

Nanocrystalline Titania catalysed oxidations of Lactic acid, Glutaric acid and Phthalic acid

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ABSTRACT

The study of carboxylic acid oxidation is required and the data may be useful for the investigations on the complete mineralization of organic substrates. Since milk and milk products, contains L-Lactic acid that are detected in appreciable amounts in the environment. Additionally it is also found in animal feed, cosmetics, milk products, vegetable products and biological samples. Such reasons cause the accumulation of carboxylic acids in the aqua environment in high concentration. Additionally, oxidations of dicarboxylic acids like Phthalic acid (PA) and glutaric acid (GA) including Lactic acid (LA) are chosen to ascertain the catalytic activity of the nano TiO₂ –NADH system. Hence, oxidation of the organic acids is an important and one among the Advanced Oxidation Processes (AOP) may be preferable. In the present work, the reaction mixture i.e. NADH and nano TiO₂, organic acid substrates are added and the progress of the oxidation is studied. The reactivity trend towards oxidation among lactic, phthalic and glutaric acid has been found out, for the nanocrystalline TiO₂ catalysis.

Keywords: Photo Catalytic Degradation; Nano Crystalline TiO₂; organic acids and NADH.

1.1 INTRODUCTION

Nicotinamide adenine dinucleotide dihydro form (NADH) is a bio precursor in every living body cell responsible in the production of ATP. It alternates between its oxidized form NAD⁺ and the reduced form NADH¹⁻⁴. In the UV – spectra the oxidation of NADH can be followed by the absorbance decrease of the 340nm characteristic wave length peak. In the presence of oxidisable organic substrates NAD⁺ is instantly converted to NADH subsequently oxidizing the substrates in the reaction mixture which can be monitored at the characteristic wavelength. With the emergence of metal nano particles as catalyst, it is well reported that NADH is catalytically oxidized to NAD⁺ in the presence of gold nano particles and many such related systems. Implementation of other metal oxide nano particles for the catalytic conversion of NADH to NAD⁺ and the subsequent oxidation of the organic substrates with the regeneration of NADH may prove to be an interesting case study. Nanocrystalline TiO₂ is a powerful photocatalytic oxidant. Nanocrystalline TiO₂ serves as a potential oxidation catalyst for many

organic substrates⁵. Also, it is assumed to use nanocrystalline TiO₂ for catalytic NADH oxidation with many reaction turn overs. Among the many organic substrates subjected to oxidation stress, carboxylic acid is commonly formed in the products and also been found in the oxidation mixture, exposed to the environment. Hence, the study of carboxylic acid oxidation is again needed and the data may be useful for the investigations on the complete mineralization of organic substrates. Since milk and milk products, wine, beer, bread and bakery goods are popularly and widely used with large consumption, largely free L-Lactic acid present in these products are detected in appreciable amounts in the environment. Additionally it is also found in animal feed, cosmetics, milk products, vegetable products and biological samples. Such reasons cause the accumulation of carboxylic acids in the aqua environment in high concentration.

Free L-lactic acid (LA) in the presence of moisture or water dimerises and the dimers do not react in the enzymatic reactions. Hence, in the presence of strong bio oxidant NAD⁺,

oxidation of lactic acid will take place proportionately, equivalently with NADH production. The consumption of NAD⁺ or generation of NADH can be quantitatively followed in the UV spectral absorbance in the 340nm peak. These transformations are non enzymatic and need stable metal oxide nano particle precursors as catalyst, and substitutes of gold nano particles. Additionally, oxidations of dicarboxylic acids like Phthalic acid (PA) and glutaric acid (GA) including Lactic acid (LA) are chosen to ascertain the catalytic activity of the nano TiO₂ -NADH system⁶. Mono and dicarboxylic acid are absorbed in high concentration in snow, rain, cloud droplets, smog and aerosols present in high concentration in urban and marine areas⁷⁻⁹. The widespread presence of organic acids consume large amount of catalysts. Hence, catalyst regenerative oxidation of the organic acids is a vital and one among the Advanced Oxidation Processes (AOP) that may be preferable. In the present work, nano crystalline TiO₂ is synthesized using combination method of Hydrothermal and Sol-Gel method. In the presence of NADH and nano TiO₂, NAD⁺ is produced. To the reaction mixture, organic acid substrates are added and the progress of the oxidation is studied. Kinetic parameters such as rate coefficient, time of completion of reactions and effect of catalytic mass are determined. The reactivity trend towards oxidation among lactic, phthalic and glutaric acid has been found out, for the nanocrystalline TiO₂ catalysis.

