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DEGRADATION OF METHYLENE BLUE USING CuO PREPARED USING CONVENTIONAL SOLID STATE METHOD

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ABSTRACT

The degradation of methylene blue (MB) dye onto copper oxide (CuO) synthesized using solid state method was investigated in a batch adsorption process. Copper Oxide (CuO) was successfully synthesized using solid state synthesis which involves heat treatment with temperatures ranging from 400 ^oC to 600 ^oC. The optimum preparation temperature was 600 ^oC resulting in 8.5% MB removal. XRD analysis shows that the crystal system of CuO is a monoclinic system and therefore all the diffraction peaks has been indexed using the CuO monoclinic phase. The obtained parameters were a = 4.6860 Å, b = 3.4280 Å, c = 5.1330 Å with a volume cell of 81.84 Å^3. SEM analysis indicates that a standard particle size for CuO is 37.0µm and that it has irregular surface. The effect of initial dye concentration (100 ppm-600 ppm), contact time (24-48 hours) and solution temperature (30 ^0C) were also evaluated. Highest removal percentage of MB was observed in MB concentration of 600 ppm. A longer contact time of 48 hours was shown to be more effective than 24 hours. The adsorption of MB onto CuO has higher efficiency at larger concentration difference, longer contact time and higher temperature used during synthesizing CuO.

KEYWORDS: *Copper oxide; methylene blue; solid-state reaction; degradation*

1.0 INTRODUCTION

Colour is the first pollutant in wastewater that can be identified by eyes and has great influences on the perception of water quality. Even at concentration of less than 1 ppm, they are highly visible and undesirable. Dyes are vastly used for product colouring in industries such as textile, paper and plastic. These industries consumes huge volume of water for this purpose and as a result, substantial amount of coloured wastewater is generated to the environment (Sreeju, Rufus, & Philip, 2017). The discharge of dye wastewater without proper treatment is very harmful to the aquatic life. Dyes can reduce light penetration and interfere photosynthetic processes. Under anaerobic conditions, some dyes may decompose into carcinogenic aromatic amines which could pose serious threat to humans and animals (Gupta & Suhas, 2009; Santhi, Manonmani, Vasantha, & Chang, 2016).

Methylene blue (MB) dye is known to cause eye burns which may lead to permanent injury to the eyes of human and animal. If it is inhaled, the affected individual may have difficulty in breathing and if it is ingested orally, it may cause burning sensation, nausea, vomiting and mental confusion (Rafatullah, Sulaiman, Hashim, & Ahmad, 2010). Hence, it is necessary to treat such effluents due to its harmful impacts to the environment and health. Adsorption using metal oxide amongst techniques used to remove unwanted materials from the wastewater.

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Amongst promising metal used for this purpose, CuO has been revealed as a good photocatalyst in many reports (Liu, Cheng, Li, & Dong, 2018; Sreeju, et al., 2017; Zhu, Meng, Wang, Di, & Diao, 2013), its photocatalytic properties for the degradation of pollutants are closely associated to the synthesis route, shape and the size of particle. Formerly, typical function of CuO as a photocatalyst degradation for methylene blue has been addressed using small particle size and varied synthesis route, (Mustafa, Tahir, Sultan & Akhtar 2013; Jiang, Wang, Meng, Wu, Wang & Chen, 2014; Li, Chan, Liu, Zhang, Liu & Li, 2017; Mageshwari, Sathyamoorthy, & Park, 2015). Earlier, Mustafa et al. produced microsize CuO ranging between 0.02 – 1 μm using aqueous precipitation method and capable to remove 88.93% of methylene blue (Mustafa et al., 2013). Meanwhile, Jiang et al. reported their finding stated that simple hydrothermal method competent to produce flower-like CuO nanostructures composed of irregular nonosheets with about 70 nm in width and 1.7 μm in length and successfully removed about 92.1% of methylene blue (Jiang et al., 2014). Thus, a study of the synthesis and applications of CuO is both particularly important.

