Synthesis of La:Co:TiO$_2$ Nanocomposite and Photocatalytic Degradation of Tartaric Acid in Water at Various Parameters

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Abstract: In this study, nanocomposites of La:Co:TiO$_2$ was prepared by the co-precipitation method. The alcoholic route of synthesis was adopted here which was gives greenish homogeneous powder of La:Co:TiO$_2$. The material was found in the nanodiamension by the SEM analysis. The rutile and anatase both phases were present in XRD analysis of the synthesized materials. The particle size was found 24 and 82 nm in case of La:Co:TiO$_2$ and pure Titania respectively. The surface area of Titania and La:Co:TiO$_2$ nanocomposites were found 6.4 and 43.2 m^2/g. The band gap energy of Titania and La:Co:TiO$_2$ nanocomposites were found 3.2 eV and 3.0 eV respectively. The photodegradation of Tartaric Acid was investigate at different parameters such as temperature, concentration, pH of reaction mixture, dose of photocatalyst and time of illumination of UV-Visible light. The photodegradation of Tartaric Acid occurs 60-80% in presence of Cobalt lanthanum modified Titania and in presence of neat Titania only 20-40% degradation was observed. It is found that photodegradation of Tartaric Acid follow the first order mechanism and its rate constant is become doubled when temperature is rise by 10°C.

Keywords: Titania, Nanocomposite, Photocatalyst, Photodegradation

1. Introduction

In photocatalysis, light is absorbed by an adsorbed substrate [1]. Today, semiconductors are usually selected as photocatalysts, because semiconductors have a narrow gap between the valence and conduction bands [2-3]. In order for photocatalysis to proceed, the semiconductors need to absorbed energy equal to or more than its energy gap. This movement of electrons forms e-/h+ or negatively charged electron/positively charged hole pairs [4-7]. The hole can oxidize donor molecules. In the photocatalysis, the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs, which generate free radicals able to undergo secondary reactions [8-13]. Its comprehension has been made possible ever since the discovery of water electrolysis by means of the titanium dioxide [14-15].

Nanoscale titanium dioxide (TiO$_2$) particles have many excellent properties, such as low cost, simple preparation, good stability, non-toxicity, and better photodegradation ability [16-20], making it a good prospect for application in solar cells [21] photocatalysis [22], and photocatalytic hydrogen production [23]. However, the wide band gap of pure TiO$_2$ nanoparticles means that they not only have low sunlight energy conversion efficiency but also a high rate of photogenerated hole and electron recombination. Therefore, improvement of the photocatalytic properties of TiO$_2$ is essential.

There are many routes to enhance the photocatalytic properties of TiO$_2$, such as metal or non-metal doping [24], compositing with other semiconductors [25], compositing with conductive materials such as graphene [26] or carbon nanotubes [27], sensitization with organic dyes and conductive polymers, such as polyaniline [28], polythiophene [29], and polypyrrole (PPy) [30].

Tartaric Acid HOOC-CH(OH)-CH(OH)-COOH, 2,3-dihydroxysuccinic acid), is a model compound from claiming a few characteristic frameworks because of its found in

plants Furthermore soils [31]. In addition to its natural abundance in the environment, Tartrate ion is often used in nanomaterials synthesis to control both the size and morphology of nanomaterials [32-33]. Because the Tartrate ion is a useful capping group that can undergo facile exchange with other functional groups, it is an important surface ligand for the preparation of a wide range of nanomaterials with complex surface functionality that can be used in a number of biomedical and sensor applications. It is an Fe (III) transport agent in living beings, an constant household and modern chelating agent utilized within those nutrition businesses What's more, over cleansers [34], Also it may be regularly utilized Likewise a lessening operator over photolytic Furthermore photocatalytic frameworks. Early reports show that Tartaric Acid may be moderately stable at close to UV-light [35], however, it will be decayed toward photolysis beneath 242 nm to items comparative should the individuals gotten under ionizing radiation [36-38]. Those accounted for last items are acetone, carbon dioxide and acetone dicarboxylic Acid (3-oxoglutaric Acid, 3-OGA), same time Acidic Furthermore acetoacetic Acids were discovered concerning illustration intermediates [39]. AOTs investigations on Tartaric Acid would not enough. Something like that far, best two reports for oxidation through UV/TiO$_2$ photocatalysis Furthermore no additives need give support to educated [40].
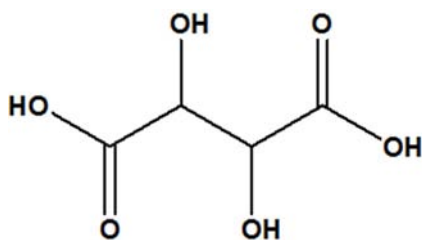

Figure 1. Structure of Tartaric Acid (2, 3-dihydroxysuccinic acid).

Over-consumption of tartaric Acid can result in unpleasant side effects. While it's unlikely that overeating foods that contain the acid will cause such side effects, those supplementing the acid in its crystalline form are at risk. Such side effects of over-consumption include increased thirst, vomiting, diarrhea, abdominal pain and gastrointestinal inflammation. People looking to lower or cease consumption of it will want to steer clear of wine, unripened fruit and any product that contains the ingredient tartrate which is a sweetener derived from tartaric acid.

