Catalytic oxidation of polyphenol trihydroxybenzene by Pd-containing poly (vinyl alcohol)

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Abstract- Simple and environment friendly Pd-containing poly (vinyl alcohol) PVA catalysts were prepared by casting from their aqueous solutions. A series of PVA containing different ratios of Pd was characterized by IR, electronic spectroscopy, thermal analysis, XRD, Field-emission scanning electron microscopy (FE-SEM) and X-ray photoelectron spectroscopy (XPS). The binding of Pd to the polymer matrix and its effect on the polymer structure was studied by means of XRD, XPS and thermal analysis. The catalytic activity of the Pd-based catalysts towards the oxidation of polyphenol trihydroxy benzene was investigated and showed a significant catalytic activity in case of the polymer sample containing the lowest Pd concentration (A_1). The oxidation mechanism was proposed. Kojic acid was used to inhibit the oxidation reaction and it has been observed to be a non competitive inhibitor.

Index Terms- polymer; inorganic compound; XRD; XPS; DTA; oxidation.

I. INTRODUCTION

Poly (vinyl alcohol) PVA is a polymer with exceptional properties such as water solubility, biodegradability, biocompatibility, non-toxicity and non-carcinogenity that possesses the capability to form hydrogels by chemical or physical methods [1–4]. PVA, as semicrystalline material, exhibits certain physical properties resulting from the crystal-amorphous interfacial effect [5]. Moreover, it contains a carbon backbone with hydroxyl groups attached to methane carbons. These hydroxyl groups can be a source of hydrogen bonding, hence they assist in the formation of polymer blends [6]. PVA is well known for its wide range of potential applications in industrial, pharmaceutical, medical fields and continues to draw much attention of the researchers [7–9] due to the role of OH group and hydrogen bonds [10]. Its fields of applicability were widely broadened during the latest years due to the development of medicine, biomaterials, controlled drug release systems, environmental protection systems, new ecological systems for water purification and conductive systems for renewable energy sources, etc. [11–13]. During the latest years many research groups focused their attention on the study of PVA films or gels obtained by the simple addition of salts to the aqueous PVA solution. Very interesting properties have been obtained. Different additives are usually added to polymer in order to modify and improve its properties. Inorganic additives such as transition metal salts have a considerable effect on the optical and electrical properties of PVA polymer [14]. Palladium is one of the most catalytically versatile transition metals, its complexes being efficient catalysts for a wide range of C C coupling, C H functionalization, and hydrocarbon oxidation reactions [15–17]. The vast majority of Pd-catalyzed reactions involve Pd^0 and Pd^{2+} oxidation states and these transformations have been extensively investigated for the past several decades [16,18–21]. Pd-catalysts are widely employed both in academia and in industry, making Pd the most extensively used metal catalyst for the synthesis of a wide variety of organic compounds [22–24], including pharmaceuticals [25,26], heteroarenes [27] and natural products[28]. Palladium compounds are interesting catalysts in the field of catalytic oxidation which is widely used in a pollution control technology for removing organic compounds. Palladium has been used in the hydroxylation of benzene [29] and oxidation of alcohols [30], ketones [31] and phenol[32].

In this study, synthesis and characterization of simply prepared and environment friendly catalysts using the easily degradable PVA and a small amount of Pd ion were presented. These catalysts were used in the catalytic oxidation of polyphenol trihydroxy benzene with and without H_2O_2 at room temperature.

II. EXPERIMENTAL SECTION

2.1. Preparation of PVA-Pd samples

1.0 gm of poly vinyl alcohol (PVA) was dissolved in about 50 ml dist. water with heating and continuous stirring. To the above solution the required amount of $PdCl_2$ was added dropwise with vigorous steering and heating at ~100 °C. The solution was poured to the Petri dish and put in the oven at 80 °C for ~ 8h to get the plastic sheet. The Petri dish was put over the water bath, so the plastic sheet was easily removed and it will be ready for usage. Four samples were prepared by this simple method; the pure polymer PVA (A_0), polymer containing 0.005 wt.% Pd (A_1), polymer containing 0.01 wt.% Pd (A_2), polymer containing 0.05 wt.% (A_3).

