

# Selective Catalytic Oxidation of Naphthol to Lawsone on Copper Phthalocyanine

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**Abstract:** A green chemistry approach is used for the synthesis of copper phthalocyanine (CuPc) and its application for the conversion of 2-naphthol to 2-hydroxy-1,4-naphthoquinone (HNQ, Lawsone) in alkaline aqueous solution using H<sub>2</sub>O<sub>2</sub> as an oxidizing agent. The product obtained was compared with that of authentic sample and was found to be identical. Further the effect of amount of catalyst, amount of NaOH, amount of starting material and amount of H<sub>2</sub>O<sub>2</sub>, on the rate of reaction was investigated. The efficiency of The reaction was checked using different solvents, temperature, use of substituted CuPc and other metals phthalocyanines.

**Keywords:** Copper phthalocyanine, 2-naphthol, Oxidation, Lawsone.

## INTRODUCTION

There is a need to develop a cleaner method of synthesis, due to the growing environmental pollution. Oxidation of aromatic alcohol to quinone is of large industrial importance [1-3]. Numerous oxidants were used in the literature such as chromic oxide [4], silver oxide [4] and ceric ammonium nitrate [5]. However, only in few reactions air or oxygen is used as oxidant [6-9]. On economic and ecological grounds there is an increased need for the development of soft processes, without toxic chemicals and which do not necessitate high temperature or high pressure. In the present work an attempt was made to synthesize 2-hydroxy-1,4-naphthoquinone (HNQ, Lawsone) from 2-naphthol using Copper phthalocyanine (CuPc) as a catalyst. CuPc is synthesized using melt method as reported in literature [10]. Lawsone is a naturally occurring compound first isolated from the leaves of *Lawsonia inermis L.* in 1959. 2-hydroxy-1,4-Naphthoquinone and related compounds have been reported to possess interesting biological activities such as antitumor, antibacterial and antifungal properties [11-12]. It is also used as hair dye and as an ultraviolet (UV) filter in sunscreen formulation. 2-hydroxy-1,4-Naphthoquinone is mainly obtained from plants [13]. Oxidation of 2-naphthol to HNQ in methanol and isopropyl alcohol using metalloporphyrine as catalyst is reported [14-15]. In the present work replacement of the organic solvents with water and metalloporphyrine to metallophthalocyanine was done, this is much economical than the former. An attempt is made to give the catalytic mechanism based on the literature [14] and the ability of Copper to go from +2 state to +1 oxidation state which is not observed in case of other metal phthalocyanines.

## EXPERIMENTAL

### Reagents

The Metalophthalocyanines catalysts were prepared from the melt method [10] and characterized using various

tools such as FTIR, UV-visible and XRD techniques. Sodium hydroxide, hydrogen Peroxide (30% aqueous solution), 2-naphthol and other reagent were purchased with purity of 99.9 % and were used without further purification.

### Catalytic Reactions

2 g of NaOH was dissolved in 50 ml of water to that 20 mg of 2-naphthol was added, followed by addition of 100 mg of CuPc. The reaction mixture was stirred for 30 min on a magnetic stirrer; stirring was stopped and to this 0.9 ml of H<sub>2</sub>O<sub>2</sub> was added. The reaction mixture was allowed to stand at room temperature for 30 min. The resulting mixture was neutralized with dilute HCl and further extracted with diethyl ether. The ether layer obtained was first washed with water twice and was dried over sodium sulphate. The ether layer was evaporated to dryness and residue obtained was crystallized in ethanol. The product obtained was compared with that of authentic sample procured from sigma Aldrich.

### Instruments

The experimental results were compared with that of authentic sample using Shimadzu FTIR IRprestige-21 (operating conditions: slow scanning speed; resolution power; 4 cm<sup>-1</sup>; wave number range: 4000 - 400 cm<sup>-1</sup> with KBr), Shimadzu UV - 2450 spectrophotometer (operating conditions: wavelength range: 800 - 200 nm, sample concentration: 4 - 20 ppm).