Previously, several reports focusing on different methods of synthesising CuO such as using solution combustion method, aqueous precipitation method and catalytic oxidation (Raizada, Ganguly & Mankad, 2014; Farrouji, Eddine, Bousit, Boualy, Mehdi, Firdoussi, Ali, 2015; Mustafa et al., 2013) leading to different properties and adsorption capacity towards methylene blue of CuO as adsorbate. In the solution combustion method, Raizada et al. reported sufficient degradation performance of CuO towards methylene blue with 80% of methylene blue removal is achieved with 20 mg/l CuO after 2 mins reaction (Raizada et al., 2014). Meanwhile, Farrouji et al. showed that using catalytic oxidation as a route to produce CuO resulted that the degradation of methylene blue insignificantly depends upon initial dye concentration (Farrouji, et al., 2015).

A trend shows that increasing of methylene blue concentration leads to decreasing of dye degradation efficiency. The decrease in catalytic activity was explained by the saturation of the catalyst (Farrouji, et al., 2015). Mustafa et al. reported that highly ordered nanowires of CuO prepared by adopting aqueous precipitation method was capable to remove methylene blue of (Mustafa et al., 2013). In addition to that, flower-shaped hierarchical CuO microspheres consisting of interpenetrating nanosheets were successfully synthesized by reflux condensation method which shows good photocatalytic activity towards methylene blue removal as reported by Mageshwari et al. (Mageshwari, et al., 2015). However, up to our knowledge, no work has been done to produce CuO using conventional solid-state method.

Thus, in this paper, we reported the properties and efficiency of CuO that has been synthesized using simple and conventional solid- state method for the adsorption of methylene blue. In this context, we report the photocatalytic activity of microsphere CuO synthesized by simple and productive solid-state method. The principle of this method is that it is economical, environment friendly, has large scale production of nanomaterials with well-defined size and shape without the use of any expensive equipment. The photocatalytic performance of the synthesized CuO microspheres was evaluated by monitoring the photodegradation of methylene blue (MB) dyes and initial dye concentrations on the photocatalytic activity of CuO was investigated.

2.0 MATERIALS AND METHOD

2.1 Synthesis of Copper Microsphere

Microspheres CuO were prepared using simple solid-state reaction method. All chemical reagents were analytical grade and purchased without further purification including copper nitrate and ethanol. In normal reaction process, 1 mol of copper nitrate and ethanol were used to prepare a copper oxide. The mass of the copper (II) nitrate were weighed with mass ratio of 1 mole of copper oxide. Different samples were calcined at different temperatures of ranging from 400 °C to 600 ºC with 50 ºC interval and 12 hrs dwelling time. Sample collected from furnace were crushed using pestle and mortar prior to characterization.

2.2 Material Characterizations

The structure of the synthesized CuO microspheres was studied using X-ray diffraction (XRD, Bruker Advanced X-ray Solutions D8) with CuKα1 radiation (λ=1.5406Å). The XRD results obtained were compared to the Joint Committee on Powder Diffraction Standards (JCPDS) Xray data file. The surface morphologies were studied by a FEI Quanta-250 Field Emission Scanning Electron Microscopy (FESEM). UV–vis spectrum was recorded on a Agilent spectrophotometer.

2.3 Photocatalysis Tests

Methylene blue (MB) (Sigma Aldrich, practical grade) were chosen as the organic pollutants to evaluate the photocatalytic performance of CuO microspheres. CuO with known amounts from 0.2 g was added into different initial MB concentration (100 ppm to 600 ppm) to shaking flasks and placed in a water bath shaker for an aspired period of time (Mustafa et al., 2013; Karagöz, Tay, Ucar, & Erdem, 2008). As the time of shaking increases, it was observed that the dye saturation of the methylene blue decreases. The products in the flask were taken out and filtered to remove the CuO. This sample is then place in the UV-spectrophotometer to analyse and quantify the amount of methylene blue. The experiments were carried out at room temperature.

3.0 RESULTS AND DISCUSSION

3.1 Structure Analysis

Figure 1 displays the XRD patterns of CuO microspheres synthesized by solid-state reaction method. As can be seen in Figure 1, all the peaks appear in the XRD pattern of CuO were corresponding to monoclinic CuO (JCPDS 45-0379) and similar observation was also reported previously (Mustafa et al., 2013; Li, et al., 2017; Rao, Sathishkumar, Mangalaraja, Asiri,Sivashanmugam & Anandan, 2018). Therefore all the diffraction peaks has been indexed according to the CuO monoclinic phase. For sample synthesized at 450ºC, the obtained cell parameters were a = 4.6860Å, b = 3.4280Å, c = 5.1330Å with a volume cell of 81.84 $Å^3$. During the XRD analysis, the peak of other components was not present in the results. This implies that the CuO produced are of high purity due to its absence of impurities.