2.2.Physico-chemical characterizations

IR spectra for PVA and PVA-Pd samples were recorded in the solid state as KBr pellet on JASCOFTIR-600 Plus with a spectral resolution of 2 cm^{-1} and accumula-tion of 100 scans at room temperature**.** X-ray diffraction (XRD) data of the samples were measured at room temperature by using a Philips diffractometer (type PW 3710). The patterns were run with Ni-filtered copper radiation ($\lambda = 1.5404$Å) at 30 kV and 10 mA with a scanning speed of $2\theta = 2.5$º/min. All electronic spectra and kinetic studies measurement were performed using Varian Cary 4 Bio UV/vis spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were obtained on a

KRATOS-AXIS 165 instrument equipped with dual aluminum–magnesium anodes using MgKα radiation as the X-ray source at a power of 150 W (accelerating voltage 12 kV, current 6 mA) in a vacuum of 8.0×10^{-8} mPa. Thermal analysis measurements (TGA, DTA) were recorded on a Shimadzu thermo-gravimetric analyzer model TGA-50H, using 20 mg samples. The flow rate of nitrogen gas and heating rate were 20 cm^3 min^{-1} and 10°C min^{-1}, respectively. Scanning electron micrographs of Pd-PVA composite films were obtained to study their morphology by an FE-SEM Quanta 200F.

2.3. Kinetic reactions for Trihydroxy-benzene (THB) oxidation

The catalytic activity of the PVA-Pd samples towards the homogeneous oxidation of trihydroxybenzene (THB) in aqueous medium at 25 °C was determined by measuring the initial rate of (THB) oxidation. The increase of the absorption at 420 nm (ε = 4583 $M^{-1}cm^{-1}$) due to the oxidation product [33] with time was obtained on a Varian Cary 3E spectrophotometer. A plot of the formation of the product with respect to time gives the initial rate. 150 μ M of the Pd incorporated in the polymer (A_1) has been used in the oxidation of different concentrations of the substrate (0.2 – 6 mM) in presence of 100 μM H_2O_2 to study the effect of THB concentration on the reaction. The rate laws were determined and rate constants obtained. The auto-oxidation rate of THB was determined under the same conditions in the absence of A_1. Inhibitions were carried out in a similar fashion as the kinetic measurements using 150 μM A_1 related to Pd^{2+} in presence of 100 μM H_2O_2 and different amounts of kogic acid and different concentrations of DMSO.

III. RESULTS AND DISCUSSION

Poly (vinyl alcohol) PVA can strongly bind with the transition metal ions because of the numerous surface hydroxyl functional groups. A series of PVA samples with different concentrations of palladium has been prepared to investigate the structure and catalytic activity of these prepared samples

3.1. Infrared spectroscopy of PVA and PVA-Pd samples

Infrared spectroscopy has been used to identify interactions in polymer chains and/or metal. The IR spectrum of the pure polymer PVA (A_0) (Fig. 1) showed two bands at 3414 and 1427 cm^{-1} corresponding to ν OH and OH bending (in plane), respectively. The band appears at 1719 cm^{-1} is corresponding to ν C=O acetate groups remained in the PVA during its synthesis [34] by hydrolysis of the poly vinyl acetate. The spectrum also, showed band at 932 cm^{-1} assigned to νC-O stretching. The band corresponding to methylene group (CH_2) asymmetric stretching vibration was detected at about 2927 cm^{-1}. By comparing the IR spectral data of the pure PVA polymer and its Pd-composites with different palladium ratios (Fig. 1), one can observe that the intensity of the band corresponding to carbonyl C=O is decreased and shifted to lower wavenumber in case of A_2 and A_3 by increasing the amount of Pd ion in the PVA polymeric matrix. This is an indication to the participation of carbonyl oxygen atom in the coordination of Pd to the polymeric matrix. At the same time the νOH band in the neat polymer PVA which appears at 3414 cm^{-1} was shifted to (3422-3347 cm^{-1}) in the Pd-polymers. The νOH band was found to be sharp in the pure polymer and