Photocatalysis might have been demonstrated on being productive should damage Tartaric Acid Furthermore, other Acids for moderately secondary concentrations, concerning illustration delegates about wastewaters nearing starting with cleaning of boilers to energy plants. Degradation of Tartaric Acid (Tar) during generally secondary focuses Eventually Tom's perusing photocatalysis through TiO$_2$/ UV-light might have been tried under different states [41].

In this study, prepared the visible light active La:Co:TiO$_2$ nanocomposites by the Impregnation of La and cobalt in neat titania. The prepared nanocomposites were characterized by the XRD, SEM, TEM, UV-Vis, FTIR and BET. It is used as photocatalyst in the visible light.

2. Methods and Materials

2.1. Synthesis of TiO$_2$ and La:Co:TiO$_2$ Nanocomposite

In this study, the precursor solution was a mixture of 5ml titanium isopropoxide, TTIP and 15 ml. A 250 ml solution of distilled water with various pH was used as the hydrolysis catalyst. The desired pH value of the solution was adjusted by adding HNO$_3$ or NH$_4$OH. The gel preparation process started when both solutions were mixed together under vigorous stirring. Hydrolysis of TTIP offered a turbid solution which heated up to 60–70°C for almost 4-6 h. After being washed with ethanol and dried at 100°C in a vacuum system for 3 h, a yellow-white powder is obtained. Finally, the prepared powder was calcined at temperature 600°C for 2 h [42].

La:Co:TiO$_2$ nanocomposites were prepared by co-precipitation chemical method. In this method, 1g of prepared TiO$_2$ was dispersed in (10 ml alcohol) alcoholic solution of Cobalt acetate (100 mg) and Lanthanum Nitrate (50 mg). The dispersion is agitated continuously for 4 hour at 80°C temperature which is just below of boiling point of alcohol. After the agitation the residue will removed through filtration and dry in oven at 60°C and will sintered for 1 hour in presence of air at 500°C by kipping it in a silica crucible inside muffle furnace. After sintering and slow anilling to room temperature, The Content was taken out from furnace and was stored in closed and air tight bottles and was used as photocatalyst.

2.2. Photodegradation of Tartaric Acids

The samples of TiO$_2$ and La:Co:TiO$_2$ nanocomposites were used as photocatalyst in visible light for the photodegradation of Tartaric Acid. A 1g/L of the photo-catalyst was dispersed in the Tartaric Acid solution and the reaction mixture was illuminated with visible light by using the Tungsten lamp of 200 W, 100V while kept under agitation. The residual concentrations of Tartaric Acid were measured by titrametrically at different time intervals. In this study, investigated the photocatalytic behavior of TiO$_2$ and La:Co:TiO$_2$ nanocomposites towards photo-degradation of Tartaric Acid.

3. Result

TiO$_2$ and La:Co:TiO$_2$ nanocomposite has been Prepared and characterized and used as photocatalyst in the photo-catalytic degradation of Tartaric Acid at different parameters. The kinetic study of photodegradation of Tartaric Acid in visible light has been investigated at different parameters.

3.1. Characterization

The prepared nanocomposites were characterized by the XRD, SEM, TEM, UV-Vis, FTIR and BET. The XRD was

used to determine the phase and crystal size of the materials. The Scanning electron microscopy was used to determine the surface morphology and average particle size of the materials. The Transmission electron microscopy was used to determine the exact particle size and surface structure of the materials. The BET was used to determine the surface area, pore volume and pore radius of the material. With the help of UV-Vis spectra we can determine the band gap energy and transition involve in the material. The FTIR spectra were used to determine the functional group present in the materials.

3.1.1. Phase Identification by X-ray Diffraction Analysis

The obtained X-Ray diffraction patterns of TiO_2 and $La:Co:TiO_2$ nanocomposites are shown in Figure 2. The observed pattern of peaks, when compared with the standard JCPDS database, suggested that, in prepared TiO_2 samples, major peaks at 2θ angles 25.5, 37.2, 48.3 and 55.4^0 correspond to anatase phase, whereas major peaks at 2θ angles 26.9, 28.2, 42.6 and 54.2° indicate the presence of rutile phase. In case of $La:Co:TiO_2$ nanocomposite sample, the observed XRD pattern indicates not only a decrease in the peak intensity, compared to TiO_2, but even the absence of some originally observed TiO_2 peaks. Some peaks are slightly sifted and their theta value increased. This is, probably, due to the change in the crystallinity, grain fragmentation and partial amorphization, when the TiO_2 samples were impregnated by lanthanum and cobalt.
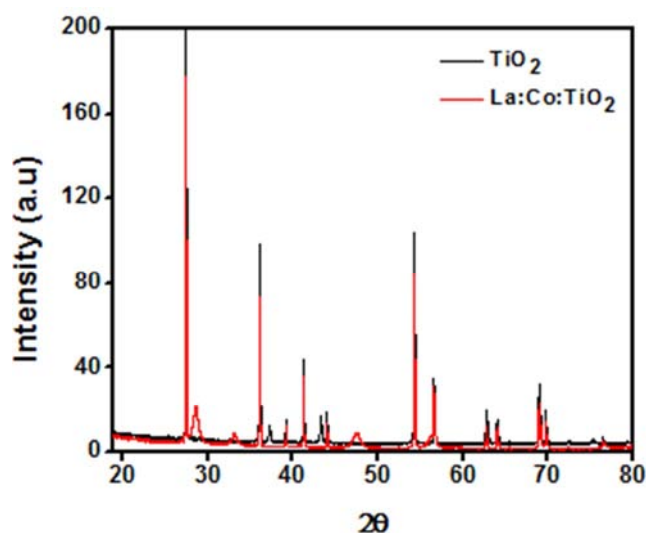

Figure 2. Observed XRD Pattern of (a) TiO_2 (b) $La:Co:TiO_2$ Nanocomposite.

