

Synthesis of Ni-TiO₂ Nanocomposites and Photocatalytic Degradation of Oxalic Acid in Waste Water

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ABSTRACT: Titania is one of the mostly used photocatalyst because of its high oxidative power, stability, and non-toxicity. Prepared nanocomposites of nickel titania by solution impregnation method. The pure TiO₂ and Ni-TiO₂ were analyzed by XRD for phase and particle size determination, SEM for the Morphology determination, BET for the surface area determination, UV-Vis Spectra for the band gap determination and FT-IR for the molecular bonding determination. XRD confirm the rutile and anatase both phases were present in nanocomposites of TiO₂ and Prepared Ni-TiO₂. The particle size were found 35 and 80 nm in case of Nickel titania and pure titania respectively by applying Scherer's calculation. SEM analysis confirms that TiO₂ and Prepared Ni-TiO₂ were in nanodimension. BET analysis was performing to determine the surface area, pore volume and pore radius of the titania and Nickel titania. UV-Vis Spectra of the TiO₂ and Prepared Ni-TiO₂ were observed at below 400 nm and also determine the band gap of TiO₂ and Prepared Ni-TiO₂. The band gap observed for TiO₂ and Prepared Ni-TiO₂ were 3.2 and 3.0 eV respectively. The FT-IR spectra also give the peak at 1025 cm⁻¹ for the formation of Ni-O bonding in Ni-TiO₂. The Prepared sample of TiO₂ and Prepared Ni-TiO₂ were subjected to photocatalytic degradation of oxalic acid. The photocatalytic degradation of Oxalic acid occurs efficiently and also investigated the effect of pH, amount of photocatalyst, Temperature, and photocatalyst. The prominent degradation was found in case of oxalic acid in the presence of nanocomposites of Ni-TiO₂. Photocatalytic degradation of oxalic acid follows the pseudo-first-order rate law. The rate constant was increased two times when temperature rises to 10 °C for photodegradation of oxalic acid in presence of TiO₂ and Prepared Ni-TiO₂.

KEYWORDS: Photocatalyst, nanocomposites, Photodegradation, Nickel titania, solution impregnation

I. INTRODUCTION

Titanium Dioxide is most widely used photocatalyst because it has many advantages. It is used as photocatalyst due to high oxidative power, high photostability, redox selectivity, stability and non-toxicity. It generates the holes, which can oxidize the all organic materials. Therefore TiO₂ is a superior photocatalyst. It is chemically inert and resistant to corrosion, and it requires little post-processing, making it inexpensive [1-2]. It can react under mild-operating conditions [3]. Titanium dioxide have great importance in the applications related to photo-splitting of water [4], photocatalyst [5], photovoltaic devices[6], etc., mostly attributed to the optical and electronic properties of nano-crystallined TiO₂ films [7-8]. The semiconductors could improve the separation of photo produced electron-hole pairs; resultantly enhance the photocatalytic activity of TiO₂ [9]. Photochemical reactions catalyzed by semiconductors have been investigated extensively in the degradation of toxic organic pollutants [10-11], in organic synthesis [12-13] and in energy conversion and storage [14]. In photocatalysis reactions, photogenerated electrons and holes migrate to the semiconductor surfaces where they can induce reduction and oxidation of adsorbed molecules. TiO₂ is commercially available and easy to prepare in the laboratory. An important requirement for improving the TiO₂ catalytic activity is to increase its specific surface area, which is certainly dependent on the crystal size. The smaller the catalyst, the larger will be its specific surface area. A number of methods have been used to prepare TiO₂ nanoparticle, such as chemical precipitation [15], microemulsion [16], hydrothermal crystallization [17] and sol-gel [18]. TiO₂ has also used in very important research for the utilization of solar energy. Titania is a wide band gap semiconductor with many attractive

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properties[19]. The TiO_2 based, dye sensitized, photo-electrochemical cells are receiving a great deal of attention as a possible candidate for converting solar energy into electricity on a large scale. Titanium dioxide, mostly in the anatase form, is a photocatalyst under ultraviolet light. In recent times it has been seen that titanium dioxide, when doped with transition metals, is also a photocatalyst under visible and UV light. The strong oxidative potential of the positive holes oxidizes water to produce hydroxyl radicals. It can also oxidize organic materials directly into water, carbon dioxide, ammonia and other small molecules [20]. Most of the semiconductors are generally selected as photocatalysts, because semiconductors have a narrow band gap [21]. When photocatalyst titanium dioxide (TiO_2) absorbs Ultraviolet (UV)* radiation from sunlight or illuminated light source (fluorescent lamps), it will produce pairs of electrons and holes. The electron of the valence band of titanium dioxide becomes excited when illuminated by light. The excess energy of this excited electron promoted the electron to the conduction band of titanium dioxide therefore creating the negative-electron (e^-) and positive-hole (h^+) pair. The positive-hole of titanium dioxide breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available.

