Bull. Chem. Soc. Ethiop. **2022**, 36(1), 197-207. ISSN 1011-3924
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DOI: https://dx.doi.org/10.4314/bcse.v36i1.16 Online ISSN 1726-801X

PHOTOCATALYTIC OXIDATION OF BUTAN-2-OL OVER MULTI WALLED CARBON NANOTUBES /COBALT PHTHALOCYNANINE COMPOSITES

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(Received December 1, 2021; Revised February 18, 2022; Accepted March 3, 2022)

ABSTRACT. This study involves synthesis of new substituted of cobalt phthalocyanine derivatives (CoPc) from starting materials naphthalene-1,4,5, tetracarbonic acid dianhydride (NDI) and phthalic anhydride by dry process. Nano composites materials were prepared from multi wall carbon nanotubes (MWCNTs), and MO (Cr_2O_3-NiO) to yield (MWCNTs/MO) nanocomposite and mixed with cobalt phthalocyanine to yield (MWCNTs/CoPc-MO). These materials were investigated using different analytical and spectrophotometric methods such as FTIR spectroscopy, X-rays diffraction (XRD), and scanning electron microscopy (SEM). Then the activity of these materials was investigated by conducting photocatalytic oxidation of butann-2-ol over a suspension of these composites under irradiation with UV light from middle pressure mercury lamp. The concentration of the produced 2-butanone was followed by spectrophotometric method using 2,4-dinitro phenyl hydrazone which was detected by measuring absorbance at 480 nm. Different reaction conditions and parameters were investigated such as effect of weight of the catalyst, temperature of reaction, reaction period and the effect of pH of reaction mixture.

KEY WORDS: Cobalt phthalocynanine, Nanocomposite, Photocatalytic oxidation of alcohols

INTRODUCTION

In 1907 Braun and Tcherniac discovered phthalocyanine (PC1) (tetrabenzotetraazoporphyrin). PC (H_2Pc) is an organic compound, it is thermally stable with the formula $(C_8H_4N_2)_4H_2$, the structure of phthalocyanines is a very similar with porphyrins, many phthalocyanine compounds has good catalytic performance. PC is an aromatic macrocycle compound, with substitution four meso-carbons in position α-γ and β-δ axis with four addition benzene rings and containing eight nitrogen atoms. The term phthalocyanine was found by Linstead and his group from the Greek words, naphtha (rock oil) and (cyaninen = blue) [1, 2]. PCs are heterocyclic aromatic compounds, used as colorant materials [3-5].

Phthalocyanines compounds are considered as important materials that have a wide range of applications, due to their optical and electrical properties and thermal stability [6]. Pcs prepared by reaction between metal salts, urea, ammonium molybdate, and NDI, phthalonitriles (phthalic anhydride, phthalimide or phthalic acid) at a temperature around 200 °C and reaction times of several hours. Mono or binuclear metal phthalocyanines are widely used in solar cells, sensors, and light-emitting devices. In 1930s Linstead and his co-workers prepared some of its metal derivatives. More than 70 different metal ions into the central cavity can be introduced to improve physical properties of the phthalocyanine [7]. Phthalocyanines are the second most important class of colorant. Pcs important materials because of electrical, optical, and their thermal stability [8]. Applications of Pcs have now been extended to many technological processes. These compounds have been prepared by reaction between urea, metal salts and phthalimide or phthalic anhydride or phthalonitrile. Typically, reaction times of several hours are needed for such reactions and temperatures around 200 °C [9]. In addition, they are used for oxidative degradation of pollutants or catalysts for photoreactions and as photosensitizers [10].

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Among different synthetic applications, photcatlytic oxidation of alcohol was investigated by many researchers. In this context, oxidation of alcohols is an environmentally friendly and important reaction to synthesize organic oxygenated compounds that can be applied in many industrial, and pharmaceutical processes. For example, in industrial applications, the gas-phase synthesis of formaldehyde can be synthesized in large scale from methanol oxidation in gas phase. This process is achieved by photocatalytic oxidation over suspension of mixed photocatalyst [11, 12].

