Photovoltaic Degradation of Methylene Blue Dye Using CuO Nanoparticles Prepared by SOL–GEL Method

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Abstract - Photocatalytic degradation is a hopeful approach for decay of dyes. Photocatalytic degradation of phenolic compounds such as methylene blue has been studied using different concentration in the range of (0.1-2) wt. % from Copper oxide CuO nano-particles. Nano-particles have been synthesized employing Sol-gel technique which is considered as a chemical engineering technique for formations of an oxides network during poly-condensation reactions of a precursor molecule in a solution. This study was carried out under special and natural conditions with and without UV source. The nanoparticles had been characterized using various techniques. The first one was X-Ray Diffraction (XRD), which shows that the structure of CuO nanoparticles are monoclinic of CuO nanoparticles, the normal crystal size of copper oxide NPs was found to be equal to 13nm. The second characterization techniques was SEM (Scanning Electron Microscopy), The SEM micrographs of prepared samples show the distribution particles and the morphology of copper oxide NPs (with size of particle~13nm). Catalysts were performed via UV–Visible spectrophotometer. The rate of degradation for methylene blue was monitored spectrophotometrically by measuring absorbance of dye. The effect of dye concentration and catalyst concentration were studied.

Keywords: Nanocomposite, Polymers, Doped.

I. INTRODUCTION

The advanced oxidations processes seem to be a perfect technique to destroy pollutants that were toxic to non-toxic compounds. Photo-catalytic oxidation reactions have been launched while photon with energy equal to band gap energy was absorbed by catalyst that leads to raise an electron (e\textsuperscript{-}) from the valence band to the conduction band at the same time, a positive hole (h\textsuperscript{+}) in the valence band is generated [1]. The photocatalytic operation is usually starting by incident UV radiation on the oxide samples which progress to electron-transfer from the filled VB to the CB. This approach was accompanied by generated of the electron and the positive whole pairs on the surface of the photo-catalyst [2]. The charge-carriers were either merge, with others or involve in mineralize of pollutants on organic origin on surface of catalyst via series of reduction and oxidation reactions. In addition, probable reactions of positive hole and electrons with oxygen and water progress to form peroxides and superoxide radicals that consider as active type in process of degradation [3]. CuO NPs are significant p-type transition metal semi-conductor, slit, band gap of 1.2 eV and resistance with low electrical value, and demonstration an interesting un-common characteristics[4], due to its anti-ferro magnetism, low-cost, non-toxicity and high stability features [5, 6]. Transition metal oxide has a significant type of semi-conductors that had applications in storage media, solar energy and catalysis [7]. Sol-gel process is a chemical engineering technique used for formations of an oxides network by poly-condensation responds of precursor molecules in solution. Chemistry of sol-gel techniques have been the preparation of inorganic polymer from liquid via transform from precursors to sol and finally to a structure of network. A gel is a case where both liquids and solid are dispersed in each other, which exhibit a solid network that involves liquid components [8]. The technique is based on mixing solutions that enable reactions in the formations of several particles [9]. The technique was according to mixing solutions which enable reaction in formation of particles. They are utilized for nanoparticle preparation. However, thus, represent an occasion for the size- and Shapes controlled synthesis of nanoparticles. Such morphological attributes are significant since they have the potentials to enhance the effectiveness of Nano-based biomaterials [10]. Concerning to a continuance published articles on nanotechnology [11–19], we focus on degradation of photo-catalytic of methylene blue dye utilizing copper oxide.

II. MATERIALS AND TECHNIQUE

General notification: Chemical compounds were stocked via Sigma/Aldrich nanoparticles was Copper oxide CuO which was prepared by sol-gel technique.

Sol-gel Technique: Copper oxide Nano-powders have been synthesized via Sol-gel technique. Aqueous liquid of CuCl\textsubscript{2}.6H\textsubscript{2}O (0.2 M) was synthesized. Glacial acetic (1 ml) was added to above liquid and heated to 1000 °C with stirring. Sodium hydroxide (8 M) was added to above heated liquid till pH equal to 7. Blue solution color becomes black immediately and the black precipitate with large amount was created promptly. Centrifuged and washed 3-4 times by deionized water. The acquired precipitate has dried for 24 h in air.

Samples: CuO nanoparticles were prepared as catalyst (0.1 g diluted in 100 ml methanol). Nanoparticles and methylene were weighed by using sensitive balance (Denver, Germany). Methylene blue as a dye often used for catalytic tests (0.05 g diluted with 500 ml methanol).