1.2 Kinetic studies

In the three necked round bottomed 100ml flask 1% wt of nano crystalline TiO₂ is added and 1mM NADH solution is added drop wise through one neck with continuous stirring. At every three minutes of regular intervals of time small aliquots are drawn and UV spectra taken. The absorbance of 260 nm characteristic peak of NAD⁺ increases gradually while the absorbance at 340nm of NADH peak decreases simultaneously. After few minutes, the absorbance of NADH reduces considerably to zero indicating the complete transformation to NAD⁺. At this stage, 10ml mM solution of carboxylic acid solution was added in drop with another neck of flask. At regular intervals of time, the small aliquots of the reaction mixture are drawn out and the UV spectra are taken. It is found that for lactic acid 290nm absorbance started decreasing significantly with time. Also simultaneously, the absorbance of NADH peak increased gradually. This observation confirms transformation of NAD⁺ to NADH. It is found

that the oxidation of carboxylic acid proceeded until all of the NAD⁺ has been transformed to NADH. If the concentration of NAD⁺ is higher than the complete oxidation of carboxylic acid takes place. After the completion of reaction, tiny bubbles of CO₂ in the reaction mixture cause effervescence. This ensures mineralization of organic substrate. This procedure is repeated with phthalic and glutaric acid. In the case of glutaric acid and phthalic acid 950nm and 290nm peaks are used for the kinetic information.

1.3 Kinetic analysis

In the absence of NADH addition when nanocrystalline TiO₂ and each of the organic carboxylic acid are reacted maintaining the same experimental conditions after more than 8hrs of time only 5% of the feed reactant are found to be oxidized. However when NADH solution is added to nano TiO₂, and within a few minutes (less than 3mts) of time when the carboxylic acid substrate is added, the absorbance values instantly started to decrease, indicating the progress of oxidation of carboxylic acids. In Fig 1.1, 1.2 and 1.3 the UV spectra of the three carboxylic acids (LA, GA and PA) are taken at various intervals of time of progress of reaction are presented. In Fig 1.4, the absorbance variations with time plots, of carboxylic acid degradation are given. Also the simultaneous decrease in the absorbance values of NAD⁺ proportionate to the decrease in the concentration of the carboxylic acid at constant time intervals. In Fig 1.5, the kinetic plots for rate coefficient determination by plotting OD₀/OD_t Vs time are given. In this case, NADH precursor concentration is kept in excess of 10times the concentration of the carboxylic acid, so that rate coefficient corresponds to the pseudo first order reactions. The presence of best fit linear plots in Fig 1.5, indicate the pseudo first order reaction to occur. The slopes of the linear plots, multiplied by 2.303, produce corresponding to the pseudo first order rate coefficient values. Also it is found that the rate coefficient values for the reduction of NAD⁺ corresponding to each of the three carboxylic acids are nearly the same with that of the rate coefficient oxidation of each of the carboxylic acid respectively. In the Table 1.1, the rate coefficient values of the oxidation of the three carboxylic acids are given. It may be seen that under the NADH mediated oxidative stress, lactic acid has been oxidized more efficiently than phthalic acid which is more than glutaric acid with regard to the extent of conversion.

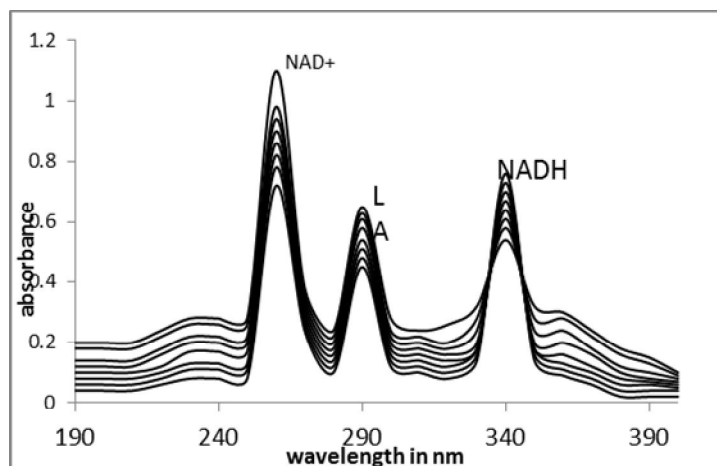


Fig. 1.1: Time dependent UV- Visible spectra of Lactic acid (LA) of 1mM concentration in the presence of nanocrystalline TiO₂ using NAD⁺ and NADH at 25°C