Meanwhile, Figure 2 shows SEM images of CuO synthesized at temperatures 450ºC. As shown in Figure 2 (b), well-developed pores were found on the surface of CuO. The solid state synthesis had resulted in porous structure of CuO with less agglomeration leading to the large

surface area. This porous structure of CuO is essential as dye adsorption site in the adsorption process. In Figure 2 (a), the diameter of a selected CuO as shown is 37.0μm. Figure 2 (b) shows a close-up view on the particle that demonstrates the ball-like shape of CuO microspheres was made of needle-like particles that agglomerates forming bigger structures. In addition to that, Figure 2 (c) denotes that the particle surface has irregularities in surface area.

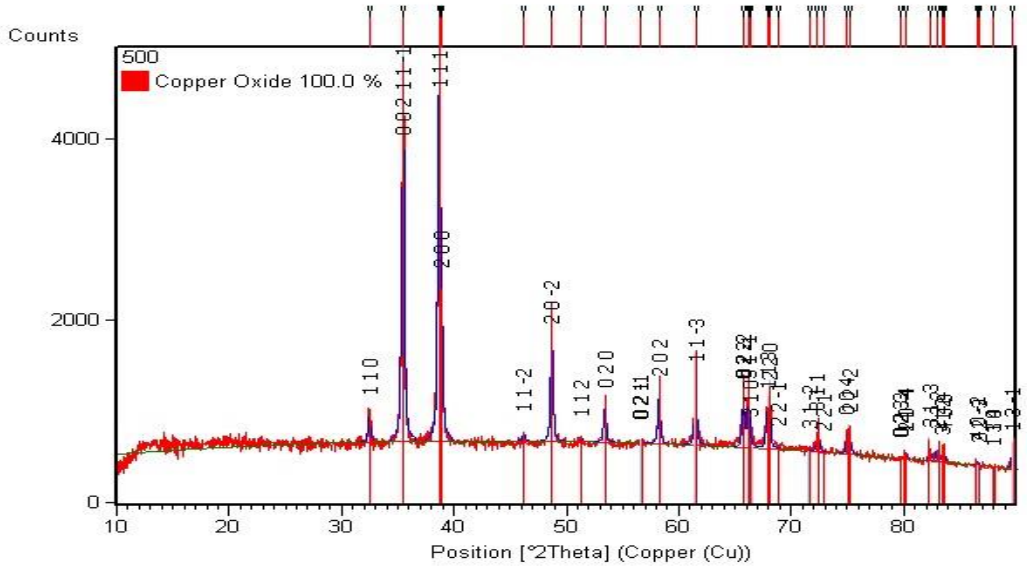

Figure 1. XRD patterns for CuO prepared by conventional solid-state reaction method