Oxalic acid is a chemical substance. At high concentrations, it is a dangerous poison, the effects of oxalic acid in the human body, when ingested in foods, flow from its ability to combine chemically with certain metals commonly found in human body, such as magnesium and calcium. When oxalic acid combines with such metals, they form "salt". These metal salts are called oxalates. The potential problems with oxalates in the human body are two. (1) they mean that the metal in them say calcium has been made unavailable to the body; if a large amount of oxalic acid is ingested, the oxalates formed mean that the body is being to some degree deprived of certain essential nutrients. For normal, healthy persons, that risk is nearly trivial provided that great amounts of oxalic acid are not consumed on a continuing, long term basis. (2) The effect is not chemical but mechanical: the crystals of oxalate, very small but very sharp, can be large enough to irritate the body [22-23].

Oxalic acid is associated with the formation of kidney stones. If you have kidney problems, your doctor may advise you against eating foods with high levels. Oxalic acid poisoning symptoms include weakness, burning in the mouth, and death from cardiovascular collapse, on the respiratory system, throat burning in the throat, abdominal pain, nausea, vomiting, diarrhea, convulsions, and coma. Individuals with gout, rheumatoid arthritis, or certain forms of chronic vulvar pain are advised to avoid foods high in oxalic acid or oxalates [24]. Oxalic acid is a representative member of the dicarboxylic acid family, the photooxidation of oxalic acid in the presence of TiO_2 and Ni-TiO_2 was done. Oxalic acid was chosen because its radiolysis and reactivity toward OH^\bullet radicals and also because it is a water pollutant. It is used in various industrial treatment processes (textile industry, metallurgy etc.) [25].

II. EXPERIMENTAL

1. Synthesis of Titania and Nickel-titania nanocomposites

25ml of diluted TiCl_4 was taken along with 1ml of concentrated H_2SO_4 and diluted to 1 l using double distilled water. Liquor NH_3 was added drop wise to the solution so as to maintain the solution pH in the range of 7–8. The precipitate is filtered and washed free of chloride and ammonium ions. The precipitate is first oven dried at 100°C for 12 h and grinded in a mortar. The obtained powder is then calcined at 500°C for 4 h to get TiO_2 [26].

Ni-TiO_2 nanocomposites were prepared by solution impregnation method. In this method, 10g prepared TiO_2 dissolve in 100 ml mixture of water and alcohol (ratio 3:1 V/V). Nickel acetate (5%) alcoholic solution added in the TiO_2 solution drop wise. The dispersion is agitated continuously for 4 hour at temperature which is just below of boiling point of alcohol. After the treatment the residue will removed through filtration and will sintered for 1 hour in presence of air at 500°C by kipping it in a silica boat inside muffle furnace. After sintering and slow anilling to room temperature. Content was taken out from furnace and was stored in closed and air tight bottles and was used as photocatalyst [27].

2. Characterization

Several techniques were employed for characterization of the powders. Powder X-ray diffraction was used to identify the crystal phase and to estimate the average crystallite size as well. The particle size and morphology of the powder were observed by scanning electron microscope (SEM), BET analysis was used to determine the surface area of nanocomposites, FT-IR spectra of nanocomposites was recorded and UV/vis absorption spectra were recorded on a spectrophotometer.

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3. Photodegradation of oxalic acid

In this study, photo-degradation of oxalic acid was investigated. Photocatalysed oxidative degradation reaction of organic substrates is holds lot of potential in pollution abatement as well as in synthetic Organic Chemistry. Although in literature several photocatalyst have been cited for this purpose many of these suffer from one or more disadvantage, particularly with regard to either then being highly expensive and chemically unstable. TiO_2 is well known semiconductor that has also been widely used as photocatalyst. In this study, to investigate the photo-degradation behavior of a prepared TiO_2 vis-à-vis synthesized Ni- TiO_2 nanocomposites towards photo-degradation of oxalic acid [26-29]. Oxalic acid was used as the model pollutants in this study because: (1) they are oxidised directly to CO_2 without the formation of any stable intermediate products; (2) they are intermediate products in the photocatalytic degradation of other larger organic compounds; and (3) they have been used previously in photocatalytic studies [28-30]

III. RESULT

In this study, TiO_2 and Ni- TiO_2 nanocomposite were prepared and characterized by various techniques and used, as photocatalyst, in the photo-catalytic degradation of oxalic acid.