### Analysis of Products

Formation of product was monitored using fluorescence active TLC. The authentic sample and product both were dissolved in ethanol and run on TLC with a mobile phase of 10% methanol in chloroform. Both authentic sample and product have same R<sub>f</sub> of 0.26. The crystal obtained was overlying IR spectra and also UV- visible spectra (when dissolved in 0.1N NaOH solution) with that of authentic sample. Further the rate of reaction with change in different parameters was studied using UV- visible spectroscopy, dissolving the sample in 0.1 N NaOH has maxima in visible region at 453 nm. Whereas the starting material (2-hydroxynaphthalene) after dissolving in 0.1 N NaOH did not show any absorbance at around 400-500 nm region. The va-

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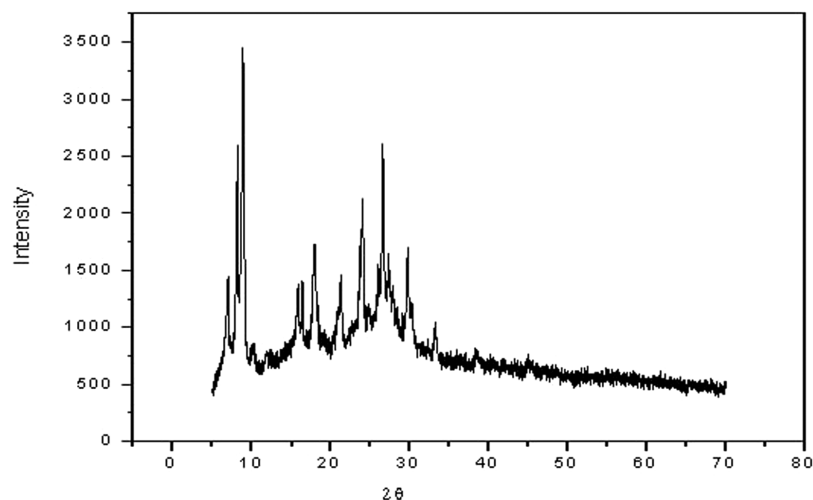


Fig. (1). XRD powder pattern of CuPc.

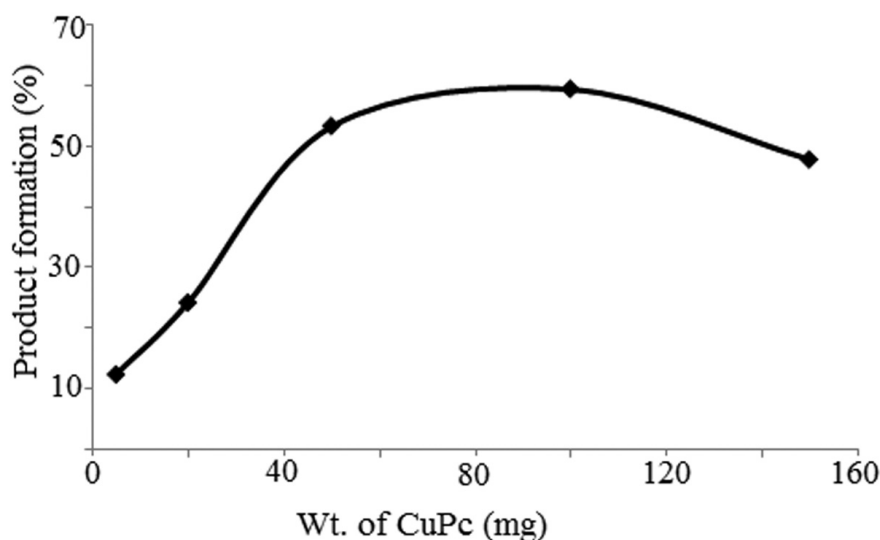


Fig. (2). Graphical representation of percentage product formation for different concentration of CuPc (mg).

lidity of this method with respect to GC method was described [10], it has a difference of less than 2%.