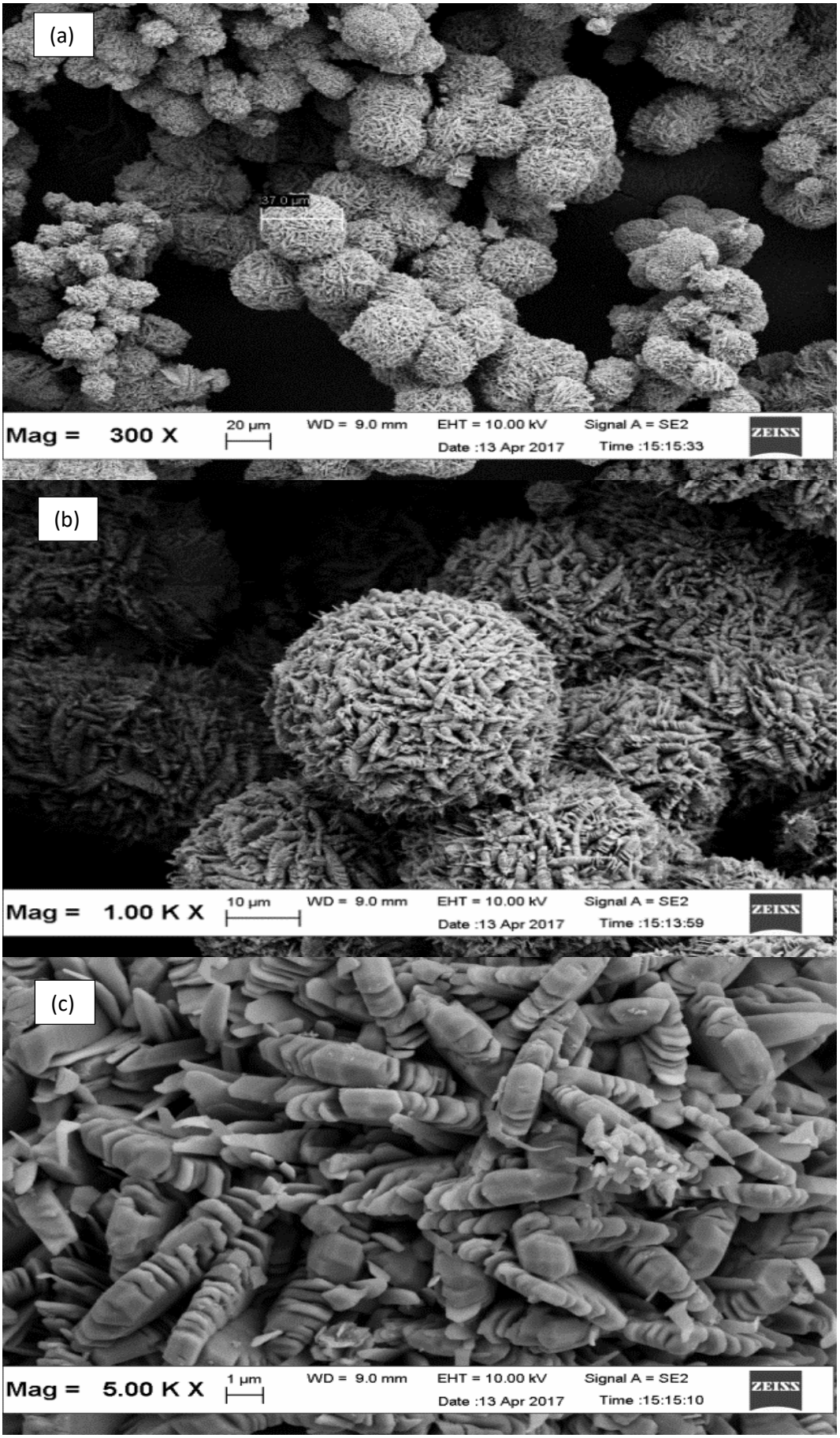

Figure 2. SEM images at different magnification of CuO

3.2 Effect of temperature on the adsorption capabilities of CuO

In order to determine the potential capability the microspheres CuO to degrade organic contaminants from wastewater, the catalytic activity of the hierarchical CuO microspheres were evaluated in the oxidation of MB without the presence of H_2O_2 under neutral condition as depicted in Figure 3. Temperature is one of the important parameter in an adsorption process. Five samples were synthesized at different calcining temperatures (400 ^{0}C, 450 ^{0}C, 500 ^{0}C, 550 ^{0}C and 600 ^{0}C) and further studied over a range of initial dye concentrations ranging from 100 to 600 ppm with 100 ppm interval. As the temperature increased from 400 ^{0}C to 600 °C, the percentage of MB dye adsorbed also increased from 4.17% to 8.50%. This result shows that when the temperature increases, the amount of adsorption of dye increases. This is probably due to the increase in number of pores when a higher temperature was used to synthesis the CuO.