Photocatalytic oxidation of liquid aliphatic alcohols including ethanol, propan-1-ol, propan-2-ol and butan-2-ol, as well as using a mixture of these alcohols was reported by Paul and co-workers over a suspension of TiO_2 (rutile form) and under irradiation with UV light of 366 nm at reaction temperature in the range of 275–313 K. It was found that, activation energy for the formation of corresponding carbonyl compounds was independent on type of alcohol. This observation can be argued to energy required to promote photoelectrons from valence band into the conduction band of rutile [13].

The present work describes synthesis of new substituted cobalt phthalocyanine derivatives (CoPc) using naphthalene-1,4,5, tetracarbonic acid dianhydride (NDI)and phthalic anhydride by dry process. The photocatalytic activity of the synthesized of these nano-composites was investigated by screening phtocatalytic oxidation of butan-2-ol alcohol over suspensions of these materials.

EXPERIMENTAL

Materials and instruments

Fourier transform infrared spectroscopy (FTIR) was used to investigate functional groups and chemical bonds in the samples using FTIR-8400S, Shimadzu Japan. X-Rays diffraction (XRD), D5000 XRD6000, Shimadzu, Japan, Raman spectroscopy, Senterra, high spatial and spectral resolution (Spectral Resolution: < 3cm^{-1})/Bruker (Germany), SEM instrument JEOL JSM-6700F instrument (Germany) were used. BET surface area was measured using Micrometrics, 2023, Germany. The absorbance was measured using UV-Visible spectrophotometer, Shemadzu (Japan) 1800 Double Beam, region (200-1100) nm. MWCNTs were purchased from Nanoshel–USA with a diameter of 13–18 nm, length in the range of 1 with a purity 99%. Sulfuric acid and nitric acid from (BDH), naphthalene-1,4,5, tetracarbonic acid dianhydride 99% from Alfa Aesar were used.

Synthesis of Copc/MWCNTs compound

A 0.15 g of activated multiwall carbon nanotubes was dissolved in 7 mL of DMF with stirring and heating to 76 °C under N_2 flush. Then, 2 mL of $SOCl_2$ was added to the mixture, after one hour (0.12 g.) NDI-Ph (Copc) was added with (2 mL) of triethylamine. Then, the mixture left with reflux for four hours at 110 °C. After that the mixture was filtered, and dried for 48 hours at 100 °C to yield compound Copc [14-16].

Synthesis of compound (NDI-Ph(1:1)/MWCNTs-MO) nanocomposite

Nanocomposite (NDI-Ph(1:1)/MWCNTs-MO) was synthesized by two steps: first step includes the addition of NDI-Ph compound to F-MWCNT in the mass ratios 0.50:100. F-MWCNTs dispersed into 100 mL and NDI-Ph into 20 mL of distilled water and sonicated for 30 min. NDI-Ph compound solution was added to the F-MWCNTs suspension with stirring and heated to 80 °C to evaporate the water. After that the composite was dried overnight in an oven at 100 °C. Second step consists of adding metal oxide to the NDI-Ph-F-MWCNT.

Photocatalytic oxidation of butanol alcohol over nanocomposites

In this part, photocatalytic oxidation of 2-butanol was performed over NDI-Ph-F-MWCNTs nanocomposite. The spectrophotometric method was used to determine the concentration of butanon that produced from the photocatalytic oxidation of 2-butanol alcohol. This method is based on the formation of 2,4-dinitrophenyl hydrazine carbonyl compound by taking 0.1 mL from the reaction mixture at different dosage (0.04, 0.08, 0.15, and 0.2 g) at fixed temperature 20 °C, and addition of 5 mL from the mixture of (3.7:5) of hexane:ethanol, respectively. The reaction temperature was 55 °C for 30 min to produce 2,4-dinitrophenyl hydrazine of the corresponding carbonyl compound. This solution was cooled to the room temperature, and diluted to 25 mL with alcoholic potassium hydroxide solution. This solution was mixed, and the absorbance was measured at 480 nm by using UV-Visible spectrophotometer instrument. The concentration of product was determined from the calibration curve of standard butanone solution [17, 18].