## RESULTS AND DISCUSSION

CuPc was characterized employing various techniques such as FTIR, the following peaks such as  $1121\text{-}1123\text{ cm}^{-1}$ ,  $1090\text{-}1095\text{ cm}^{-1}$ ,  $1067\text{-}1070\text{ cm}^{-1}$ ,  $947\text{-}949\text{ cm}^{-1}$ ,  $872\text{-}885\text{ cm}^{-1}$ , and  $754\text{ cm}^{-1}$  are assigned to the phthalocyanine skeletal vibration. The peak observed at  $1286\text{-}1290\text{ cm}^{-1}$  is due to C-N stretching,  $900\text{-}905\text{ cm}^{-1}$  is due to C-N bending and  $1332\text{-}1335\text{ cm}^{-1}$ ,  $1419\text{-}1425\text{ cm}^{-1}$  is due to aromatic phenyl rings. In addition to this, the peak observed at  $1610\text{-}1616\text{ cm}^{-1}$  is due to C=C, C=N and ring stretching. Also peak at  $770\text{-}730\text{ cm}^{-1}$  and  $1165\text{ cm}^{-1}$  are due to C-H out of plane bending and C-H in plane bending vibration were observed.

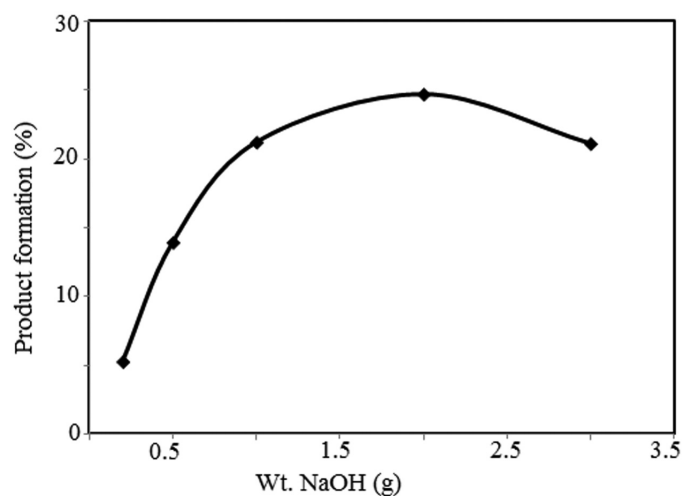
The UV-Visible data was recorded in DMSO, it showed characteristic B-Band at 287 nm and Q-band at 670 nm, which was well in agreement with that reported in literature. Further thermal studies using TG-DSC were carried out to

study the thermal stability of the molecule, the molecule was found to be stable up to  $301^\circ\text{C}$  and was found to undergo decomposition with increase in temperature.

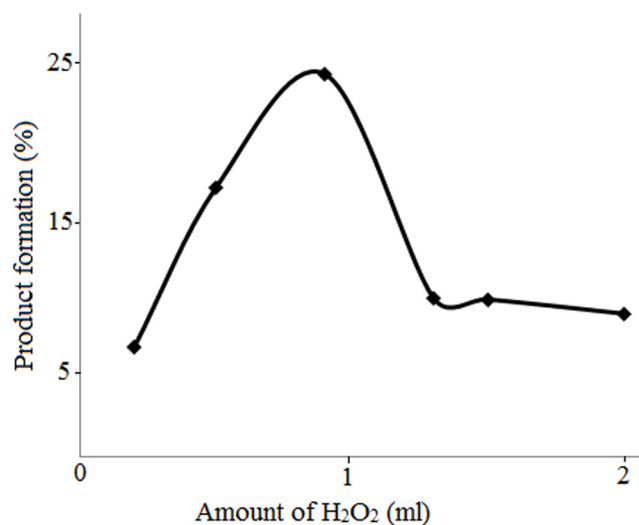
Fig. (1) shows the XRD powder patterns of the CuPc. The  $2\theta$  values were in good agreement with the corresponding JCPDS files and it indicated that this CuPc has a  $\beta$  planar monoclinic structure.

### Effect of on Amount of Catalyst

This reaction was carried out with different concentration of catalyst (CuPc), rest of the reaction conditions were kept constant, 50 ml of water, 20 mg of 2-hydroxy naphthalene, 2g of NaOH and 0.9 ml of  $\text{H}_2\text{O}_2$ . After 30 min on addition of  $\text{H}_2\text{O}_2$ , 8 ml of the reaction mixture (on filtration) was neutralized with dilute HCl and extracted with diethyl ether. The ether layer obtained was first washed with water twice and was dried over sodium sulphate. The ether layer was evaporated to dryness and residue obtained was dissolved in 0.1 N NaOH and diluted to 50 ml with 0.1 N NaOH. The percentage of product obtained is shown in Fig. (2).