abroad in case of A_3 which may be due to the existence of water molecule accompanied by a relatively large amount of palladium coordinated to the polymer. The assumption of Pd coordination to the polymeric matrix through carbonyl oxygen atom and OH alcoholic was supported by shifting of the in plane OH bending which appear at 1427 cm^{-1} in the PVA spectrum to (1419-1412 cm^{-1}) in the Pd-PVA samples.
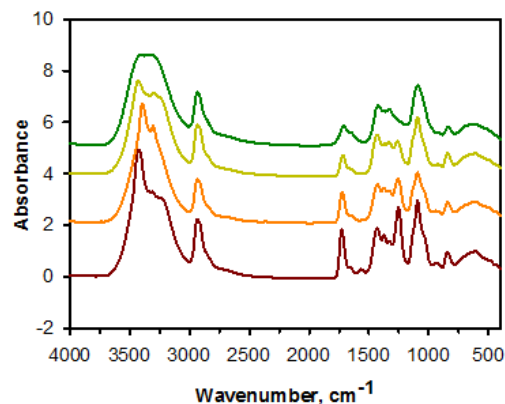

Fig. 1. IR spectra of PVA and PVA-Pd samples

3.2. XRD studies

In order to study the effect of Pd and its interaction to PVA with different ratios, wide-angle X-ray diffraction study was employed for all samples and the obtained patterns are presented in Fig.2. Generally, when the polymer contains crystalline domains, the diffraction peaks are sharp and their intensities are high whereas for amorphous polymer they are broad. From Fig.2, it is observed that the diffraction pattern of pure polymer PVA exhibits a typical peak at 2θ = 20° which can be assigned to the mixture of (1 0 1) and (2 0 0) crystalline planes [35,36]. After the addition of Pd with different ratios to PVA, the intensity of this peak was increased in case of A_1 then decreased gradually in case of A_2 and A_3 as can be seen from the XRD patterns. The crystallinity was high in case of pure PVA (A_0) due to the presence of hydroxyl groups in its side-chain. At the same time the crystallinity of A_1 may be due to that the small amount of Pd doesn't affect extensively on the hydroxyl group side chain. However in cross linked the hydroxyl groups of PVA reacted with Pd molecules resulting in a decreased crystallinity and increased amorphous domains in cross linked Pd-PVA.

3.3. Surface morphology

Field-emission scanning electron microscopy (FE-SEM) photographs of the surface morphology of the (A_1) which contains 0.005 wt.%Pd, (A_2) which contains 0.01 wt.%Pd and (A_3) which contains 0.05 wt.%Pd composites are shown in Fig. 3. The surface morphology of the A_1 composite sample shows that the Pd particles in the range of 140 – 850 nm are dispersed in the surface of the polymeric matrix. The surface morphology of A_2 and A_3 which contain a larger amount of palladium ions than that contains in A_1, show a lot of large irregular palladium particles aggregates and are randomly distributed on the top surface of A_2 and embedded in PVA matrix in case of A_3.
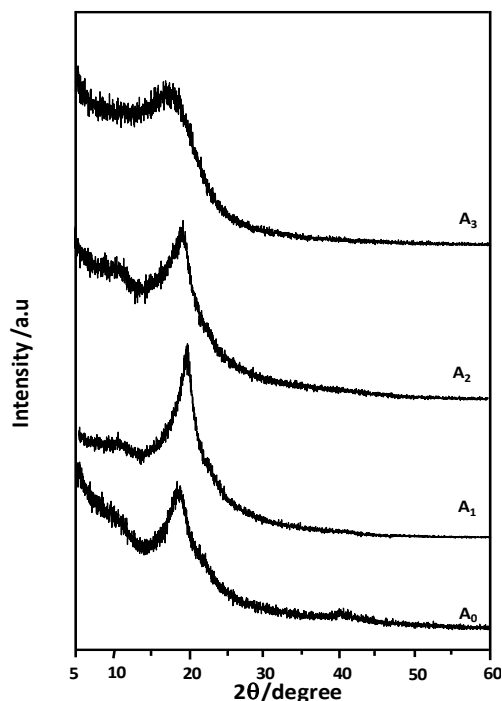
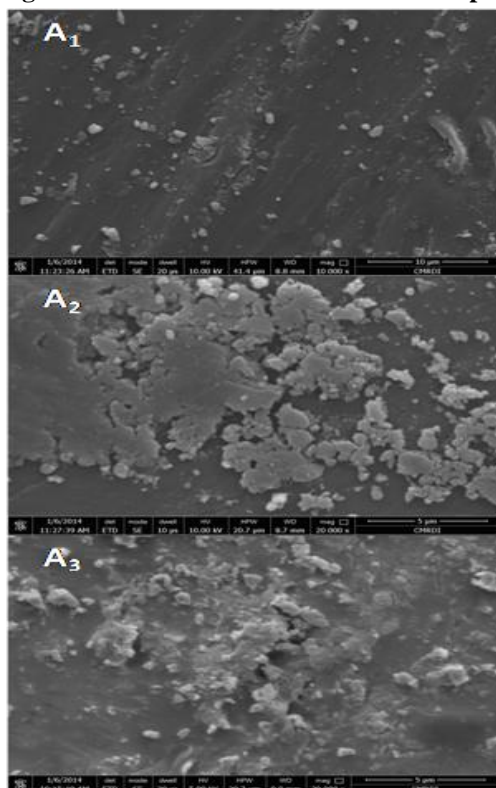**Fig. 2. XRD of the PVA and PVA-Pd samples**