Scherrer's calculations were attempted to know the average size of crystal in the samples. Although, Scherrer's calculations are only approximate in nature, but definitely provide a first-hand idea of the average size of the crystal in the samples, which may be quite accurate, provided the size of crystal is below 100 nm. The results of Scherrer's calculations are presented in Table 1. The Scherrer's formula is given in equation 1 [43]. The results suggest average size of the crystal in the samples lying in nm range.

$$B = \frac{0.9\lambda}{t\,Cos\theta} \quad (1)$$

Table 1. Average size of crystal by Scherrer's calculation.

Sample	Size of Crystal (nm)
TiO_2	82
$La:Co:TiO_2$	24

3.1.2. Scanning Electron Microscopy (SEM)

The morphology of the samples was investigated by scanning electron microscopy and it resumes the most interesting outcomes. Figure 3a and 3b clearly shows that both the prepared samples are obtained agglomerate in nanometric dimension. The impregnation of Lanthanum and Cobalt are indicating that the particle size reduce due the penetration of Lanthanum and Cobalt in the lattice of titanium dioxide.
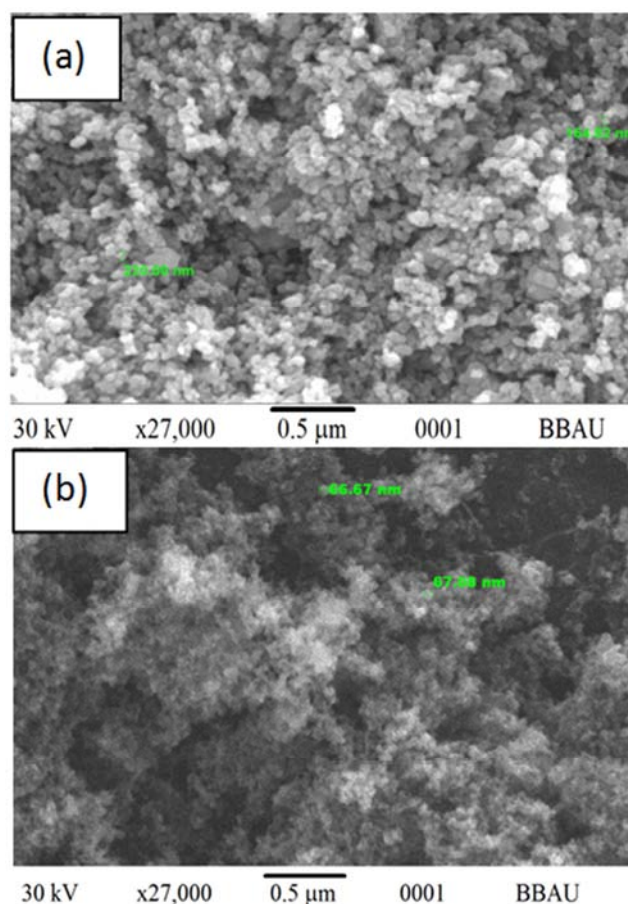

Figure 3. Observed SEM image of (a) TiO_2 (b) $La:Co:TiO_2$ nanocomposite.

3.1.3. Transmission Electron Microscopy (TEM)

TEM analysis of materials was used to examine the crystallite/particle size, morphology. The prepared TiO_2 powders consist of both cube and hexagonal shape; on the contrary, the particle of $La:Co:TiO_2$ nanocomposite has mostly hexagonal morphology. It can be estimated that the particle size of TiO_2 $La:Co:TiO_2$ nanocomposite powders in Figure (5a) and (5b) are nanoscale with the grain size less
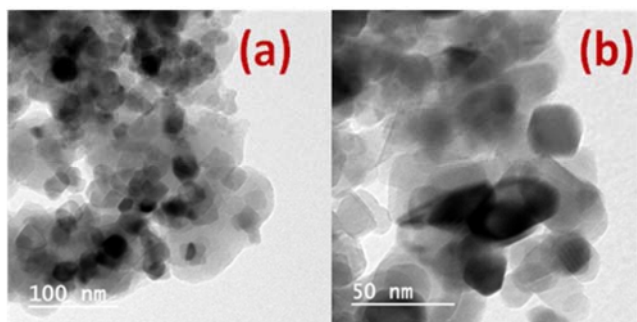
than 100 nm.

Figure 5. Observed TEM image of (a) TiO₂ (b) La:Co:TiO₂.