Photocatalytic Technique: The photocatalytic technique consists of UV- source as a lamp (6 watt) of cylindrical shape of (22cm) as a body length and 16cm are length which was used as a photo source. This lamp was positioned in a container of
the sample (mixture of copper oxide and methylene blue) and then placed on magnetic stirrer to mix and disperse solutions. Methylene blue concentration Impact: Various concentrations of the methylene blue were used (0, 1, 0.2, 0.5, 1, 1.5 and 2) wt% and 0.1 wt% from CuO nanoparticles. The samples were withdrawn from the mixture without photo-catalysts and after 15 min. for each concentration of methylene blue. The samples were investigated by UV-visible spectrophotometer to measure the optical absorbance.

CuO nanoparticles concentration Impact: Various concentrations of the CuO nanoparticles were used (0.1, 0.5, 1.5 and 2) wt. % and 0.1 wt.% of methylene. The samples were withdrawn from the mixture without photo catalysts and after 15 min. For each concentration of CuO nanoparticles. The samples were investigated by UV-visible spectrophotometer to measure the optical absorbance.

Optical absorption measurements: A double beam UV-VIS SP-80001 spectroscopy (Shimadzu Co. Japan) was used to measure the absorption when changing dye concentration, irradiation time at different conditions in the range of (200-1200) nm. The absorption data of samples can be used to calculate absorption coefficients of all samples at different wavelengths that were utilized to determine the optical energy band gap.

Characterization Techniques:

X-Ray Diffraction (XRD): The crystallinity of CuO powders have been studied by X-Ray Diffraction technique in National University of Malaysia (UKM). In order to study the structural properties and crystallite size of CuO nanoparticles.

SEM: Morphology surface of copper oxide NPs were examined in National University of Malaysia (UKM) using scanning electrons microscope (model, quanta450, company FEI/USA).

III. Results

Methylene blue concentration impact: The effect of variation in concentration of methylene blue shown in fig.1, the degradation rates have been observed in the range from 0.1 wt% to 0.5 wt%. It has been spotted that the proportion of degradation will increases with rising of concentration of methylene blue up to 3% for CuO nanoparticles catalyst. Further increase in concentration beyond this limit leads to decreasing in degradation rate. Methylene blue with higher concentrations will reduce radicals' generation on catalyst surface since active sites have been covered by methylene blue ions, also, the UV-screening impact of the methylene blue itself. At a high dye concentration, a significant amount of UV could be absorb by molecules of methylene blue rather than by CuO particles that reduce the efficiency of catalytic reaction because of decreasing in the concentrations of peroxide or superoxide radicals.

CuO nanoparticles concentration effect: A series of experiments have been done to find the influence of CuO concentrations (0.1, 0.5, 1.5, and 2) wt%. Methylene blue was fixed 0.1 wt%. The degradation of methylene blue was increased after period time of 15 min. As the concentration of CuO NPs was increased to 1.5 wt%, more radicals would produce to attack the Methylene blue and so, the average of reaction increase, as it is showed in fig. 3. When CuO NPs was utilized in excess, OH radicals would react with CuO and produce HO2; in addition OH radicals have been created at high concentration. Moreover, the H2O2 could accept the photo-generated electrons from the conduction band to form hydroxyl radicals, which prevent charges recombination. CuO could shift the absorption spectrum of photo-catalyst to visible region via formation of complexes on its surface, also it produce O2 through its photo-chemical reactions.
Characterization Techniques:

Copper oxide XRD: XRD have been used to show the CuO phase formation. Reflections have been well indexed to monoclinic phase of CuO. From Fig. 4, parameters of XRD of CuO NPs listed in tab. 1 with a space group of C 1 2/c 1 (15) and lattice parameters of $a=4.6809 \, \text{Å}$, $b=3.4176 \, \text{Å}$ and $c=5.1220 \, \text{Å}$, $\alpha=90^\circ$, $\beta=99.784^\circ$ and $\gamma=90^\circ$ are obtained. The perfect crystallinity and absence of impurities could be concluded as a result of sharpness of peaks and accurate peaks number in pattern of XRD. Moreover, it appears that the output is a single phase. The average crystallite size of CuO NPs was around ~13nm that was estimated by Scherer’s equation.

V. CONCLUSIONS

Maximum increasing of absorbance was noticed when the concentration of methylene blue increased from 0.5 wt% to 1 wt% and this behavior leads to increasing in degradation of methylene blue up to 3% for CuO catalyst. XRD measurements show that the CuO nanoparticles were monoclinic of CuO nanoparticles, the size of copper oxide NPs were 13nm.
REFERENCES