Fig.3. FE-SEM photograph of the surface morphology of PVA-Pd samples

3.4. Thermal analyses

The DTA thermogram of PVA and PVA-Pd composites (not shown) reflects the phase transition of polymer composite, where the glass transition temperature Tg, is an important parameter for identifying the amorphous or the semicrystalline solids. The DTA of pure polymer PVA illustrated two distinct endothermic phase transitions at 96 and 195 ^{o}C. These transitions are corresponding to glass and melting phase transitions, respectively. On the other hand the glass transition was not observed in case of A_1, A_2 and A_3. This result indicates that the presence of Pd doesn't lead to a decrease in the overall lamellar size of the PVA. However, the presence of Pd caused a decrease in the decomposition temperature from 253 ^{o}C in A_0 to 180 ^{o}C, 165 ^{o}C and 80 ^{o}C in A_1, A_2 and A_3, respectively. This confirms a strong interaction between PVA and Pd. It is known that the crystalline nature of PVA results from the strong intermolecular interaction between PVA chains through the intermolecular hydrogen bonding [37]. Thus, it is possible that in our study the interactions between PVA chains and Pd particles led to the decrease of intermolecular interaction between the PVA chains and thus the crystalline degree [38] as shown in XRD.

TG for the pure PVA polymer A_0 and its Pd-polymers A_1, A_2 and A_3 (Fig. 4) shows inflection points within the range of 25-600 ^{o}C. The pure polymer shows four inflection stages. The first one in the rage of 56-114 ^{o}C with weight loss 4.6% is corresponding to the loss of adsorbed moisture and/or evaporation of the trapped water. The decomposition stages started with the second inflection stage at 253 ^{o}C with weight loss 59.4%. At the same time, the TG of the Pd-polymer samples shows two inflection stages. The first stage in the range of 65-120 ^{o}C with weight loss 2.6% and at the range of 78-149 oC with weight loss 4.3% for A_1 and A_2, respectively, are corresponding to removal of adsorbed water. Moreover, the decomposition process in the Pd-polymer samples started with the second inflection stage in A1 at 180 ^{o}C with weight loss 81.6% and A2 at 165 ^{o}C with weight loss 70.9%. It is noticed that the thermal degradation of sample A_3 started early with the first inflection point at 80 ^{o}C with weight loss 35.8% and finished at 460 ^{o}C. This may be due to destroying the network crossliking between the polymeric chains as a result of incorporation of more Pd in the polymeric matrix.
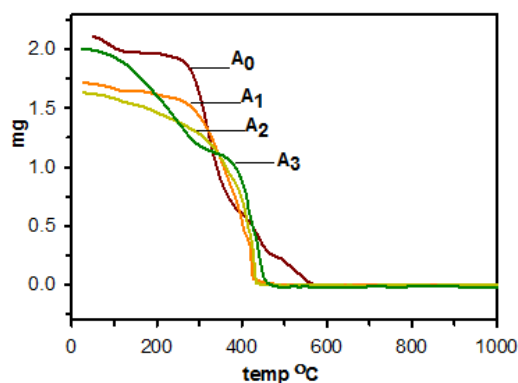

Fig. 4. TGA of PVA and PVA-Pd samples

3.5. 3.5. X-ray photoelectron spectroscopy (XPS)

To obtain information about the structural features of the PVA-Pd catalysts, X-ray photoelectron spectroscopy (XPS) studies have been performed on the neat polymer PVA and its Pd-composites.