X-Rays diffraction

Crystal structure of the prepared nanocomposite was investigated using XRD technique, Phillips X-rays diffraction with CuKα radiation (1.542 Å, 40 KV, 30 MA), in the 2θ range, 10-80 degrees. XRD6000, Shimadzu, Japan. XRD data were employed to calculate the average crystalline sizes (D) by Scherer's equation in the following equation [19].

$$D = \frac{k\lambda}{\beta cos\theta}$$

where: D is the average crystal size, k is the shape factor depends on the shape of the crystal, equal to 0.89 for heterogeneous shape and homogeneous equal to 0.94 for shape, $\lambda = 0.154$ nm is the X-rays wavelength of Cu Kα, β is the full width of the peak measured at half maximum intensity and θ is the Bragg's angle of the peak, β is measured in degree and it converted into radian as follows:

$$\beta_{rad} = \beta_{deg} * \pi/180$$

Fourier transform infrared spectroscopy

Surface functional groups of the prepared materials were investigated using Fourier transform infra-red spectroscopy (FTIR), 8400S Shimadzu, Japan. FTIR spectra were recorded in the range from 400-4000 cm^{-1}, materials were mixed with powder of (KBr) in a ratio of 1.20.

Raman spectroscopy

Raman spectroscopy was used to characterize each of D and G band of carbon nanotubes and their diameter. It is a powerful method for determining the degree of structural ordering and investigating the presence of contaminants materials.

Scanning electron microscope

Surface morphology of the prepared materials was investigated using SEM instrument JEOL JSM-6700F instrument (Germany). SEM technique was also utilized in the investigation of the average particle size of the prepared composites.

RESULTS AND DISCUSSION

XRD diffraction patterns for the prepared NDI-Ph(1:1)/MWCNTs

XRD patterns for the prepared materials (NDI-Ph(1:1)/MWCNTs) are shown in Figure 1 and 2. These patterns show a strong intense peaks at (2θ = 12.215, 12.283, 17.538, 21.271, 24.606, 25.166, 26.526, 27.672, 28.081, 32.739, 33.158). In addition to that, there are a low intense peak at $2\theta = 43.3^{\circ}$. These patterns peaks are corresponding to the F-MWCNTs, and β-NDI-Ph (1:1) MWCNTs. Compared to the MWCNTs, $2\theta = 25.2^{\circ}$ and $2\theta = 44.0^{\circ}$. In general, all these peaks are shown a downhill shift due to mutual interaction among materials in these composites materials.

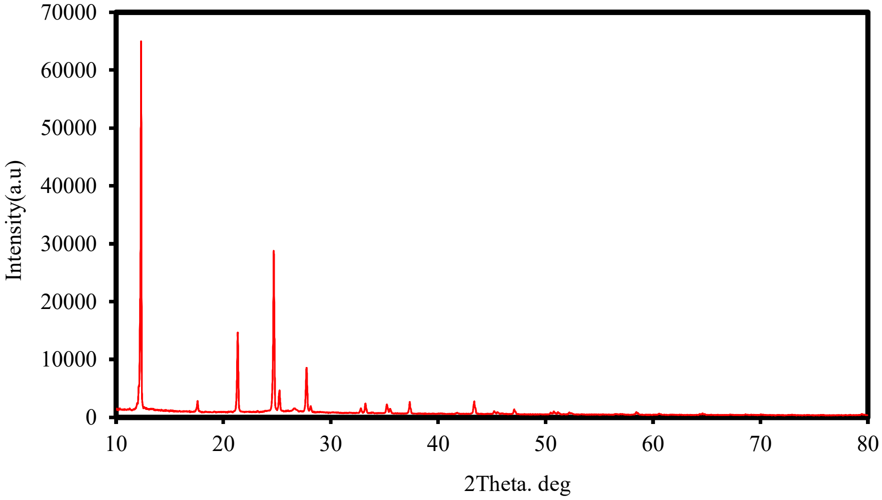

Figure1. XRD patterns for the prepared NDI-Ph(1:1)/MWCNTs.

