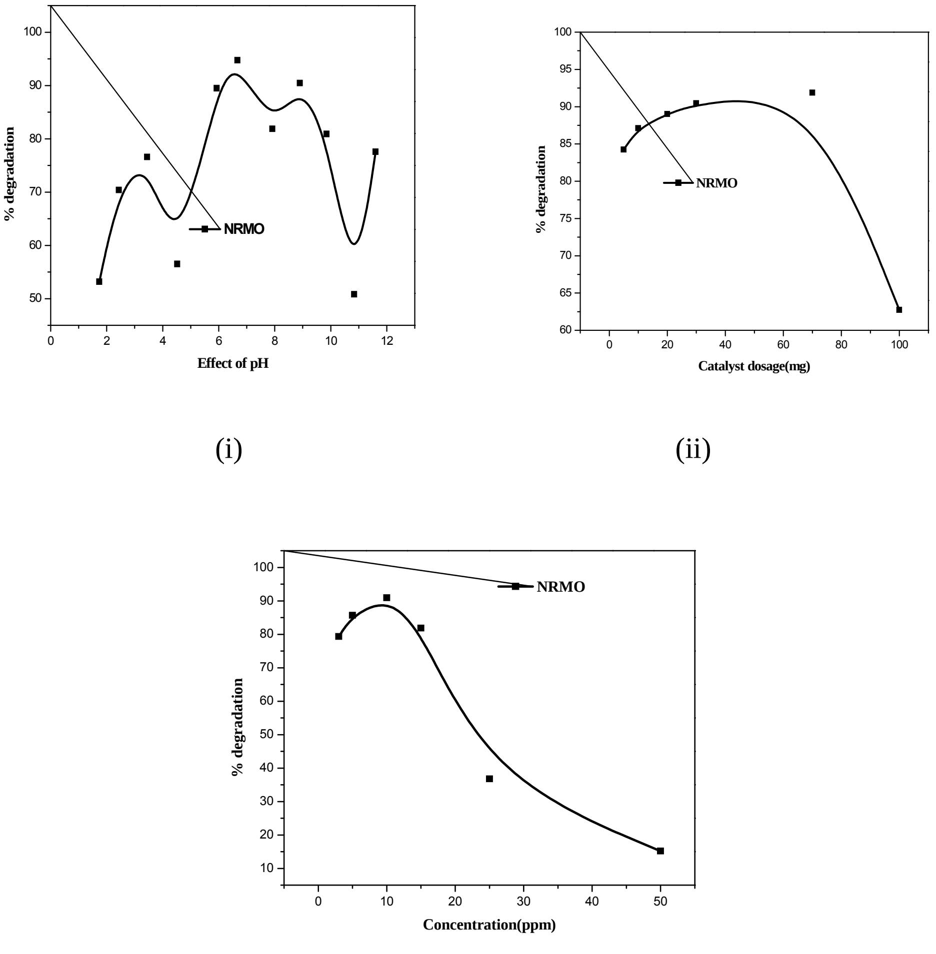
D. FESEM Analysis

FESEM image of NRMO shows the uniformly distributed nanorods with a hexagonal structure as shown in Fig.4 .The length of the NRMO is approximately of 80nm.



IV. PHOTOCATALYTIC ACTIVITY

The photocatalytic activity of the NRMO was evaluated by the photodegradation of hydroquinone under UV light irradiation. Effect of pH on oxidation of hydroquinone was studied (Fig. 5). Neutral pH was found to be optimum for the effective degradation of hydroquinone. A catalyst dosage of 70 mg of NRMO photocatalyst loading produced >90 % photocatalytic activity. At lower doses, photons are absorbed better on the surface of the catalyst. Thus, the production of OH radicals is enhanced thereby leading to the degradation of a greater number of hydroquinone molecules. On the other hand, at higher loading levels, the penetration of light into the solution is lower due to the scattering effect of the catalyst particles [12]. The effect of initial hydroquinone concentration on the degradation of hydroquinone and was carried out in the range of 5 to 25 ppm. The extent of degradation decreased as hydroquinone concentration increased. The reason for this is the shielding effect caused by hydroquinone molecules in solution.



(i) (ii)

(iii)

Fig. 5 shows the photocatalytic studies on the (i) Effect of pH (ii) variation of catalyst dosage and (iii) concentration of initial dye concentration of NRMO .