The C 1s, O 1s and Pd 3d core level spectra have been collected and analyzed. Fig. 5 shows the C1s binding energy of

PVA at 287.88 and 284.07 ev attributed to C=O [39,40] and single C-C, respectively, [41]. The C1s binding energy for A_1, A_2 and A_3 shows no significant change in the B.E. corresponding to C-C, while the binding energy attributed to C=O appeared at higher B.E. (288.37-288.54) due to the participation of the carbonyl group in binding to Pd. XPS of A_2 and A_3 show shoulder at 286.06 and 286.02 e.v. attributed to C-O-Pd [41].
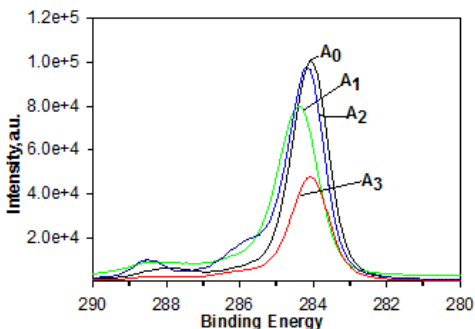

Fig. 5. C 1s XPS of PVA and PVA-Pd samples

The binding energy of O1s (Fig. 6) in the pure polymer A_0 is 531.48, while the binding energy of O1s in the A_1, A_2 and A_3 is shifted to higher B.E. (532.26-532.44). The results show that the lone-pair of electrons on oxygen atom transfers to palladium and the electron cloud density around oxygen atom decreases due to the participation of oxygen atom in the coordination to Pd atom.
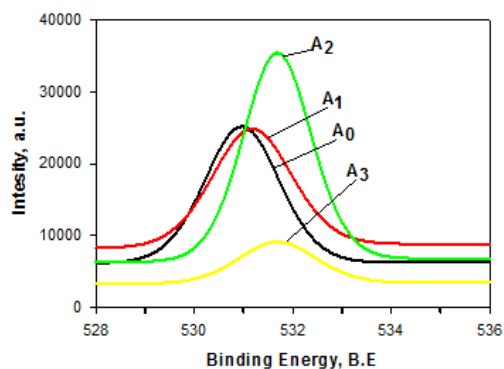

Fig. 6. O 1s XPS of PVA and PVA-Pd samples

The Pd 3d spectrum of A_2 (Fig.7) showed two peaks for the 3d5/2 and 3d3/2 components at binding energies of 335.59 and 340.69 eV, respectively. Such values for the binding energies indicate that the Pd in the A_2 are exactly the same as those of zero-valence Pd species (Pd^0) [42,43]. At the same time the Pd 3d spectrum for A_3 (Fig.7) revealed the presence of palladium in a +2 oxidation state with binding energies 336.84 eV (3d5/2) and 342.08 eV (3d3/2).

3.6. Electronic spectroscopy

The electronic spectra of the pure polymer PVA and its palladium composites (not shown) show a small peck at 270 nm attributed to n→ π* for pure polymer A_0. This band is shifted to higher wavelength at 305 nm for A_1, A_2 and A_3. The spectra of PVA-Pd show a peak for Pd^{2+} at around 423 nm, which results from ligand to metal charge transfer transition (LMCT).
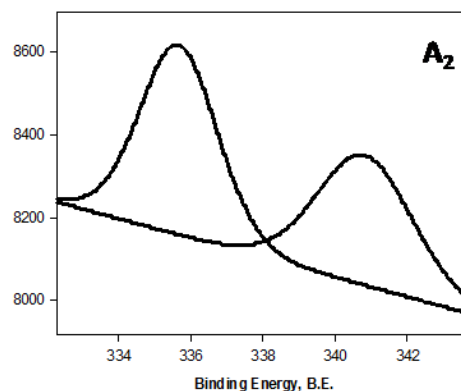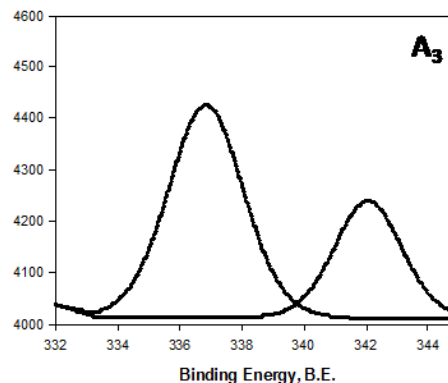