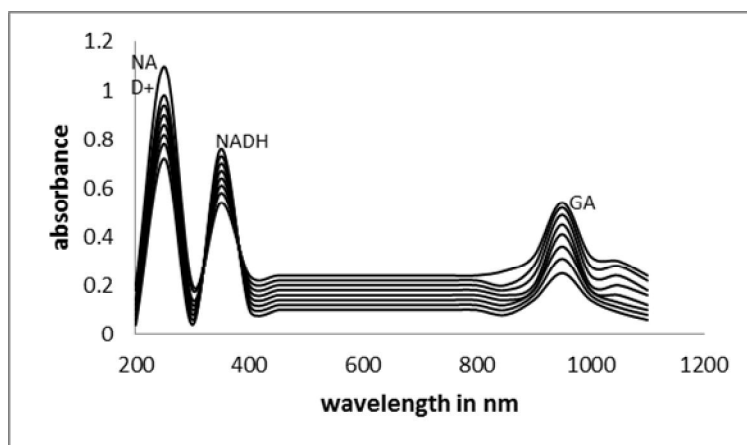


Fig. 1.2: Time dependent UV- Visible spectra of Glutaric acid (GA) of 1mM concentration in the presence of nanocrystalline TiO₂ using NAD⁺ and NADH at 25°C

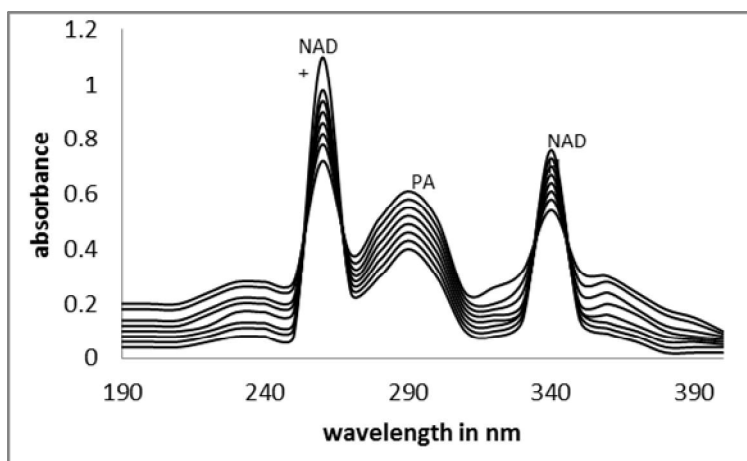


Fig. 1.3: Time dependent UV- Visible spectra of phthalic acid (PA) of 1mM concentration in the presence of nanocrystalline TiO₂ using NAD⁺ and NADH at 25°C

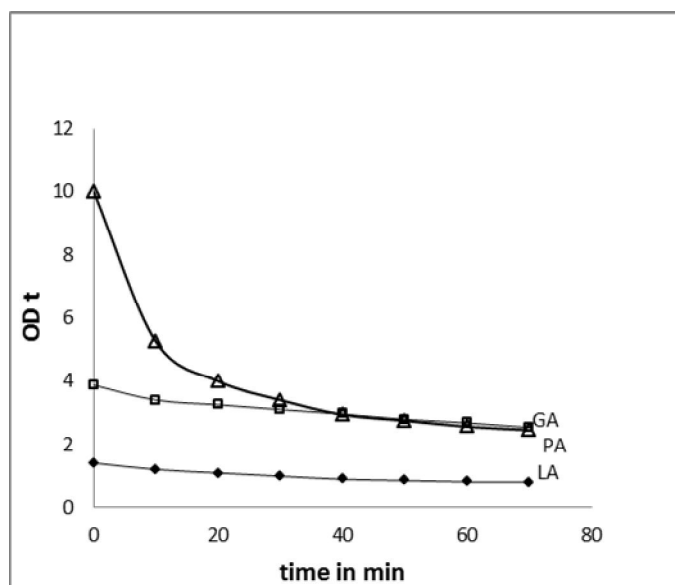


Fig. 1.4: Absorbance Vs time plots for the three drugs (Lactic acid (LA), Glutaric acid (GA) and Phthalic acid (PA) with nanocrystalline TiO₂ of 1 wt% at 25°C