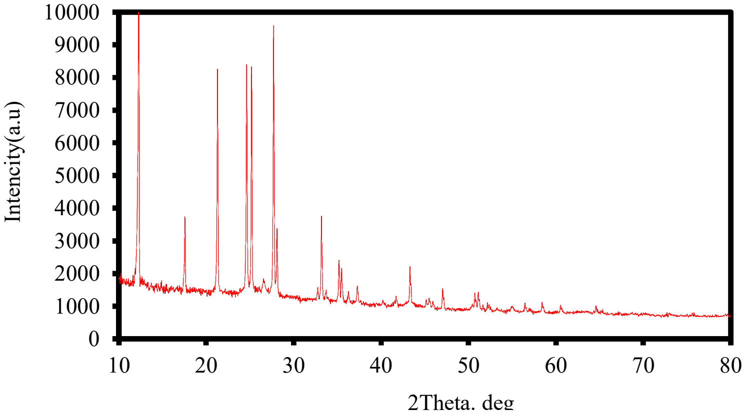

Figure 2. XRD patterns for the prepared NDI-Ph(1:1)/MWCNTs-Cr_2O_3-NiO.

XRD patterns for the prepared NDI-Ph (1:1)/MWCNTs

XRD patterns of the nano composites NDI-Ph(1:1)-MWCNTs/Cr_2O_3-NiO show an average crystalline size of 87.91 nm. XRD patterns for the prepared composites are shown in Figure 2, from these patterns it can be seen that, there is a high similarity to that of co-oxide catalysts with a slight shifting in peaks position. At 26.5°, 33.69°, 43.34° appears peak for MWCNTs. Also at (24.56°, 25.63°, 29.64°, 31.74°, 33.69°) appears peak for α-Co-Phthalocyanin when comparing with ICCD card No. 44-1994. XRD patterns for NDI-Ph(1:1)MWCNTs/Cr_2O_3-NiO show an important peaks corresponding to the β-Co-Phthalocyanin (12.248°, 17.536°, 21.267°, 24.601°, 25.165°, 26.550°, 27.686°, 28.073°, 32.727°, 33.172°) by comparing with ICCD card No.14-0948 [20, 21] .

SEM of multi-walled carbon nanotubes with NDI-phthalicanhydride (1:1), Cr_2O_3-NiO

Surface morphology of MWCNTS- NDI-phthalicanhydride (1:1), Cr_2O_3-NiO are shown in Figure 3.