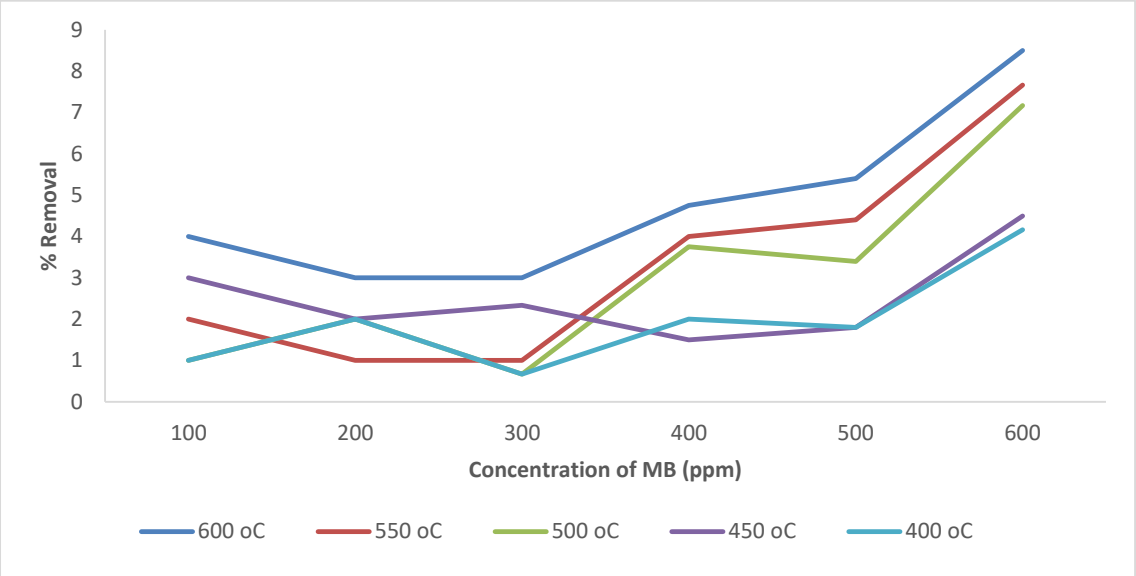

Figure 3. Adsorption capabilities of microspheres CuO at different synthesized temperature

3.3 Effect of CuO contact time on the degradation of the MB analysis

Despite the effect of synthesized temperature towards the degradation capability of CuO, the effect of contact time on adsorption of MB onto CuO at various initial dye concentrations (100-600 mg/L) at 30^{0}C also studied and presented as in Figure 4. From the figure, microspheres CuO is able to adsorb more amount of MB after exposed for a longer time of 48 hrs. This however does not last as shown in the figure as for concentrations of MB above 300 ppm, the adsorption capabilities of CuO seems to become stagnant. The results obtained is different than previous research whereas time increase , the absorption capabilities shows a decreasing trend. From the Figure 4 also can be seen that when adsorption reaches equilibrium, the rate of adsorption decreased with increase in contact time. Therefore, when given sufficient time, CuO is able to adsorb significant amounts of MB until it reach equilibrium.