3.1.4. Surface Area Analysis (B.E.T)

The specific surface area, pore volume and average pore size of the TiO_2 and $La:Co:TiO_2$ nanocomposite prepared photocatalyst were characterized by using the N_2 adsorption technique *BET (belsorp Japan)*. Figure 6 shows the adsorption desorption plot for the TiO_2 and $La:Co:TiO_2$ nanocomposite and Table -2 summarizes their physical properties. The TiO_2 modified by Lanthanum and Cobalt are fragmentized to some extent during thermal treatment, leading to a marked increase of the surface areas and the average pore radius size and decreasing of the pore volume [44].
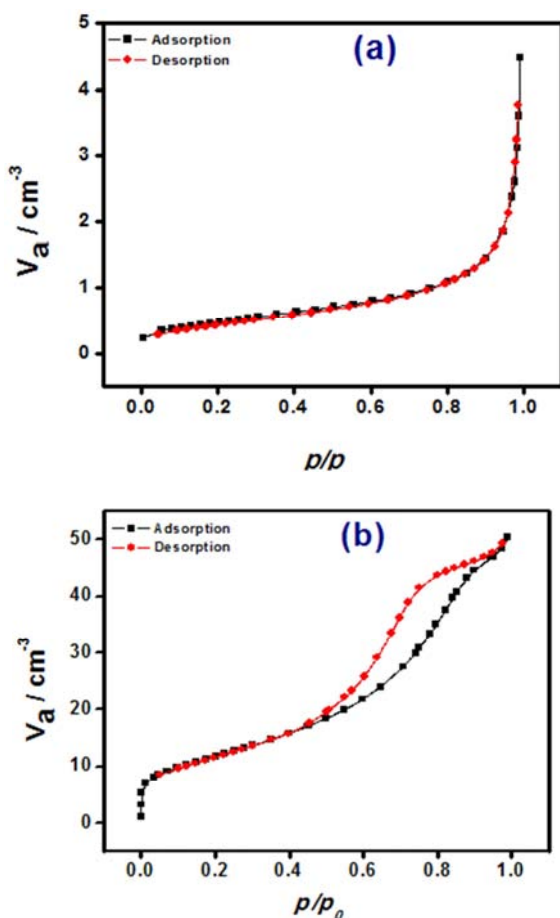

Figure 6. Adsorption desorption plot of the (a) TiO₂ (b) La:Co:TiO₂.

Table 2. *Phase ssurface area, pore volume, pore radius of TiO_2 and $La:Co:TiO_2$.*

Sample	Surface area (m²/g)	Pore volume (cm³/g)	Pore radius (nm)
TiO_2	6.4	0.018	11
$La:Co:TiO_2$	43.2	0.031	6

3.1.5. UV-Vis Diffuse Reflectance Spectroscopy (DRS)

The absorption spectrum of TiO_2 consists of a single broad intense absorption around 300 nm due to the charge-transfer from the valence band to the conduction band [45]. Figure.7. shows the absorbance of prepared samples. The undoped TiO_2 showed absorbance in the shorter wavelength region while $La:Co:TiO_2$ nanocomposite results showed a red shift in the absorption onset value in the case of La and Ni impregnated Titania. The impregnation of La and Co ions into TiO_2 could shift its optical absorption edge from UV into visible light range, due to prominent change in TiO_2 band gap was observed [46]. Aqueous suspensions of the samples were used for the UV absorption studies. The blue shift that is observed in the absorption spectra with the decrease in particle size has been reported earlier [47].
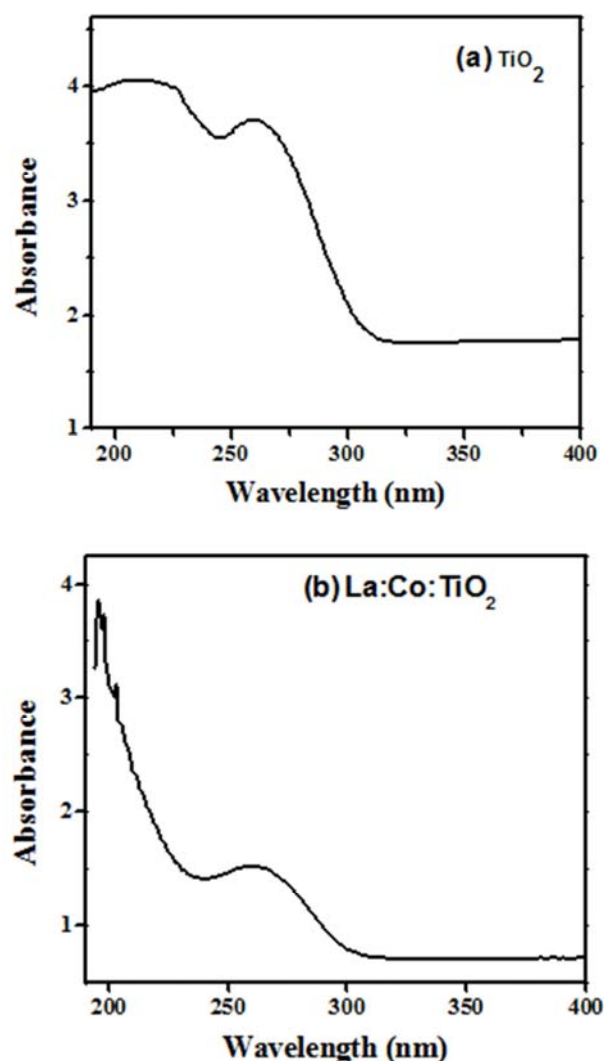

Figure 7. UV- Vis. Spectra of (a) TiO₂ (b) La:Co:TiO₂.