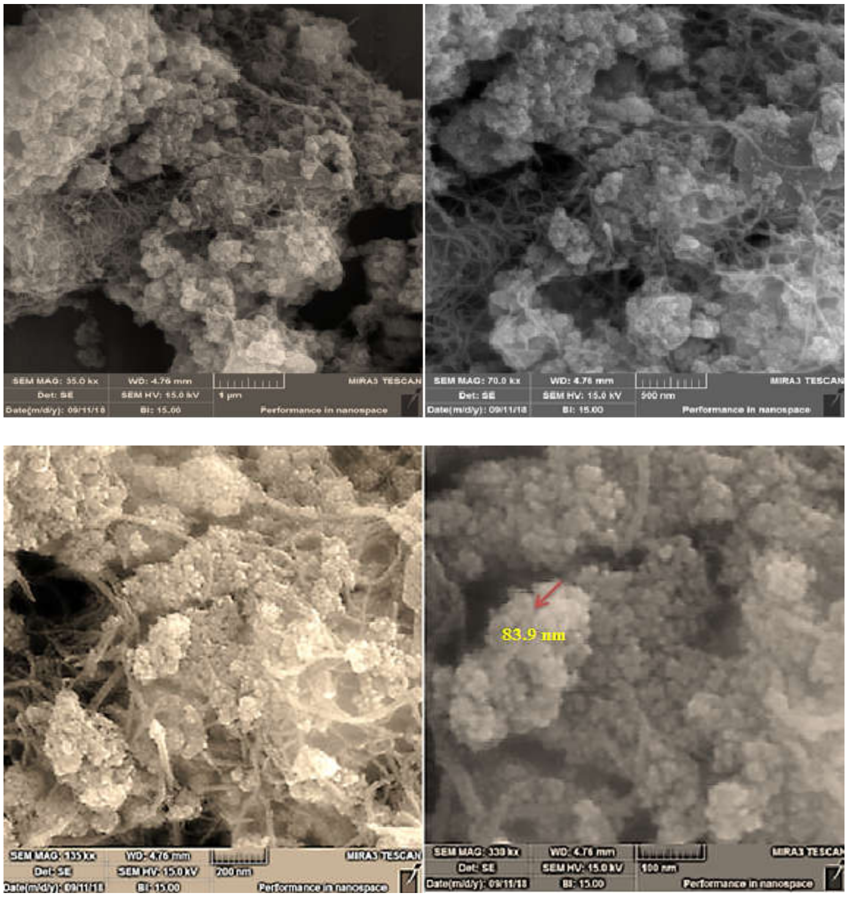

Figure 3. SEM images of F-MWCNTs-NDI-ph(1:1)-Cr_2O_3-NiO (1.0:0.5 g).

From these images it can be seen that both of tube and particles of co-oxide are present. The SEM image of nano composite shows that the MWCNTs are homogenously distributed throughout the co-oxide, and Copc matrix with an obvious agglomeration of the MO particles. Also the result of average particles size are approximately similar to that calculated from XRD patterns that was calculated by applying Sherrers equation [22].

Raman spectra of NDI-Ph(1:1)/MWCNTs-MO nanocomposite

Figure 4 shows the Raman spectrum of NDI-Ph(1:1)/MWCNTs–MO. To investigate interaction between CoPc molecules and F-MWCNTs/MO, Raman spectra can be utilized in finding interaction between F-MWCNTs and CoPc/F-MWCNTs. The peaks at (324, 459, 757, 850, and 902 cm^{-1}) in CoPc sample were obtained due to vibrations of isoindole moieties [17]. The peaks between 1200 and1600 cm^{-1} can be assigned to pyrrole groups and the bands at 1587 cm^{-1}, and 1571 cm^{-1} corresponds to cobalt ion, which is in a good agreement with that reported in previous studies [23, 24].

Raman spectra show a combination of their individual characteristic Raman peaks with a change in peak positions and their intensities. The intensity ratio of D band to the G band (ID/IG), that is represents a ratio of sp^3 hybridized carbon atom relative to sp^2 bonded carbon atom, it was around 1.07. This small variation of ID/IG ratio indicated that CoPc were attached to the surface of F-MWCNTs through a non-covalent bond. Raman spectra of CoP-F-MWCNTs/MO, NDI-PH (1:1)-F-MWCNTs/MO, exhibit the characteristic G-band around 1587, 1571 which is related to C–C vibration of the carbon material with a sp^2 orbital structure around. The peaks around 1366 cm^{-1} is associated with sp^3 hybridization carbon with defects. The peaks 2984, 2976 cm^{-1} are associated with G band of F-MWCNTs at the composite materials.