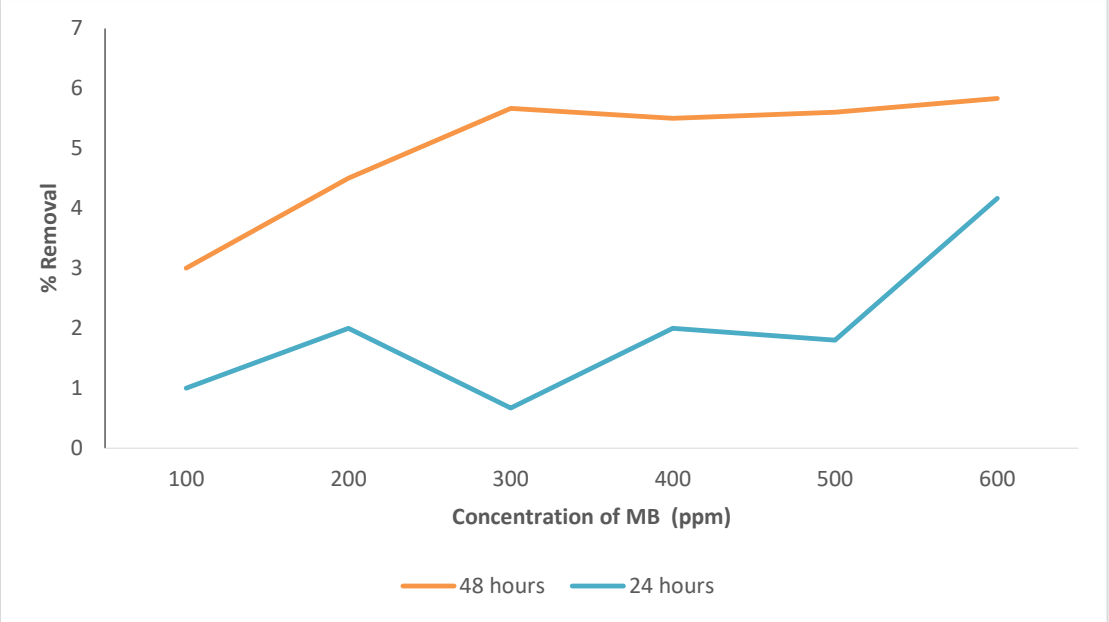

Figure 4. Rate of removal of MB using micropsheres CuO at different contact time

3.4 Effect of CuO catalyst towards different initial concentrations of MB

The effect of initial MB concentrations (between 100 ppm and 600 ppm) was studied parallel to the work done earlier by Karagöz et al., 2008. By varying the concentration of the methylene blue (MB) dye, the adsorption of methylene blue was carried out using 0.2 g of CuO synthesized at various temperatures. Figure below shows that the percentage of removal of MB increases when the concentrations of MB in the solution increases. This may be due the powerful driving force to overcome mass transfer resistance between the liquid and solid phase. This trend of results shown similar as Karagöz et al. (2008) which also reported on effect of initial MB concentration on adsorption. Freundlish plots were obtained using different temperatures in the range of 400 ^{o}C – 600 ^{o}C as shown in Figure 5 and the values of 'k' and 'n' are further presented as in Table 1. Low values of k indicates temperatures that are less favorable for adsorption such as temperatures at 600 ^{o}C whereas high values of k indicates temperatures that are more favorable for adsorption such as temperatures at 500 ^{o}C and 550 ^{o}C.

Table 1. Value of 'k' and 'n' for microspheres CuO at different synthesized temperature

Temperature (^{o}C)	k	n
400	3.35	0.65
450	3.34	0.65
500	4.78	0.54
550	4.84	0.54
600	3.46	0.64

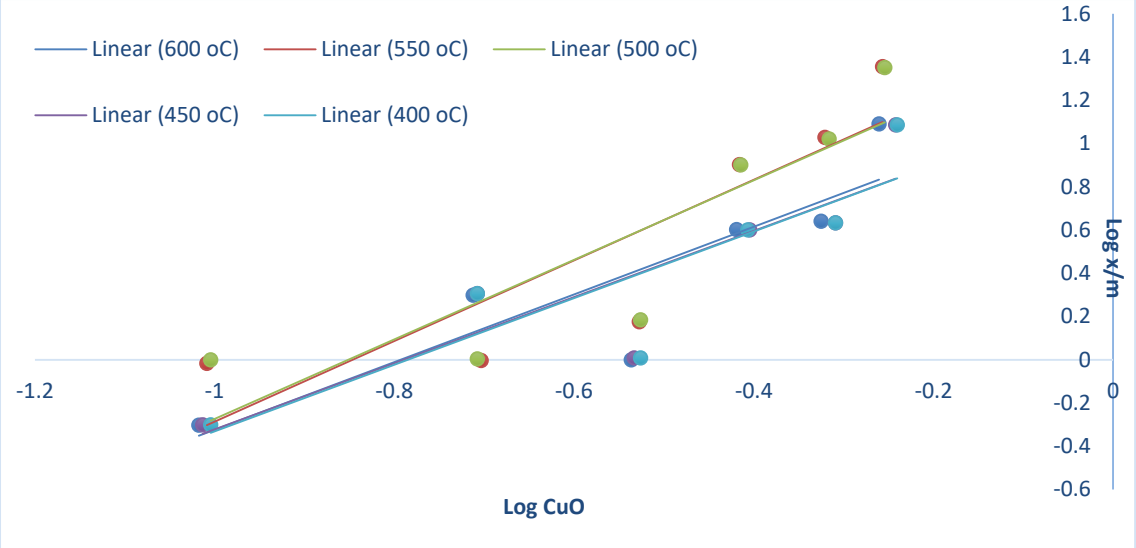

Figure 5. Effect of miscropshere CuO at varied initial concentrations of MB

4.0 CONCLUSION

In summary, a highly purity micronsize CuO was prepared by simple conventional solid-state reaction process at temperatures of 600ºC in which resulted with 8.5% MB removal. The spherical CuO having a particle diameter 37.0 µm presents an irregular surface with sufficient porosity for the adsorption activity. The as-synthesized monolithic spherical CuO exhibits superior degradation performance for MB without presence of H_2O_2. It is found that the high degradation efficiency of CuO mainly results from the uniform shape and size of CuO structure and its porous surface that leads to effective contact between MB and the catalyst.

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