3.1.6. Band Gap Energy Determination

The band gap of TiO_2 as calculated from the extrapolation of the absorption edge onto the energy axis is 3.2 eV and this is well reported. Figure 8 shows the $(\alpha h\nu)^2$ versus $h\nu$ for a direct transition, where α is the absorption coefficient and $h\nu$ is the photon energy, $h\nu = (1239/\lambda)$ eV, where λ is the wavelength in nanometers. The value of $h\nu$ extrapolated to $\alpha = 0$ gives an absorption energy, which corresponds to a band gap Eg. The extrapolation of graph yields an Eg value of 3.2 eV which is in fact the band gap of Titania. But for the sample of $La:Co:TiO_2$ nanocomposite the indirect plot yield band gap values of 3.0 eV [48]. The band gap energy is decrease in $La:Co:TiO_2$ nanocomposite because the lanthanum and Cobalt forms a sub band level between valence band and conduction band.
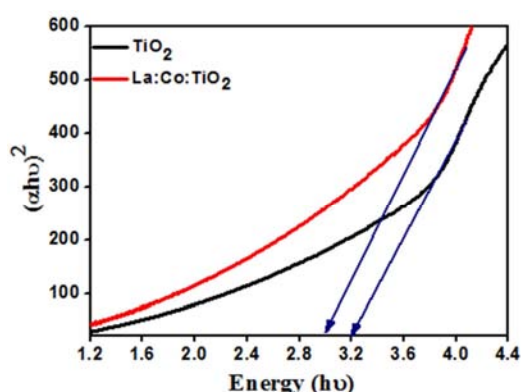

Figure 8. Band Gap energy of (a) TiO_2 (b) $La:Co:TiO_2$.

3.1.7. FT-IR Spectroscopy

FT-IR spectra of undoped and 5.0% La and 10.0% Co impregnated TiO_2 samples (Figure. 9) show peaks corresponding to stretching vibrations of the O-H and bending vibrations of the adsorbed water molecules around 3350-3450 cm^{-1} and 1620-1635 cm^{-1}, respectively. The broad intense band below 820, 804, 592 and 456 cm^{-1} is due to Ti-O-Ti vibrations The shift to the higher wave numbers and sharpening of the Ti-O-Ti band from "a" to "b" in Figure. 9 may be due to decrease in size of the catalyst nanoparticles. In addition, the surface hydroxyl groups in TiO_2 increase with the increase of La and Co loading, which is confirmed by increase in intensity of the corresponding peaks.
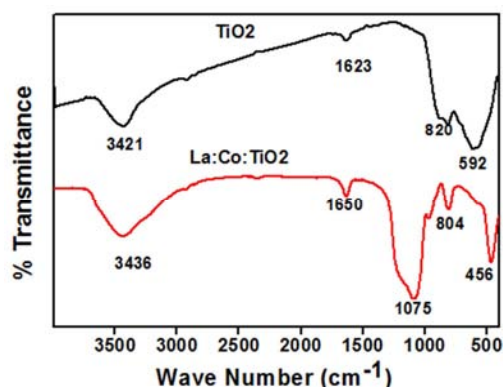

Figure 9. FT-IR Spectra of (a) TiO_2 (b) $La:Co:TiO_2$.

The FT-IR spectra shows strong band at 1075 cm^{-1} corresponds to the vibration of Co–O bond and it is confirm the penetration of Lanthanum and Cobalt in Titania [49].

3.2. Photo-Degradation of Tartaric Acid

In this study, photo-catalytic degradation of Tartaric Acid was investigated. The measured values of residual concentration of Tartaric Acids in the reaction mixture at different times of illumination (or reaction time) have been shown in Figures 11-13. It is clear from the results shown that both TiO_2 and $La:Co:TiO_2$ nanocomposites are proving as an effective photo-catalyst for the degradation of Tartaric Acids. However $La:Co:TiO_2$ nanocomposite seems to be more effective as photo-catalyst for the degradation of Tartaric Acid [50].

3.3. Factors Affecting Photodegradation of Tartaric Acid

Photodegradation of Tartaric Acid is affected by the temperature of reaction, pH of the solution, the concentration of Acid, Amount of photocatalyst, type of photocatalyst and time of illumination of radiation. In this study, we are investigating the factors which are affecting the photodegradation of Tartaric Acid.

3.3.1. Effect of Temperature

In present research, it is found that the temperature has a great effect on the photodegradation of Tartaric Acid. The photocatalytic efficiency can be increased about 2-3 times if the temperature increased from 30°C to 40°C Because the solar energy include UV light, which can be used to activate the photocatalytic course, which is increase the temperature of photocatalytic system. The experiments showed that Tartaric Acid cannot be photodegraded if TiO_2 or UV light was not used, indicating that Tartaric Acid cannot be pyrolyzed by heating with the heating temperature which was less than 40°C and self degraded by absorbing irradiation. Only when TiO_2 and UV light were both used, the Tartaric Acid was efficiently degraded shown in Figure.10. The obvious decrease of concentration of Tartaric Acid shows that the TiO_2 and $La:Co:TiO_2$ nanocomposite can serve as an effective photocatalyst [51].
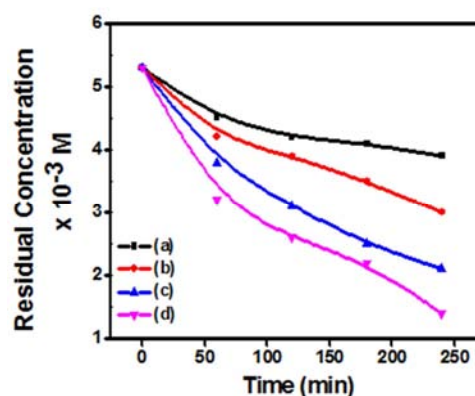

Figure 10. Effect of temperature on Photodegradation of Tartaric Acid (a) TiO_2 at 30°C (b) TiO_2 at 40°C (c) $La:Co:TiO_2$ at 30°C (d) $La:Co:TiO_2$ at 40°C.