**Fig. (3).** Graphical representation of percentage product formation for different concentration of NaOH (g).



**Fig. (4).** Graphical representation of % product formation for different concentration of H<sub>2</sub>O<sub>2</sub> (ml).

#### Effect of Amount of NaOH on the Rate of Reaction

This reaction was carried out with different concentration of NaOH, rest of the reaction conditions were kept constant. 50 ml of water, 20 mg of 2-hydroxy naphthalene, 20 mg of CuPc and 0.9 ml of H<sub>2</sub>O<sub>2</sub>. After 30 min on addition of H<sub>2</sub>O<sub>2</sub>, same procedure was followed as above. The percentage of product obtained is shown in Fig. (3).

#### Effect of Amount of H<sub>2</sub>O<sub>2</sub> on the Rate of Reaction

This reaction was carried out with different concentration of NaOH, rest of the reaction conditions were kept constant. 50 ml of water, 20 mg of 2-hydroxy naphthalene, 20 mg of CuPc and 0.9 ml of H<sub>2</sub>O<sub>2</sub>. After 30 min on addition of H<sub>2</sub>O<sub>2</sub>, same procedure was followed as above. The percentage of product obtained is shown in Fig. (4). From the graph it is clearly observed that there is sudden decrease in the amount of product formed when there is increase in the concentration of H<sub>2</sub>O<sub>2</sub> from 0.9 to 1.3 ml, the main reason is that the nature of reaction is very exothermic that the product formed gets further oxidized and degraded to smaller fragment.

#### Effect of Amount of 2-hydroxy Naphthalene on the Rate of Reaction

This reaction was carried out with different concentration of 2-hydroxy naphthalene rest of the reaction conditions were kept constant. 50 ml of water, 100 mg of CuPc, 2g of NaOH and 0.9 ml of H<sub>2</sub>O<sub>2</sub>. After 30 min on addition of H<sub>2</sub>O<sub>2</sub>, same procedure was followed beofre. The percentage of product obtained is shown in Fig. (5).

#### Effect of Solvent

The reaction was also studied in different solvents such as methanol, isopropyl alcohol (IPA) and acetone. In case of methanol 20% yield was obtained after 24 h at room temperature and 14% yield after 24 h at 0-5°C. In case of IPA formation of product was observed along with some other side product as observed in TLC. In case of acetone, formation of product was not encountered.

#### Effect of Temperature

At lower temperature, 0 - 5°C the rate of reaction was very slow, after 24 h the starting material was observed

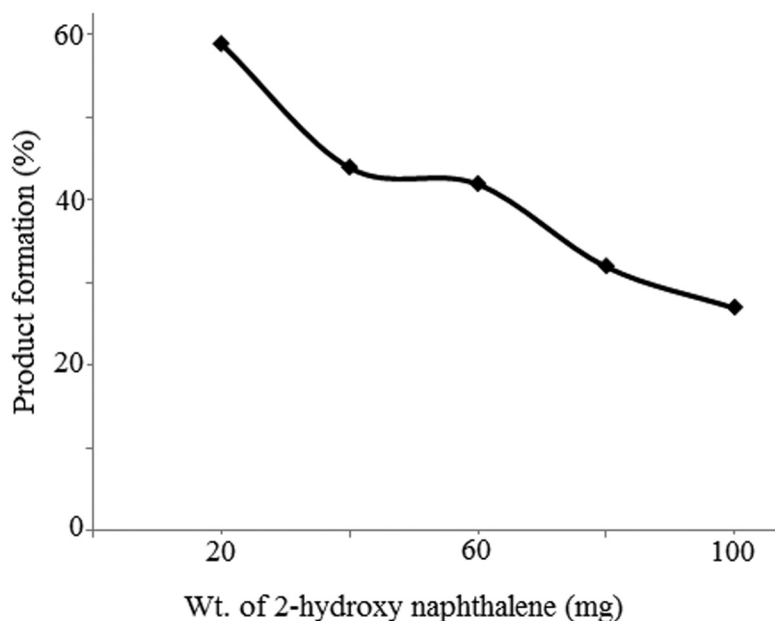
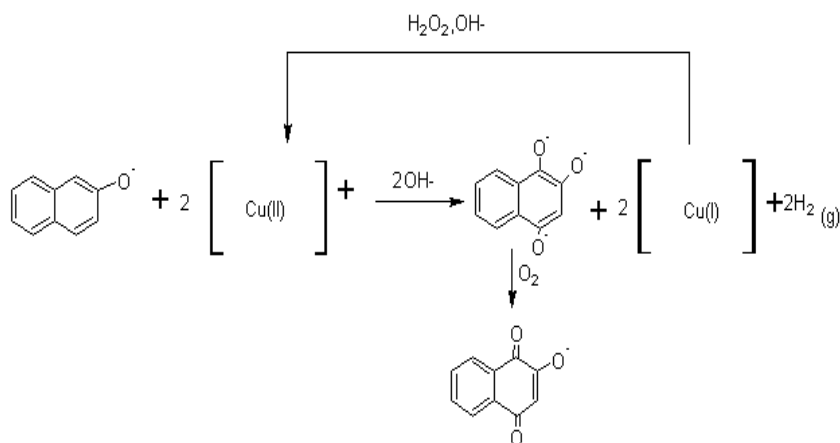