Fig. 7. Pd 3d XPS of A_2 and A_3

3.6. Catalytic reaction

   3.6.1.   Oxidation of trihydroxy benzene THB

Hydrogen peroxide constitutes a potentially green and environmentally friendly oxidant because it releases only water as a by-product. Thus, many efforts have been put into the research for ideal conditions for its use in oxidation reactions. In this study, the simply prepared and easily degradable Pd-PVA samples, with and without hydrogen peroxide, were used in an aqueous medium and at room temperature in the oxidation of polyphenol trihydroxybenzene. THB has been employed as a substrate to investigate the catalytic activity of the Pd-PVA samples towards the oxidation of polyphenol compound. The activities and reaction rates of the oxidation can be determined using electronic spectroscopy by following the appearance and increasing of the absorption maximum of the quinone. Prior to a detailed kinetic study, it is necessary to get an estimation of the ability of the pure polymer PVA (A_0) and its Pd-PVA samples towards the oxidation of THB. The pure polymer PVA showed a negligible observed rate towards the oxidation, while the A_3 showed a small observed rate of 1.5×10^{-5} mM/s. At the same time A_1 and A_2 showed the high observed rate of 0.016 and 0.13 mM/s respectively, as shown in the Fig. 8. These results revealed that A_1 which contains the lowest concentration of palladium incorporated into the polymeric matrix showed the highest catalytic activity. To determine the dependence of the rates on the substrate concentration and study the catalytic activity of A_1 and its interaction with H_2O_2 towards the oxidation of 1,2,3-trihydroxybenzene, A_1 was treated with increasing amounts of THB. A first order dependence was observed at low

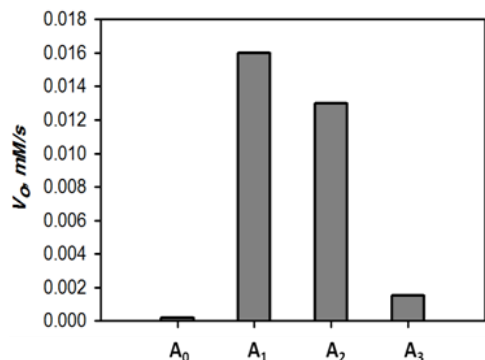concentrations of the substrate, whereas saturation kinetics was found at higher concentrations.

Fig. 8. Oxidation of THB using PVA and PVA-Pd samples in the presence of H_2O_2 at 25 °C

The oxidation rates of THB by A_1 containing 150 μM pd at different concentrations of THB (Fig. 9) were determined in the presence of 100 μM H_2O_2. The rate of THB oxidation is found to be nonlinear, reaching saturation at high THB concentrations. The oxidation reaction produces a first-order rate constant $k = 0.316$ s^{-1} ($t_{1/2} = 2.2$ s). The catalysis shows 1.2×10^5 times rate enhancement in terms of the first-order rate constant (k/k_o, wherein $k_o = 2.53 \times 10^{-6}$ s^{-1} is the rate constant for the uncatalyzed reaction. The oxidation of THB in the absence of H_2O_2 (Fig.9) showed the same trend as that has been showed in the oxidation of THB in the presence of H_2O_2 with a first order rate constant $k = 0.486$ s^{-1} ($t_{1/2} = 1.4$ s)
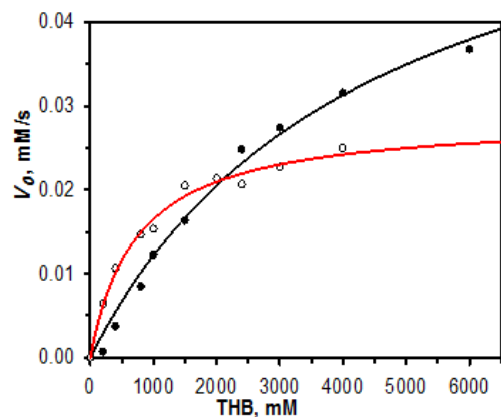