3.3.2. Effect of Concentration of Tartaric Acid

Effect of carboxylic Acid concentration Keeping the catalyst loading constant at 1g/liter of the Acid solution, the effect of varying amounts of the Acid was studied on its rate of its degradation (from 3.4×10^{-3} to 1.5×10^{-3} M) as given in Figure 10-13. With increasing concentration of Tartaric Acid the rate of degradation was found to decrease. This is because as the number of Acid molecules increase, the amount of light (quantum of photons) penetrating the Acid solution to reach the catalyst surface is reduced owing to the hindrance in the path of light. Thereby the formation of the reactive hydroxyl and superoxide radicals is also simultaneously reduced. Thus there should be an optimum value maintained for the catalyst and the Tartaric Acid concentration, wherein maximum efficiency of degradation can be achieved [52].
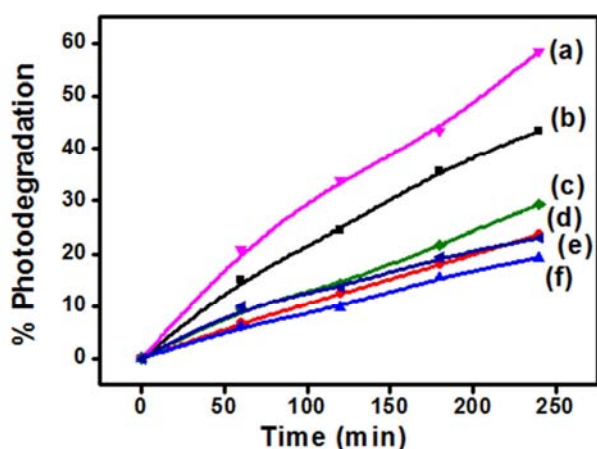

Figure 11. *Effect of Concentration on photodegradation of Tartaric Acid (a) 1.32×10^{-3} M with La:Co:TiO$_2$ (b) 1.32×10^{-3} M with TiO$_2$ (c) 2.65×10^{-3} M with La:Co:TiO$_2$ (d) 2.6×10^{-3} M with TiO$_2$ (e) 5.3×10^{-3} M with La:Co:TiO$_2$ (f) 5.3×10^{-3} M with TiO$_2$.*

3.3.3. Effect of Photocatalyst

It is clear from the results shown in Figure 10-13 that both TiO$_2$ and La:Co:TiO$_2$ nanocomposites are proving as an effective photo-catalyst for the degradation of Tartaric Acids. However La:Co:TiO$_2$ nanocomposite seems to be more effective as photo-catalyst for the degradation of Tartaric Acids. The prominent degradation of Tartaric Acids was found in 3 hour study in the presence of La:Co:TiO$_2$ nanocomposites in comparison to the prepared TiO$_2$. This is because the surface area of La:Co:TiO$_2$ nanocomposites are greater than TiO$_2$. Hence La:Co:TiO$_2$ nanocomposites is absorbing the more photon on its surface than TiO$_2$ [54]. Hence the adsorption of Tartaric Acid molecule on the surface of photocatalyst increased and photodegradation of Acid become increase.

3.3.4. Effect of pH

The photodegradation reaction was also carried out under varying pH conditions from (2 to 7), by adjusting with NaOH, with TiO$_2$ kept at constant amounts of 200 mg in 20 ml of tartaric acid solutions. The reaction was found to have low rates at neutral ranges of pH. While at lower cases it was

found to increase at 2 to 3 pH. The photodegradation is maximum at 2-3 pH, but at 6 pH the photodegradation is rapidly decreasing and after increasing pH the photodegradation slightly increase (Figure 12). This implies that acidic conditions are favourable towards the formation of the reactive intermediates that is hydroxyl radicals is significantly enhanced, which further help in enhancing the reaction rate. On the other hand in neutral medium conditions the formation of reactive intermediates is relatively less favourable and hence less spontaneous.
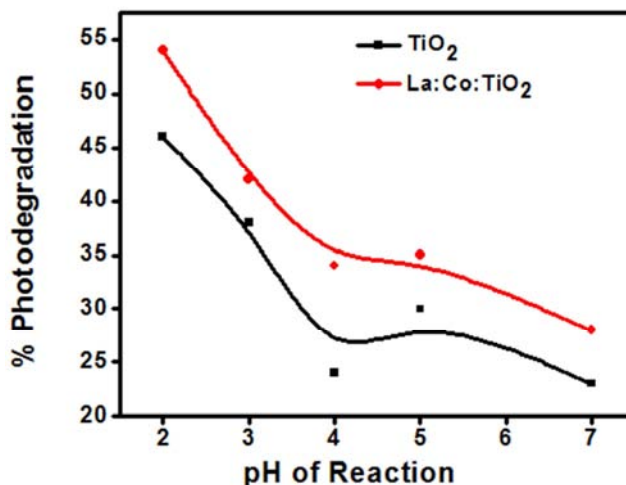

Figure 12. *Effect of pH on photodegradation of Tartaric Acid with photocatalyst.*