1. Preparation of Ni- TiO_2 nanocomposite powder by solution impregnation method

Ni- TiO_2 nanocomposite was prepared by solution impregnation method using aqueous solution of Nickel acetate in alcohol. The obtained yield of the product was more than 90% of the expected theoretical yield.

IV. CHARACTERIZATION

1. Phase identification by X-ray diffraction analysis

Phase identification in the samples was attempted by analyzing them using X-Ray Diffractometer (Bruker AXS D8 Advance System, Germany). The obtained X-Ray diffraction patterns of few representative samples are shown in Figures 1(a) and 1(b). 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 correspond to anatase phase, whereas major peaks at 2θ angles 26.9, 28.2, 42.6 and 54.2^o indicate the presence of rutile phase. In case of Ni- TiO_2 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. This is, probably, due to the change in the crystallinity, grain fragmentation, when the samples were wet impregnated by nickel acetate [31].

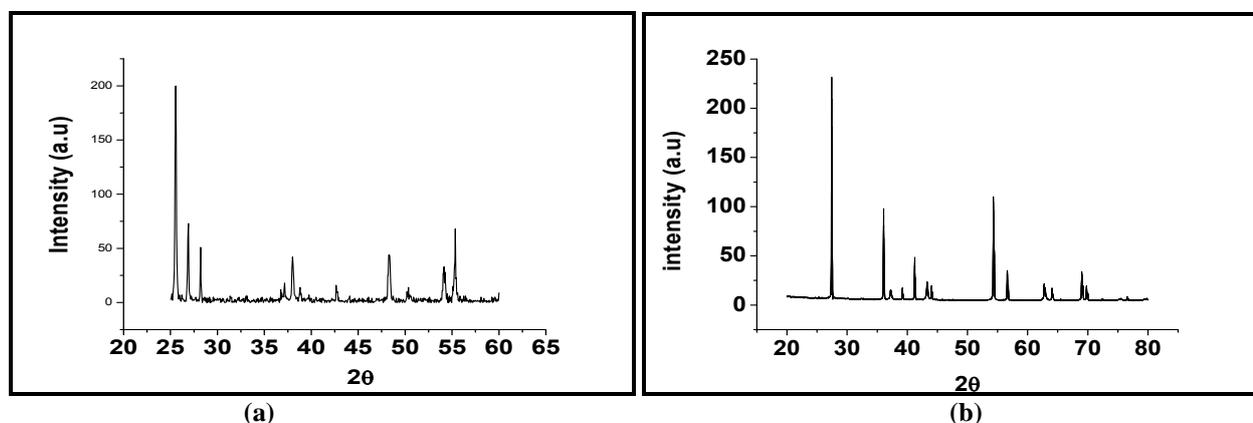


Fig.1 Observed XRD pattern of (a) TiO_2 (b) Ni- TiO_2

2. Determination of Average size of Particles/ Grains in samples

Utilizing the observed X-ray diffraction data of TiO_2 and Ni- TiO_2 , Scherrer's calculations were attempted to know the average size of particles/grains in the TiO_2 and Ni- TiO_2 samples. Although, Scherrer's calculations are only approximate in nature, but definitely provide a first-hand idea of the average size of the particles/ grains in the samples, which may be quite accurate, provided the size of particles/ grains is below 100 nm. The Debye-Scherer formula given

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in equation (1) and Bragg's equation given in equation (2). The results of Debye-Scherer calculations are presented in Table 1 [32]. The results suggest average size of the particles/ grains in the samples lying in nm range. The particles size is reducing from 80 nm to 35 nm due to fragmentation of TiO₂ lattice when Ni impregnated in TiO₂.

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

$$n\lambda = 2d \sin \theta \quad (2)$$

Where, λ is wave length of X-Ray (0.1540 nm), β is FWHM (full width at half maximum), θ is diffraction angle, d is d-spacing and D is particle diameter size.

TABLE -1: Average size of particles/grains in the samples of TiO₂ and Ni-TiO₂

sample	Particle size from Scherrer's calculation *(nm)
Ni-TiO ₂	35
TiO ₂	80

3. Scanning electron microscopy (SEM)

The morphology of the samples was investigated by scanning electron microscopy and it resumes the most interesting outcomes. Fig 2 (a) and 2 (b) clearly show that both the prepared samples are obtained agglomerate in nanometric dimension. The impregnation of Nickel is indicating that the particle size reduce due the penetration of Ni in the lattice of titanium dioxide.