Fig. 9. Oxidation of different concentrations of THB using A_1 (●) in the absence of H_2O_2 and (○) in presence of H_2O_2

3.6.2.   Mechanism of oxidation of THB

The saturation pattern which has been observed during determination of the oxidation rates may suggest an enzyme-like pre-equilibrium kinetics. This kinetics can be described as the binding of THB with the catalyst A_1 to form an intermediate THB-A_1 complex, followed by conversion of the bound substrate (THB) into products. On the other hand, the oxidation reaction may also follow free radical mechanism. To investigate the existence of free radical in the reaction mechanism, various concentrations of dimethyl sulfoxide $(CH_3)_2SO$ have been used in the oxidation of 1.0 mM THB in presence of H_2O_2 using A_1 (Fig. 10). The free radical scavenger $(CH_3)_2SO$ [44] was found to inhibit the oxidation reaction under the experimental conditions showing $IC_{50} = 11$μL, suggesting the presence of free radical inducing the oxidation reaction of THB.
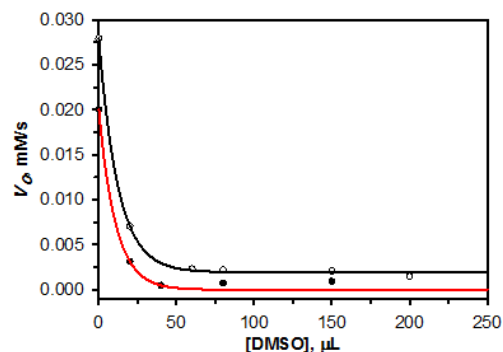

Fig. 10. Effect of DMSO on the oxidation of THB using A_1 (○) in the absence of H_2O_2 and (●)in the presence of H_2O_2.

As shown in scheme 1, THB is oxidized by Pd^{2+} to semiquinone radical (A), then, by aerobic oxidation, the semiquinone radical was oxidized to the quinone structure and superoxide radical was produced (B). The superoxide radical reacts with the hydrogen atoms to form hydrogen peroxide (C). Hydrogen peroxide oxidize Pd^0 to Pd^{2+} and is reduced producing free hydroxyl radical OH$^{\cdot}$, which is widely known as an active oxidizing agent via a single electron process (step D). The OH$^{\cdot}$ radical oxidize THB to the quinine structure (step E) and produce water molecules as side products. The observed rate constant of the THB oxidation in the presence of H_2O_2 is found to be lower than the observed rate measured in the absence of H_2O_2, indicating that the addition of hydrogen peroxide may be push the reaction (step C) somehow to the left side and decreases the formation of OH$^{\cdot}$. Upon addition of DMSO, the oxidation rate is dramatically inhibited in the absence and in the presence of H_2O_2. The inhibitory effect of DMSO on the THB oxidation may be due to the oxidation of DMSO itself to form dimethylsulfone [45] eq. 1
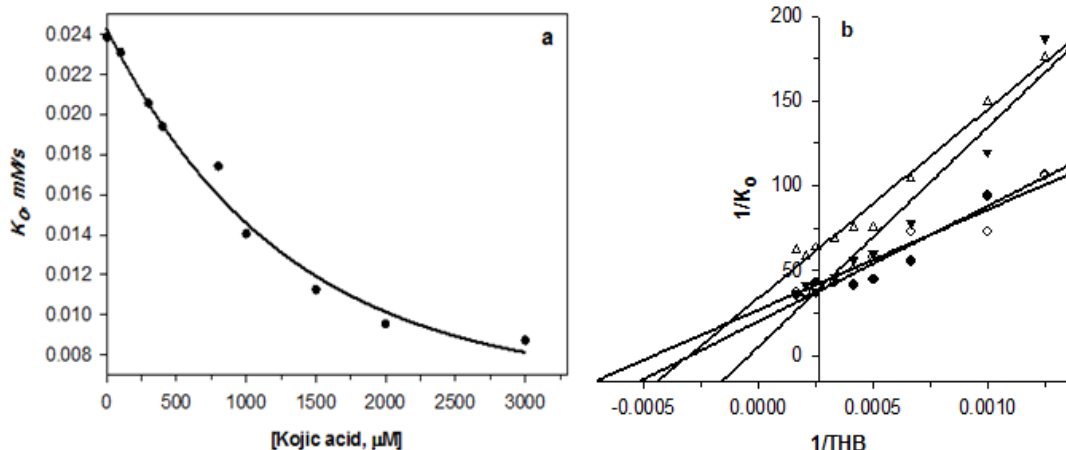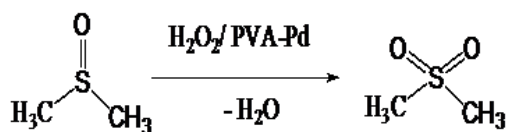
Fig. 11; (a) Inhibition of THB oxidation using kojic acid. (b) Inhibation of THB oxidation at (●) without kojic acid, (○) 300 μM kojic acid, (▼) 600 μM kojic acid, (Δ) 1000 μM kojic acid.