3.3.5. Effect of Photocatalyst Amount

It is clear from the results shown in Figure 13 that both TiO$_2$ and La:Co:TiO$_2$ nanocomposites are proving as an effective photo-catalyst for the degradation of Tartaric Acid. But when the amount of photocatalyst increases the photodegradation of Tartaric Acid also increase, because the number of active site increases.
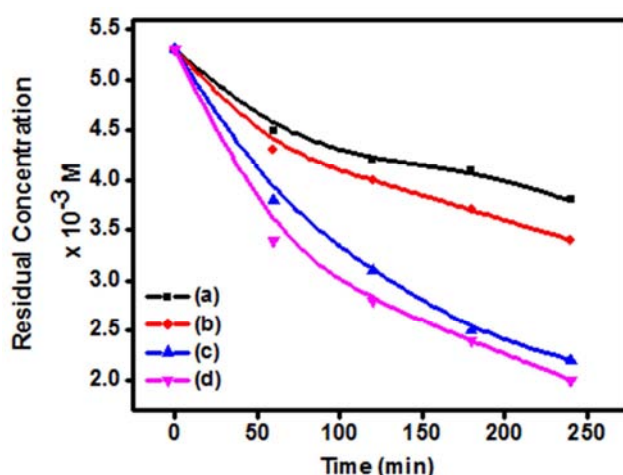

Figure 13. *Photodegradation of Tartaric Acid at different amount (a) at 20g/l with TiO$_2$ (b) at 40g/l with TiO$_2$ (c) at 20g/l with La:Co:TiO$_2$ (d) at 40g/l with La:Co:TiO$_2$.*

It is observed that La:Co:TiO$_2$ nanocomposites is the more effective photocatalyst than neat TiO$_2$ because the

La:Co:TiO$_2$ nanocomposites have large surface area and low band gap energy than the titania. It is shown in Figure 13.

3.4. Recyclability of Photocatalyst

The photocatalyst recyclability has been studied. The photocatalyst and Tartaric Acid mixture was agitated, illuminated with UV-Visible light and after desired time, the mixture was centrifuge to remove the photocatalyst. The obtained photocatalyst washed three times with distilled water and finally kept in oven for 24 h at 60°C temperature and further it is reuse for the degradation of Tartaric Acid.
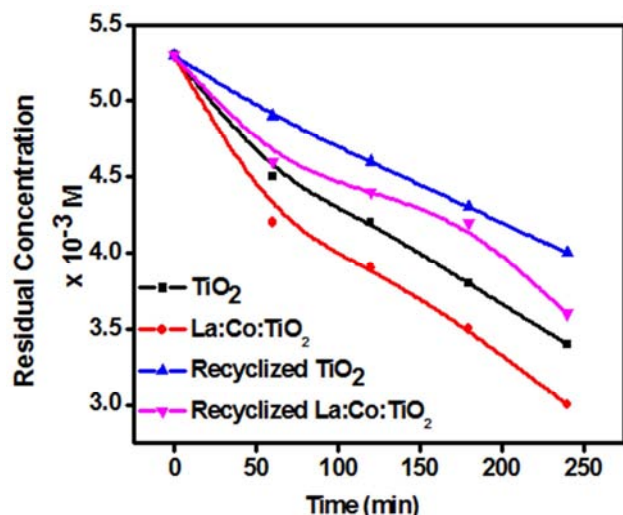

Figure 14. *Photodegradation of Tartaric Acid by recyclable Photocatalysts with time.*
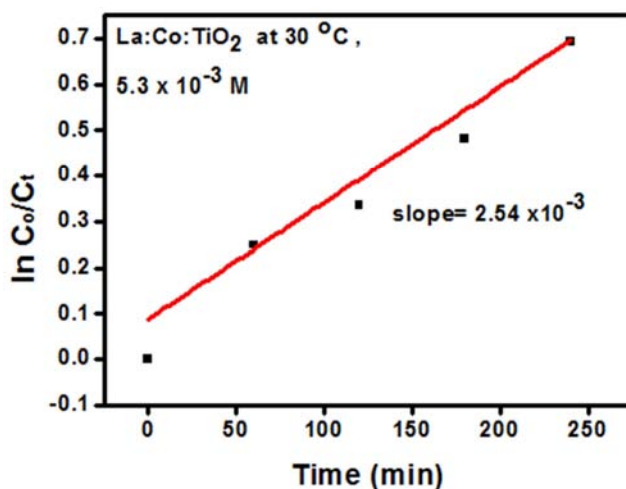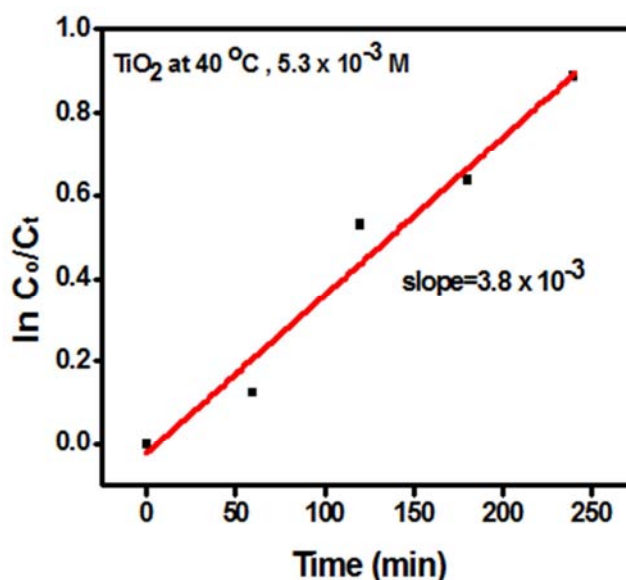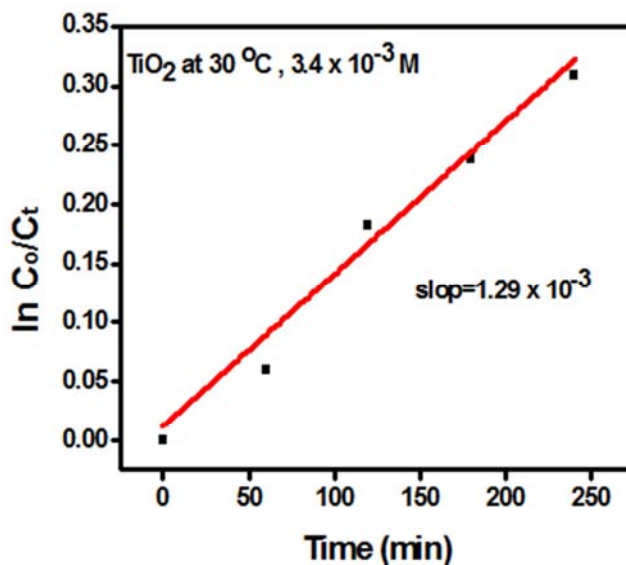
The photodegradation of Tartaric Acid by the recyclized Photocatalyst are showing in Figure 14. The result shows that the recyclized photocatalyst efficiency is decreased due to the lost of some active sites and decrease of collection efficiency of photon.