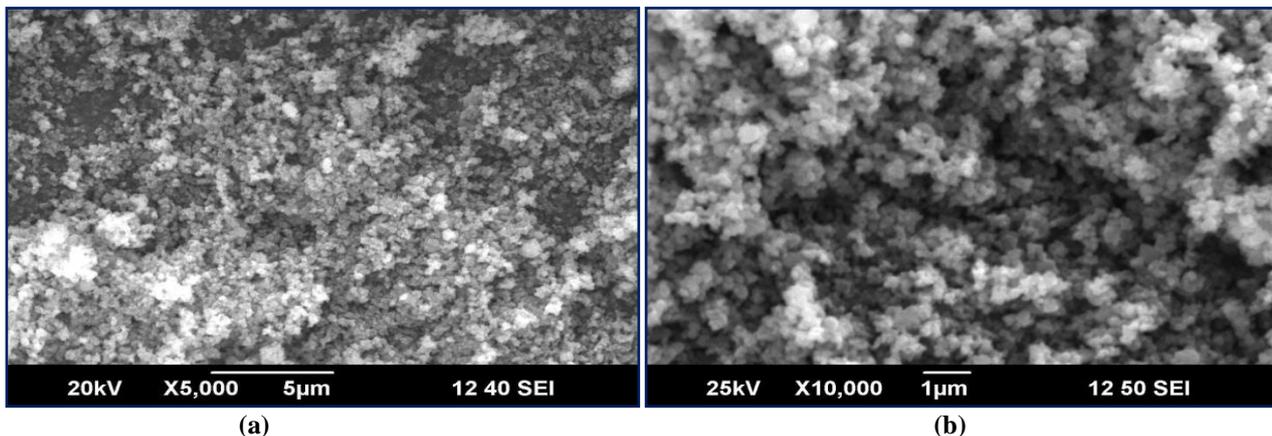


Fig. 2 Observed SEM image of (A) TiO₂ (B) Ni-TiO₂

4. Surface area analysis (B.E.T)

The specific surface area, pore volume and average pore size of the TiO₂ and Ni-TiO₂ as-prepared photocatalyst were characterized by using the N₂ adsorption technique BET (*belsorp Japan*). Table -2 summarizes their physical properties. The TiO₂ modified by Nickel are fragmented 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 [33].

Table-2: Phase surface areas, pore volume, pore radius of TiO₂ and Ni-TiO₂

Sample	Phase	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore radius (nm)
TiO ₂	R+A	6.4	0.018	11
Ni-TiO ₂	R+A	13.2	0.031	6

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5. UV-Vis Diffuse Reflectance Spectroscopy (DRS)

The absorption spectrum of TiO₂ consists of a single broad intense absorption around 400 nm due to the charge-transfer from the valence band to the conduction band [34]. The undoped TiO₂ showed absorbance in the shorter wavelength region while Ni/TiO₂ results showed a red shift in the absorption onset value in the case of Ni added titania. The impregnation of Ni ions into TiO₂ could shift its optical absorption edge from UV into visible light range, but no prominent change in TiO₂ band gap was observed [35]. 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 [36].