A. Kinetics of hydroquinone degradation

The effect of initial hydroquinone concentrations (5, 10, 15, and 25 ppm) on the kinetics of photo degradation of hydroquinone with photo catalyst was studied under atmospheric conditions. The kinetic data was analyzed using first order rate equation (Fig.6 (ii)).The photodegradation process followed a pseudo first order kinetics (eq.1). The values of k_{obs} were determined using least square regression analysis and the calculated periods of half life t½ (t½ =0.693/k) are given in Tab.1. The Degradation of hydroquinone molecule was also confirmed through chemical oxygen demand (COD) measurement before and after the reaction. (Fig. 6 (i))

$$\ln(Co/Ce)=k_{obs}t \qquad (1)$$

TABLE I.

Initial hydroquinone concentration (ppm)	**Metal oxide photocatalyst**	
	$k_{obs} \times 10^{-3}$ (min^{-1})	$t_{1/2}$
5	**0.472**	**1.4682**
10	**0.298**	**2.3255**
15	**0.287**	**2.4146**
25	**0.236**	**2.9364**

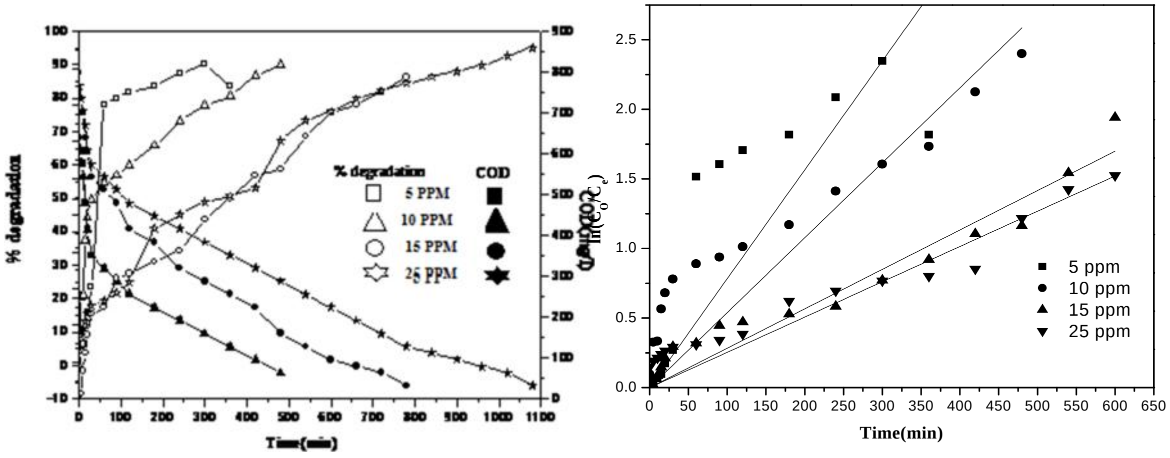


Fig. 6 shows the (i) kinetics of photocatalytic degradation of hydroquinone by NRMO with a comparison of COD measurement and (ii) Pseudo-first order Kinetic plots for the degradation of hydroquinone by NRMO.

B. Absorption spectra of hydroquinone degradation

UV-visible spectrum of samples withdrawn at various time intervals during the hydroquinone photo degradation of hydroquinone with NRMO photo catalyst is shown in Fig. 7. As the reaction proceeded, the height of the original peaks diminished gradually and completely disappeared after 480 min when NRMO photocatalyst was employed. The results indicated that synthesised NRMO showed high photocatalytic activity since 100% hydroquinone removal was observed at 480 min for 10 ppm concentrations of hydroquinone.

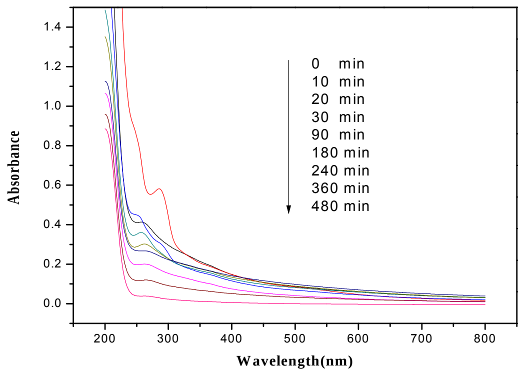


Fig. 7 shows the absorption spectrum of the prepared NRMO.

CONCLUSION

The synthesized photo catalyst was characterized employing XRD, UV-DRS, FT-IR and FESEM analysis. In order to increase the efficiency of degradation and to facilitate easy setting of catalyst on slurry reactors photo catalyst was developed. NRMO photo catalyst was employed as the catalyst for degradation of hydroquinone in the presence of UV radiation. The photo degradation followed the pseudo first order rate equation. Photo degradation of hydroquinone confirmed by analyzing chemical oxygen demand of the aqueous phase solutions before and after irradiation of hydroquinone solutions.It is observed that the lower hydroquinone concentrations produced minimum amount of COD. It shows that hydroquinone could be easily degraded with NRMO catalytic systems.

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