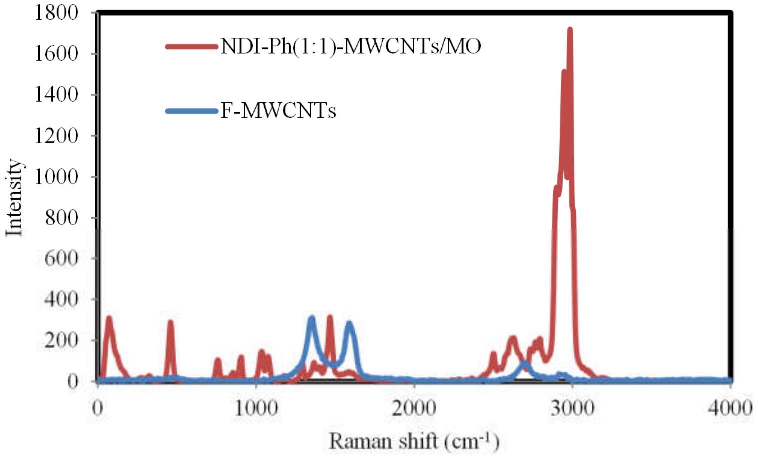

Figure 4. Raman spectrum of NDI-Ph (1:1) compounds with MWCNTs/MO.

Surface area measurement by BET method

The results of surface areas, average pore volumes and average pore diameters of the prepared NDI-phthalic anhydride (phthalocyanin)/MWCNTs-MO at different ratios are shown in Table 1. The obtained results, show decreasing of the surface area, average pore volumes and average pore diameters for the NDI-ph(1:1)-MWCNTs/MO in comparison with Copc-MWCNTs/MO. This observation is probably due to strong interaction between materials in the composite that leads to formation of chemical bonds. Also the strong interaction makes bland pores with reduces of the surface area for the Copc-MWCNTs/MO composite [24].

Table 1. Surface areas, average pore volumes and average pore diameters of the composite.

Samples	Surface area (BET)(m^2/g)	Average pore volume (cm^3/g)	Average pore diameter (nm)
Copc-MWCNTs/MO	9.000	0.980	59.568
NDI-ph(1:1)-MWCNTs/MO	33.800	0.989	93.277

FTIR of multi-walled carbon nanotubes with NDI-phthalicanhydride(1:1)- Cr_2O_3-NiO

FTIR spectra of the synthesized composites are shown in Figure5. From these spectra, the peaks of F-MWCNTs/ phthalocyanine are appeared around 3547-3392 cm^{-1} (NH_2), 2972 cm^{-1}, 2742 cm^{-1} (C-$H_{alph.}$), 1701-1697 cm^{-1} (C=O_{amide}) ,1400 cm^{-1} (C-N), 1471 cm^{-1} (C=C), 1570 cm^{-1} (C=N), metal (Co) peaks at 441 cm^{-1}, and 565,813 cm^{-1}.

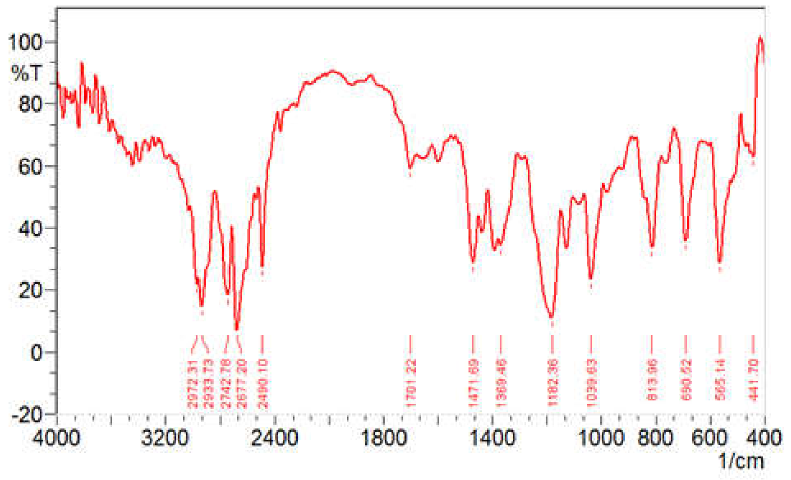

Figure 5. FT-IR spectrum of compound NDI-phthalicanhydride(1:1), Cr_2O_3-NiO.