Fig. (5). Graphical representation of % product formation for different concentration of 2-naphthol.



Scheme 1. Mechanism for catalytic reaction.

whereas at 45 °C, the product formed was found to undergo degradation under reaction condition.

#### Catalytic Activity Over Various Catalysts

The oxidation were studied using CuPc, Tetranitro Copper Phthalocyanine (TNCuPc) and Tetraamino Copper Phthalocyanine (TACuPc), no other transition metal phthalocyanines were able to catalyze this reaction. Only CuPc, TNCuPc and TACuPc were able to catalyzed the reaction out of which CuPc showed total product formation of 59% where as TACuPc 11.8% and TNCuPc only 1.72%.

#### Proposed mechanism

Based on the observation there is absolutely no change in FTIR spectra of CuPc before and after catalytic activity. On washing with water and heating at 105 °C for 1 h, this catalyst can be re-used without loss in activity. The mechanism for catalytic reaction is proposed as shown in scheme 1. The CuPc showed much better activity than any other metal phthalocyanines. The main reason is that Cu can

very well perform redox mechanism. It can act as an oxidizing as well as reducing agent such as  $\text{Cu}^{2+}$  to  $\text{Cu}^{1+}$  which is essential for this reaction. The attack of Hydroxyl group is possible at 1 and 4 position of the 2-Naphthol only when there is someone to abstract the hydride ion present on 1 and 4 position, the ability of CuPc to go from +2 to +1 oxidation state helps it to take an electron with the evolution of Hydrogen gas. The hydroxyl group attached to the ring at 1 and 4 position, being present in an alkaline medium exists in the form of an ion as shown for the starting material. This further oxidizes to final product. The intermediate formed is very unstable that it is not analyzed during reaction. Though the Cu is in center of the molecule, but having planer structure, it is able to interact with other molecule, without any damage to the parent structure. It is difficult for other transition metal phthalocyanines to perform such redox mechanism as shown above in Scheme I.  $\text{Cu}^{2+}$  helps to oxidize 2-naphthol with alkali thereby reducing its state and the reduced  $\text{Cu}^{1+}$  then oxidizes with  $\text{H}_2\text{O}_2$ . The reaction continues till all the reactant is exhausted forming lawsone.

## CONCLUSION

The oxidation of 2-naphthol to 2-hydroxy-1,4-Naphthoquinone was found to be very economical and as well as in accordance to that of Green chemistry approach. The catalyst initiates the reaction with H<sub>2</sub>O<sub>2</sub> as oxidant whose byproduct is water. The reaction was carried out in water and at room temperature without any external pressure. The purification of the product was also very simple and catalyst can be recycled. From different studies it is found that the ideal conditions for the active reaction are 20 mg of 2-naphthol, 100 mg of CuPc, 2 g of NaOH, 50 ml of water, 0.9 ml of H<sub>2</sub>O<sub>2</sub> and the reaction time as 30 minutes. This reaction also focuses light on the ability of Cu in CuPc to get reduce to +1 oxidation state, without affecting the phthalocyanine ring.

## CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

## ACKNOWLEDGEMENTS

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