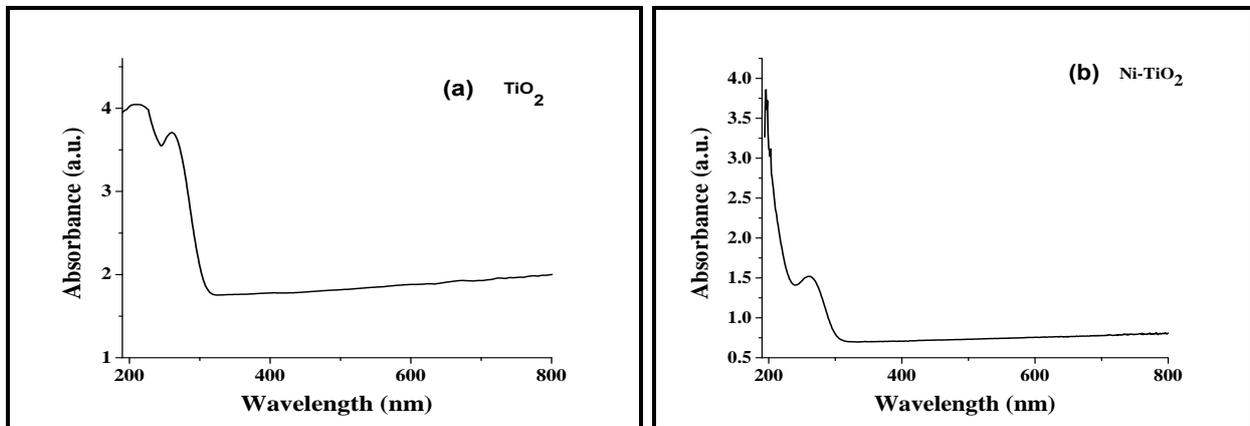


Fig-3 UV- spectra of (a) TiO₂ (b) Ni-TiO₂

6. Band Gap Energy determination

The band gap of TiO₂ as calculated from the extrapolation of the absorption edge onto the energy axis is 3.2 eV and this is well reported. Fig. 4 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 E_g . The extrapolation of graph yields an E_g value of 3.2 eV which is in fact the band gap of titania. But for the sample of Ni-TiO₂, the indirect plot yield band gap values of 3.0 eV [37]. The band gap energy is decrease in Ni-TiO₂, because the nickel forms a sub band level between valence band and conduction band.

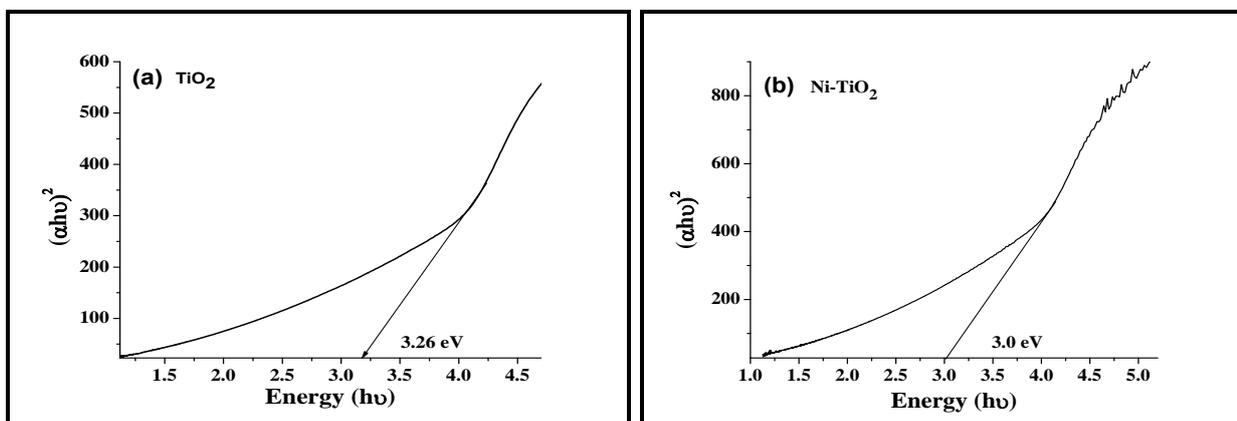


Fig. 4 Band Gap energy of (a) TiO₂ (b) Ni-TiO₂

7. FT-IR Spectroscopy

FT-IR spectra of undoped and 5.0% Ni-doped TiO₂ samples (Fig. 6) 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 Fig. 6 may be due to decrease in size of the catalyst nanoparticles. In addition, the surface hydroxyl groups in TiO₂ increase with the increase of Ni loading, which is confirmed by increase in intensity of the corresponding peaks. The FT-IR spectra shows strong band at 1075 cm⁻¹ corresponds to the vibration of Ni-O bond and it is confirm the penetration of nickel in Titania [38].