Effect of nanocomposite weight on the photocatalytic oxidation of 2-butanol over NDI-ph(1:1)-MWCNTs/MO

The results of photocatalytic oxidation of butane-2-ol over nano composite NDI-ph (1:1)-MWCNTs/MO are shown in Figure 6. The dosage of Nano composite that were used 0.04, 0.08, 0.15, and 0.2 g., with 30 mL, 5 M of 2-butanol aqueous solution under irradiation with UV radiation at 20 °C for a period of 90 minute. From the obtained results, the best weight that gave higher efficiency for alcohol photocatalytic oxidation was 0.15 g of the used material in the reaction suspension [25]. These observations can be argued to the effect of mass of the used materials on adsorption of reacting species as well as absorption of photon of light. With increasing of material doses, this means that more photon will be absorbed from the radiation source which leads to activate more molecules of reacting species to incorporate in photoreaction. This can be seen with increasing of the efficiency of alcohol oxidation upto 0.15 g. At masses more than 0.15 g (0.20 g), it can be seen that, there is a reduction in the efficiency of alcohol oxidation. This can be attributed due to formation a dense solution which leads to formation inner filter that absorbs photons of light and prevents them from passing to other side of reaction mixture. This would lead to reduce number of molecules that can absorb photons of radiation under these circumstances. These finding are in a good agreement with that were reported in the previous works [26-28].

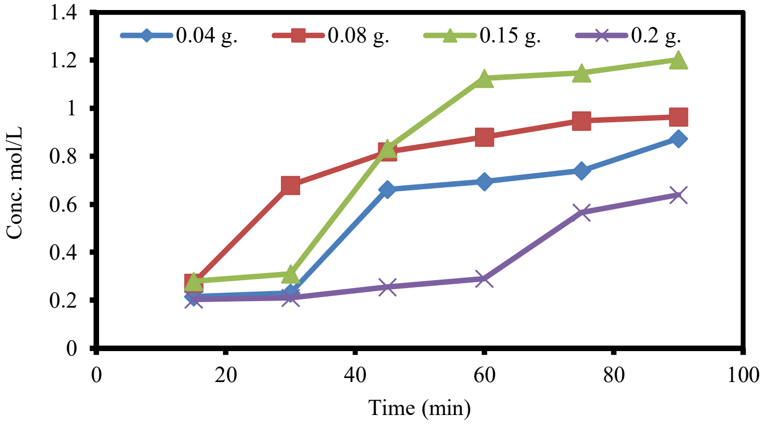

Figure 6. Photocatalytic oxidation of butane-2-ol over NDI-ph(1:1)-MWCNT/MO for different dosage at 20 ^{O}C , and time 90 min.

The first step in the photocatalytic oxidation of alcohol over used photocatalyst surface is the excitation of photocatalyst particles by absorption of ultraviolet light ($\lambda < 400$) nm. This process produces (e-h) pair in conduction band and valence band of MO particle, respectively.

These redox species are contributed in the formation of reactive radical species at the surface such as hydroxyl radical, HO_2, and $O^{\cdot}_2$ radicals. These radicals then would contribute in the dehydrogenation of the used alcohol by proton abstraction from hydroxyl group of alcohol reacting molecule. This result in formation of carbonyl compound from reacting molecules of the used alcohol. The role of MWCNTs in composite in this process is preventing back electron transfer from conduction band of MO into valence band which leads to reduce the efficiency of the photocatalytic process, in this case it can act as a sink for electrons. Then these electrons would be captured by adsorbed oxygen to produce reactive radicals that are participated in redox reaction at the surface of the composite [28, 29].

Effect of temperature on the photocatalytic oxidation of butane-2-ol over NDI-ph(1:1)-MWCNT/MO

The effect of temperature on photocatalytic oxidation of butane-2-ol was investigated at different temperatures. These are 283, 293, and 303 K with using a suspension of 0.15 g. of nano composite with constant of other reaction parameters. The obtained results are presented in Figure 7. From these results, it can be seen that, the concentration of formed butanone increases with increasing of reaction temperature. This can be attributed to the effect of temperature on adsorption/ desorption processes and increase rate of formation of free radicals with elevation of reaction temperature. Also increase of reaction temperature can effect on the amount of adsorbed particles and increase rate of diffusion of reacting species which leads to accelerate rate of conversion of alcohol to its corresponding ketone [30, 31].