Eq. 1. Oxidation of DMSO using PVA-Pd in presence of H_2O_2

3.7. Inhibition of trihdyroxybenzene oxidation by kojic acid:

Since Kojic acid is a well known compound for inhibition of polyphenol oxidation [46]. It was used to inhibit A_1 complex towards oxidation of trihydroxybenzene. Fig. 11 shows that the Kojic acid inhibits the oxidation of THB with IC_{50} ~ 650 μM. The inhibitory effect of the kojic acid was studied in the oxidation of different THB concentrations. Various concentrations of kojic acid were used in the oxidation reaction in the presence of H_2O_2. Kojic acid has been observed to be a non competitive inhibitor towards the oxidation of THB (Fig 11)

3.8. Effect of temperature

The effect of temperature on the first order rate constant of the catalytic oxidation of trihydroxybenzne using A_1 in the presence of hydrogen peroxide was studied in the temperature range of 10– 50 °C. The activation energy value was calculated by using Arrhenius equation   (eq. 2):

$$\ln k = \ln A - \left(\frac{E_a}{RT}\right) \qquad (2)$$

where A is Arrhenius constant, k is the rate constant, Ea is the apparent activation energy, R is the ideal gas constant (R = 8.314 J K^{-1} mol^{-1}) and T is the absolute temperature (K). The Ea was calculated from the slope of the plot (ln k vs. 1/T), Fig. 12, and found to be 14.8 kJ/mol.
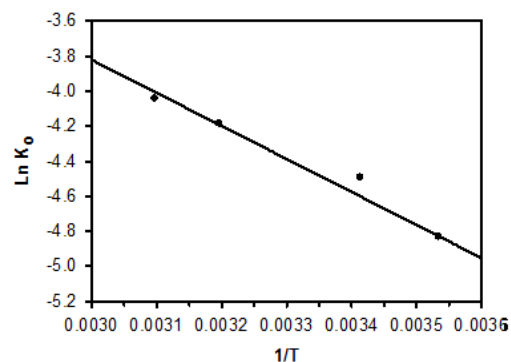

Fig. 12. Effect of temperature on THB oxidation.

This small value of the activation energy indicates that the oxidation reaction can proceed more quickly.

IV. CONCLUSION

A Series of Pd-containing poly(vinyl alcohol) was prepared and fully characterized by different tools. The Pd ion coordinated to the polymeric matrix through oxygen atoms. The Field-emission scanning electron microscopy (FE-SEM) photographs showed that the polymeric matrix contains particles in a nano scale on the surface of A_1. In case of A_2 and A_3 (FE-SEM) showed a lot of large irregular palladium particles aggregates and are randomly distributed on the top surface of A_2 and embedded in PVA matrix in case of A_3. The oxidation rate of THB using A_2 in the absence of H_2O_2 was found to be higher than the oxidation rate in the presence of the H_2O_2. Thus, the catalyst reveals an excellent catalytic system which contains a small amount of Pd and can be simply prepared. This system also can be used without H_2O_2 to give a significant catalytic activity towards the oxidation of polyphenolic compound. The oxidation reaction of THB follows the free radical mechanism and dramatically inhibited by kojic acid and DMSO.

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