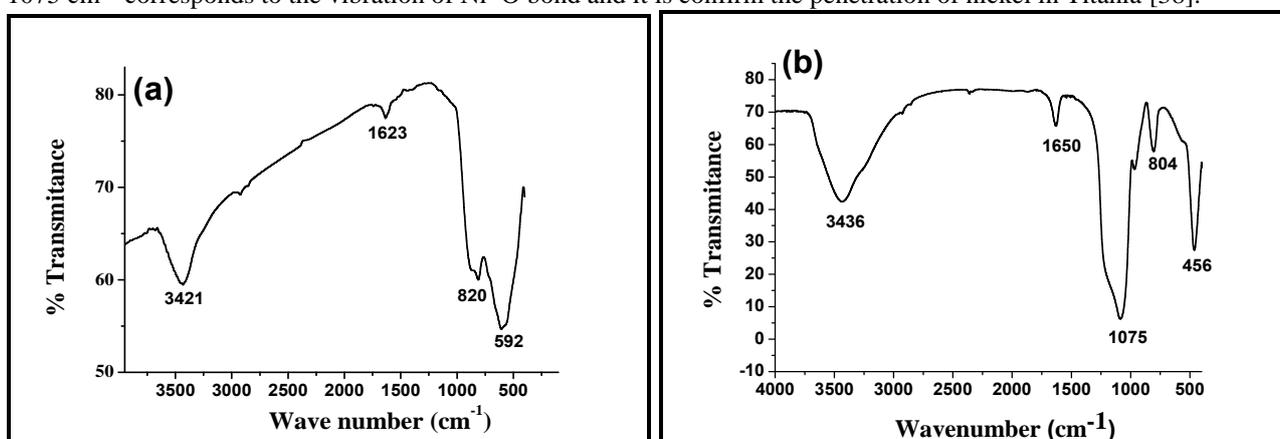


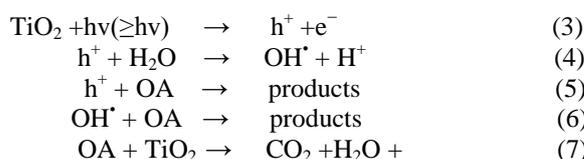
Fig. 5 FT-IR Spectra of (a) TiO₂ (b) Ni-TiO₂

V. PHOTODEGRADATION STUDY

In this study, photo-catalytic degradation of Oxalic acid was investigated. The samples of TiO₂ and Ni-TiO₂ were used as photocatalyst in the photo-degradation of Oxalic acid, 20g/l of the photo-catalyst was dispersed in the 5.2 mM solution of Oxalic Acid and the reaction mixture was illuminated with UV light, while kept under agitation. The results presented in this Section comprise the residual concentrations of Oxalic Acid in the reaction mixture, measured at different time intervals. The measured values of residual concentration of acids in the reaction mixture at different times of illumination (or reaction time) have been shown in Fig. 6. It is clear from the results shown that both TiO₂ and Ni-TiO₂ are proving as an effective photo-catalyst for the degradation of oxalic acid. However Ni-TiO₂ seems to be more effective as photo-catalyst for the degradation of Oxalic acid.

1. Photo-degradation of Oxalic acid

When photocatalytic reaction is conducted in aqueous medium, the holes were effectively scavenged by the water and generated hydroxyl radicals OH•, which are strong and unselected oxidant species in respect of totally oxidative degradation for organic substrates. Both holes and hydroxyl radicals have been proposed as the oxidizing species responsible for the degradation (mineralization) of the organic substrates [39]. The Photocatalytic degradation of oxalic acid mechanism are as follow



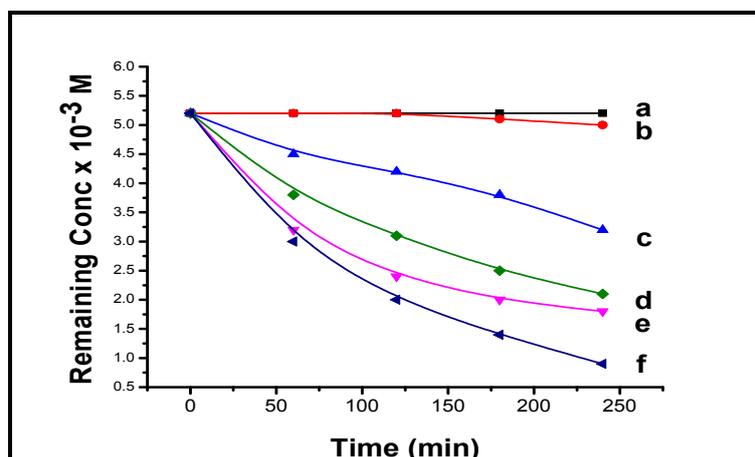


Fig. 6 The effect of temperature and photocatalyst on photodegradation of oxalic acid (a) without photocatalyst at 30°C (b) without photocatalyst at 40°C (c) TiO₂ as photocatalyst at 30°C (d) TiO₂ as photocatalyst at 40°C (e) Ni-TiO₂ as photocatalyst at 30°C (f) Ni-TiO₂ as photocatalyst at 40°C.

2. Effect of Temperature

The effect of system temperature on photocatalysis has not attracted enough attention. But In present research, it is found that the temperature has a great effect on the photodegradation of carboxylic acids. 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 carboxylic acids cannot be photodegraded if TiO₂ or UV light was not used, indicating that carboxylic acids cannot be pyrolyzed by heating with the heating temperature which was less than 40 °C and self degraded by absorbing irradiation. Only when TiO₂ and UV light were both used, the oxalic acid was efficiently degraded shown in fig 6. The obvious decrease of concentration of carboxylic acids shows that the TiO₂ and Ni-TiO₂ can serve as an effective photocatalyst [40-42].