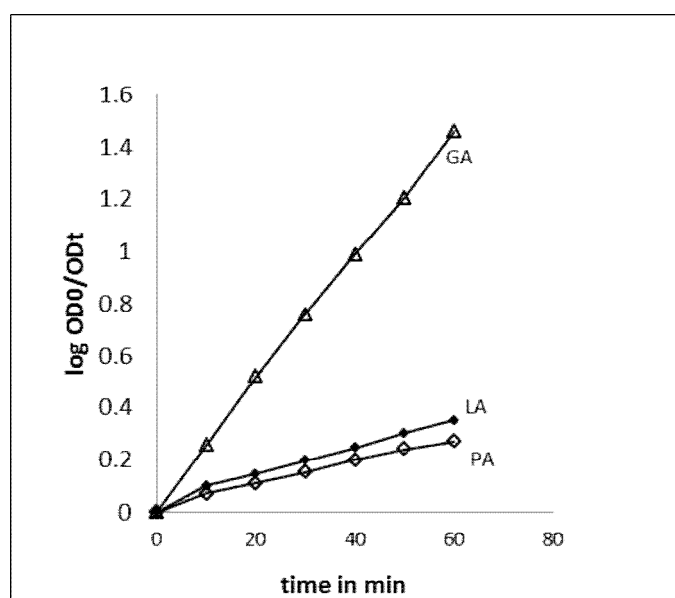


Fig. 1.5: Kinetic plots of log [OD₀/OD_t] Vs time for three organic acids LA, GA and PA in the presence of nanocrystalline TiO₂ of 1 wt% at 25°C

Table 1.1: Pseudo first order rate coefficient values of the three organic acids (LA, GA and PA) of 1mM concentration at 25°C

S.No	Name of the organic acid	k X 10 ⁻³ s ⁻¹
1	Lactic acid (LA)	1.59
2	Glutaric acid(GA)	1.22
3	Phthalic acid(PA)	5.74

Incidentally, it is found that in presence of lactic acid, the rate of NAD⁺ conversion to NADH was found to be more rapid in Lactic acid than in the

Phthalic acid, which is more than, in the case of Glutaric acid. The rate at which NAD⁺ and the lactic acid reacts determines the overall rate of

oxidation. After the completion of reaction in all the three carboxylic acid system which takes more than 2 hrs of time, it is found that NADH peak retraced with that of the original spectrum of NADH after the start of the reaction. When the tiny bubbles subsided by, cooling the reaction system in ice cold water bath, and filtered, if any organic residues are present. The filtrate is once again fed to the flask consisting of the originally added catalyst nano TiO₂. Again UV-spectroscopically the NADH conversion to NAD⁺ can be followed. At this stage, again when, a solution of carboxylic acid is

added the oxidation is found to proceed and the absorbance of the carboxylic decreased in the similar way. The number of turnovers of the reaction for 1wt% of the nano crystalline TiO₂, and 10ml of 1mM NADH solution for the oxidation of Lactic acid is found to be 6 times. In the case of phthalic and glutaric acid the number of turn over cycles are reduced to 4 and 3 respectively. This effect can be attributed to the transformations of nano TiO₂ to hydroxyl carbonates or else to the breakdown of TiO₂ nano solids.

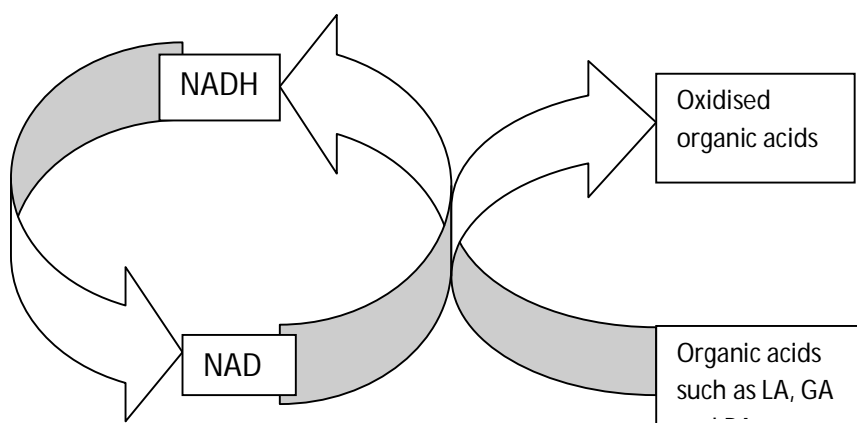


Fig. 1.7: Schematic diagram showing oxidative degradation of organic acids (LA, GA and PA) using NAD⁺

1.4 CONCLUSION

In the present work, nanocrystalline TiO₂ catalyst and NADH mediated oxidation reactions of Lactic acid, Phthalic acid and glutaric acid are kinetically studied. It is found that in the absence of NADH, only less than 2% of reaction proceeded with nanocrystalline TiO₂ during the 5hrs of reaction time. In the presence of NADH and nanocrystalline TiO₂, oxidation of lactic acid proceeded instantly and proportionately to the extent of conversion of NAD⁺ to NADH. The catalytic trend for the oxidation was found to be more efficient in the case of Lactic acid which is more efficient than phthalic acid followed by glutaric acid. Glutaric acids being an aliphatic dicarboxylic acid, longer reaction periods are required for mineralization. In the future studies, this method has been proposed to mineralize of dicarboxylic and tri carboxylic acids.

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