3.5. Kinetic Study

The pseudo-first-order rate constant (k, min^{-1}) for the photodegradation reaction of Tartaric Acid was determined through the following relation where, k can be calculated from the plot of ln (C_o/C_t) against time (t), C_0 and C_t denote the initial concentration and reaction concentration, respectively.

$$\ln C_o/C_t = k_1 t \qquad (2)$$

In addition, the linear feature of plots of ln (C_o/C_t) versus time (Figure 15) indicates that this photocatalytic degradation reaction follow the pseudo-first-order rate law [55]. The rate constant depends on temperature. If we increase 10°C temperatures then the rate constant becomes double or triple. Table.3 showing the effect of temperature on rate constant for synthesized Titania and La:Co:TiO$_2$ nanocomposite but in case of La:Co:TiO$_2$ nanocomposite the rate constant is greater than Titania.
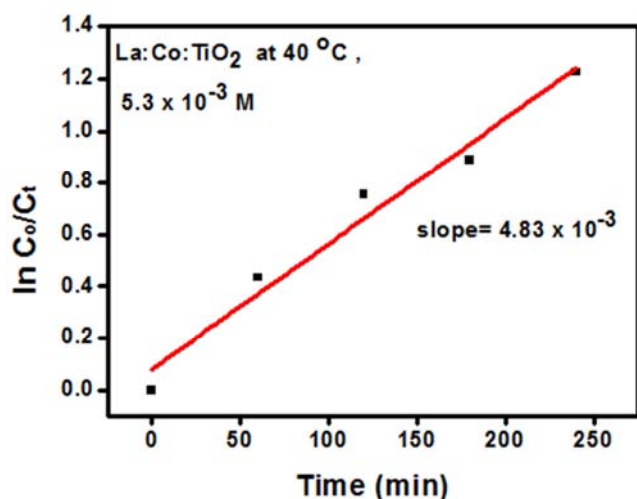
Figure 15. *Concentration Vs time graphs for the determination of rate constant K (slope value) at different temperature and concentration (a) TiO2 at 30°C, 5.3 x 10-3 M (b) TiO2 at 40°C, 3.4 x 10-3 M (c) La:Co:TiO2 at 30°C, 5.3 x 10-3 M (d) La:Co:TiO2 at 30°C, 5.3 x 10-3 M.*

Table 3. *Effect of temperature on rate constant.*

Photocatalyst	Temperature	Rate constant (min^{-1})
TiO$_2$	30°C	1.29 x 10^{-3}
TiO$_2$	40°C	3.8 x 10^{-3}
La:Co:TiO$_2$	30°C	2.54 x 10^{-3}
La:Co:TiO$_2$	40°C	4.83 x 10^{-3}

4. Conclusions and Discussions

In the present study, prepared the nanocomposites of Titania by chemical method and photocatalytic degradation of Tartaric Acid in the presence of nanocomposites of Titania and La:Co:TiO$_2$ was done. The prepared material was subjected to XRD analysis which gives the rutile and anatase both phases were present in the prepared sample. SEM analysis also proves that material was in nano dimension. Applying the Scherrer's calculations through which particle size was found 24 and 82 nm in case of La:Co:TiO$_2$ nanocomposite and pure Titania respectively. The prepared sample of Titania and La:Co:TiO$_2$ nanocomposite was subjected to photocatalytic degradation of Tartaric Acid was done. The prominent degradation was found in case of La:Co:TiO$_2$ nanocomposites. The photodegradation of Tartaric Acid investigated at various parameters, such as pH, Concentration, temperature, photocatalyst nature and amount of photocatalyst. The photo catalytic degradation of Tartaric Acid follows the pseudo-first-order rate law.

Acknowledgements

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