3. Effect of pH

The photodegradation reaction was also carried out under varying pH conditions from 2 to 7, by adjusting with NaOH, with TiO₂ kept at constant amounts of 25 g/ L of carboxylic acids 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 4 pH the photodegradation is rapidly decrease and after increasing pH the photodegradation rapidly decrease. 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 [43].

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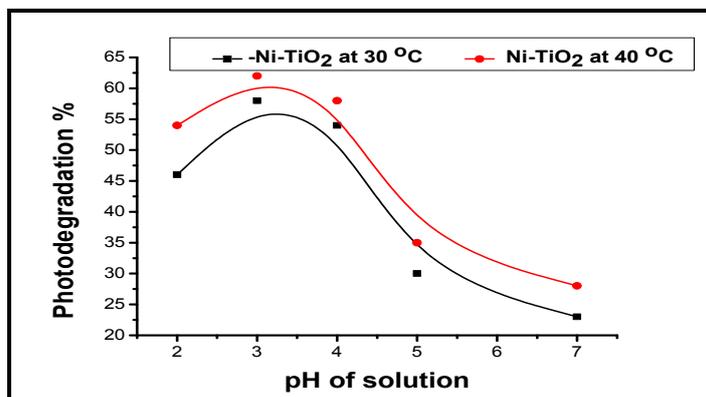


Fig. 7 Effect of pH on photodegradation of acids with temperature

4. Effect of photocatalyst

It is clear from the results shown in fig.6 that both TiO₂ and Ni-TiO₂ are proving as an effective photo-catalyst for the degradation of Oxalic Acid. However Ni-TiO₂ seems to be more effective photo-catalyst for the degradation of Oxalic acid. The prominent degradation of acids was found in 3 hour study in the presence of prepared Ni-TiO₂ in comparison to the TiO₂. This is because that Ni form a sub band in TiO₂, hence band gap energy decrease which favour the photocatalytic degradation of Oxalic acid.

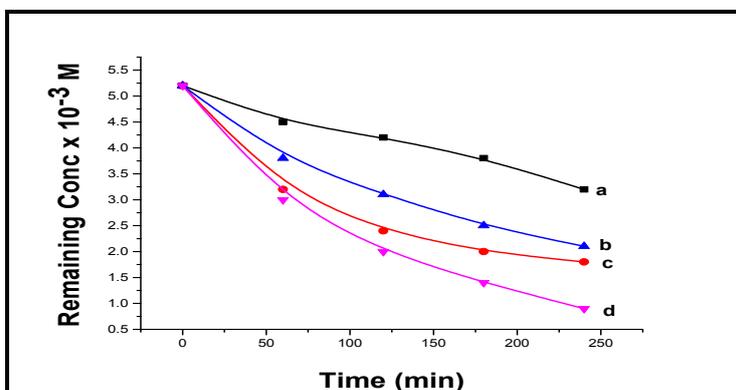


Fig.8 Effect of Photocatalyst Amount on photodegradation of oxalic acid (c) TiO₂ 20g/l (d) TiO₂ 40g/l (e) Ni-TiO₂ 20g/l (f) Ni-TiO₂ 40g/l

5. Effect of photocatalyst amount

It is clear from the results shown in fig.8 that both TiO₂ and Ni-TiO₂ are proving as an effective photo-catalyst for the degradation of Acids. But when the amount of photocatalyst increases the photodegradation of acids also increase. It is observed that Ni-TiO₂ is the more effective photocatalyst than TiO₂ [44]. When the photocatalyst amount increased, the number of active site increase for the reaction of oxalic acid. The amount of photocatalyst increases two times the rate of photodegradation increase about 30% and 60 %, in presence of TiO₂ and Ni-TiO₂ respectively.

VI. KINETIC STUDY

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

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$$\ln C_0/C_t = k_1 t \quad (8)$$

In addition, the linear feature of plots of $\ln(C_0/C_t)$ versus time (Fig.9) indicates that this photocatalytic degradation reactions follow the pseudo-first-order rate law [45-47]. For comparison, the photocatalytic activity of a pure TiO_2 and Prepared Ni-TiO_2 respectively, was also tested. The calculated degradation rate constants k (min^{-1}) at 30°C and 40°C are listed in Table.3.