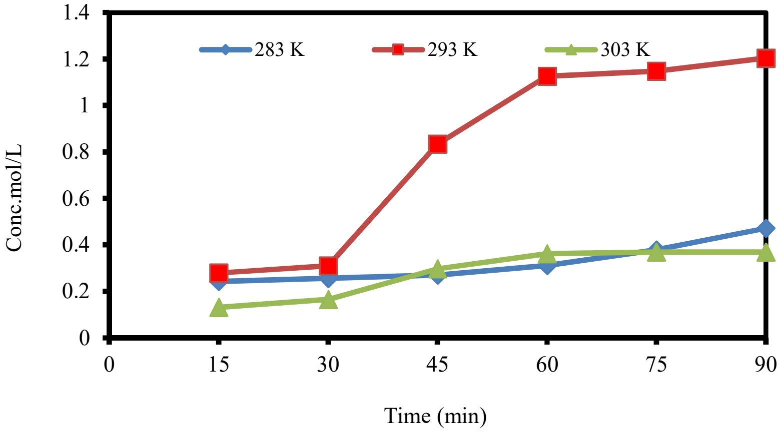

Figure 7. Effect of temperature on the photocatalytic oxidation of butane-2-ol over NDI-ph(1:1)-MWCNTs/MO.

Confirmation conversion of butane-2-ol into its corresponding 2-butnanone in a reaction mixture, this can be conducted by utilizing of FTIR spectra at the beginning and at the end of reaction time. By comparing FTIR spectrum for the two cases, it can be seen that, appearance of carbonyl group around 1620-1680 cm^{-1} in FTIR spectrum for the product mixture after 90 min, and this peak is not appeared at FTIR spectrum for reaction mixture. This observation indicate oxidation of alcohol in to its corresponding ketone [32].

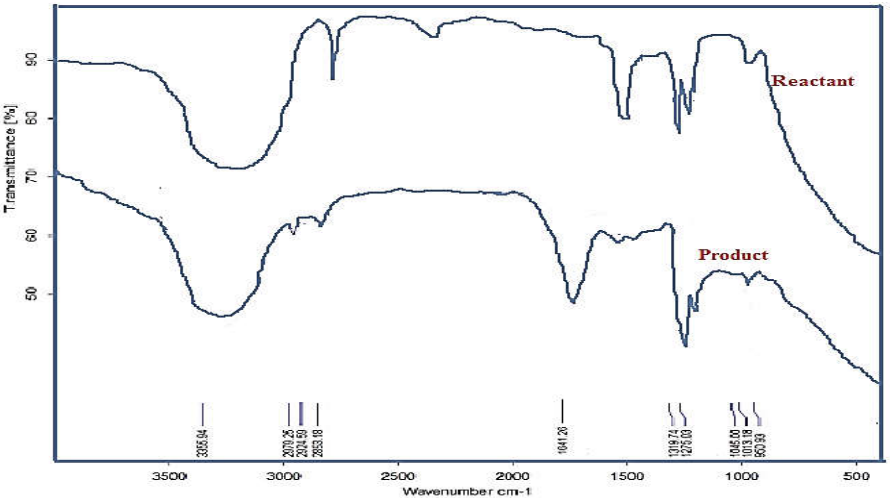

Figure 8. FT-IR spectrum of the product mixture.

CONCLUSION

From the obtained results in this study it was found that the composite of multi walled carbon nanotubes/cobalphthalocyanine was prepared successfully and it showed an efficient photocatlytic activity in conversion of 2-butanol alcohol to 2-butanone via phtocatalytic reaction over a suspension of the used materials. The efficiency of reaction was enhanced with increasing of reaction temperature with using an optimum mass (0.15 g) of the used materials.

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