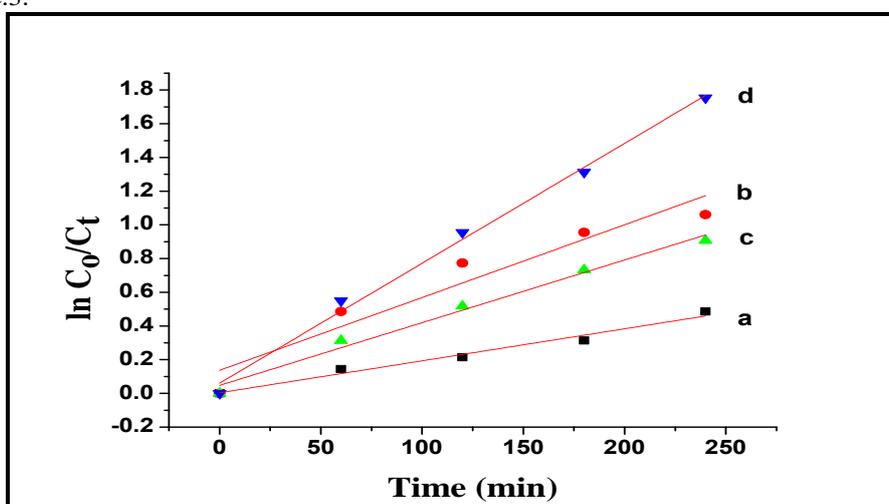


Fig.9 Graph plotted between $\ln C_0/C_t$ vs Time, The obtained slope gives rate constant (k) at different temperature (a) TiO_2 as photocatalyst at 30°C (b) TiO_2 as photocatalyst at 40°C (c) Ni-TiO_2 as photocatalyst at 30°C (d) Ni-TiO_2 as photocatalyst at 40°C .

Table.3 Rate constant of first order for TiO_2 and Ni-TiO_2 at 30°C and 40°C Temperature.

Sample	Temperature $^\circ\text{C}$	K Rate constant (slope)
TiO_2	30	0.0019
TiO_2	40	0.00432
Ni-TiO_2	30	0.00372
Ni-TiO_2	40	0.00712

The rate constant value increased about two times when temperature raises 10°C . In both TiO_2 and Ni-TiO_2 , the rate constant value increased due to the increase kinetic energy of molecules, which increase the effective collision in molecules.

VII. CONCLUSION AND DISSCUSION

Titanium dioxide (TiO_2), commonly known as titania, is one of the most commonly used photocatalysts. Because of its high oxidative power, stability, and non-toxicity, it promises a broad range of uses as a photocatalysts. Advantage of using TiO_2 as photo-catalyst are (a) using TiO_2 , the process occurs under ambient conditions (b) using TiO_2 , the oxidation of the substrate to CO_2 is complete in most cases and (c) it is comparatively inexpensive and remains quite stable in contact with different substrate. TiO_2 has also played a leading role in the active research for the utilization of solar energy. Titanium dioxide's photocatalytic characteristics are greatly enhanced due to the advent of nanotechnology. Nanoparticles or nanocrystals of titanium dioxide are of interest for their electrical, optical and chemical properties. At nano-scale, not only the surface area of titanium dioxide particle increases dramatically but also it exhibits other effects on optical properties and size quantization. An increased rate in photocatalytic reaction is observed as the redox potential increases and the size decreases.

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In the present study, TiO₂ and Ni-TiO₂ nanocomposites was prepared by solution impregnation method. The alcohol route of synthesis was adopted here, yielded dark black homogeneous powder of Nickel titanium dioxide. The obtained yield of the product was more than 90% of the expected theoretical yield. In which the material has the nanodiamonds. The prepared material was subjected to XRD analysis which gives the rutile and anatase both phases were present in the prepared sample. It is found that, in samples sintered at 400 °C both anatase and rutile phases were presented and rutile phase was more dominant, while in samples without sintered the exclusive formation of polycrystalline anatase and rutile phase separately was occurred. Applying the Scherrer's calculations through which particle size was found 35 and 80 nm in case of Nickel titania and pure titania respectively. The prepared sample of titania and Nickel titania were subjected to photocatalytic degradation of oxalic acid was done. The degradation of oxalic acid occurs efficiently. The photodegradation of Oxalic acid was investigated at different conditions such as temperature, amount of catalyst, pH of solution and type of catalyst. The prominent degradation was found in case of oxalic acid in the presence of nanocomposites Ni-TiO₂ at 40°C in 3 hour study.

VIII. ACKNOWLEDGEMENT

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