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AG DOPED TIO$_2$ NANOPARTICLES PREPARED BY HYDROTHERMAL METHOD AND COATING OF THE NANOPARTICLES ON THE CERAMIC PELLETS FOR PHOTOCATALYTIC STUDY: SURFACE PROPERTIES AND PHOTOACTIVITY

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Abstract
In this work, Ag doped nano TiO$_2$ photocatalysts were synthesized in powder form by hydrothermal method at 180 ºC in 120 min. using different reduction agents. The synthesized powders were characterized by powder X-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDS), Surface area measurements (BET), Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) analyses. The effect of reduction agents on the morphological properties of Ag doped nano TiO$_2$ has been studied. We have been observed that the use of different reduction agents affects the particle size and surface area. Ag doped nano TiO$_2$ photocatalysts were coated to the ceramic pellets by dip coating technique for photocatalytic study. Photocatalytic properties of the synthesized powder were examined in a circulating aquarium filled with indigo blue (IB) solution under UV irradiation. Periodical UV spectrophotometric analysis showed that indigo blue (IB) has been degraded and its concentration has decreased under UV irradiation by time.

Keywords: Ag doped, Nano TiO$_2$, Hydrothermal process, ceramic pellets, indigo blue dye

1. Introduction

Dyes are largely used as coloring agents in the cosmetics, leather, textiles, food, plastics, and other industries [1, 2]. However, most industrial dyes are toxic, mutagenic and carcinogenic, and have low biodegradability [3]. Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds. If they do not discharge in environment without any treatment, they can cause skin problems and harmful for humans. In many cases, the efficiency of photocatalytic degradation has been demonstrated on several kinds of dyes i.e. reactive, azo, cationic dyes. Thus, the removal of dyes prior to the discharge of wastewater from dye industries is of great importance. Textile dyes can be degraded in the presence of TiO2 powder as a photocatalyst under strong ultraviolet light [4-8].

TiO2 is the most effective because of its high photosensitivity, non-toxicity, chemical stability, low cost, easy availability and environmental friendly [9-12]. However, a major disadvantage of TiO2 is the large band gap of 3.2 eV which limits its activity when sunlight and UV light is used. To overcome these restrictions of TiO2, many studies have been perform to enhance the electron–hole separation and to extend the absorption range of TiO2 into the visible region and UV region. These studies included incorporation of metal ions or non-metal ions into the TiO2 lattice [13-16], dye photosensitization onto the TiO2 surface [17-20] and deposition of noble metals onto the TiO2 surface [21-26]. The use of noble metal/TiO2 nanocomposites is an efficient way to enhance the photocatalytic efficiency of TiO2 owing to the efficient electron-hole separation by noble metals [27-30]. Among the metallic species which can be incorporated onto TiO2 surface, Ag has shown an enhanced electron-hole separation and interfacial charge transfer ability, as well as the increase of the visible light and UV light excitation of TiO2 [31-33]. Silver is especially favourable for industrial and environmental applications owing to its easy preparation and low cost. The effects of Ag doping on the surface or lattice of TiO2 have been study [34-37]. TiO2 load with silver enable the catalyst to implement more effectively and shortens the illumination period [36]. Scientists have researched the effect of silver including on the microstructure and photocatalytic activity of TiO2 prepared by various method [25, 28, 33, 38-40].

In recent years; organic pollutants, like methanol, methylene blue, methyl orange, alizarin salt dye and Rhodamine B could also be more efficiently degraded by the metale TiO2 nano composite. Reactive oxygen species, and particularly hydroxyl radicals (HO-·), produced by the irradiated metale TiO2 has been considered to be the dominant species contributing to the degradation of several organic pollutants [39, 41-46].

There are several techniques for the preparation of Ag-modified TiO2 such as sol–gel [28, 47] photocatalytic deposition [21], deposition precipitation [22], electrospinning technique [39], Photo reduction method [45], miniemulsion method [38] and hydrothermal process [44, 48]. Hydrothermal synthesis controls the thermodynamic and no thermodynamic variables [49, 50]. In recent years, hydrothermal synthesis is used in the synthesis of various inorganic materials to control grain size, particle morphology, microstructures, phase composition and surface chemical properties [48, 51, 52]. Moreover, the hydrothermal process is environmentally friendly since the reactions are carried out in a closed system and the contents can be recovered and reused after the synthesis [53]. In the present study, Ag doped nano TiO2 particles with higher surface area were synthesized by a single step hydrothermal method at 180 C0/ 120 min in the presence different reduction agents. Looking at the studies; the preparation Ag doped nano TiO2 for the reduction of Ag+ ions to metallic Ag^o is used reduction agent such as L-tyrosine, polyols, ascorbic acid, sodium citrate tribasic dehydrate, polyethylene glycol(PEG) and hydrazine [26, 28, 33, 40, 54].

The on current study, Ag doped anatase nano TiO2 was synthesized by hydrothermal synthesis. Herein, the synthesized Ag doped anatase nano TiO2 catalyst was characterized by various techniques such as XRD, EDS, SEM, TEM and BET techniques. We report the preparation method of Ag doped TİO2 nanoparticles by hydrothermal synthesis, as the most common surfactant and reducing using such as SDS, oleic acid, sodium borohydride, PEG-600, Hydrazine and ascorbic acid were chosen for our investigation. The effect of reduction agent used for preparation on the photocatalyst structure, surface area, crystallinity, and efficiency of removal of model organic compound and aqueous phase were systematically investigated. İndigo blue dye (İB) was used as a dye which is frequently encountered in wastewater as dangerous organic pollutant.

2. Materials and methods

2.1 Materials

For the synthesis of nano TiO_2 powder, titanium (IV) isopropoxide $Ti\{OCH(CH_3)_2\}_4$, Fluka, 100%) was used as TiO_2 source, glasiyel acetic acid (Merck, 37%) was used as synthesis catalyst, and deionized water was used for the hydrolysis of titanium isopropoxide. Propan-2-ol (C_3H_8O, Merck, 99. 5%) was used as solvent in every step of the synthesis. Silver nitrate used as the starting material for the silver nanoparticles. Hydrazine anhydrous ($N_2H_4.H_2O$, %98), Polyethylene glycol (PEG-600), sodium borohydride and ascorbic acid (99%) were purchased from Merck and used as reducing agent. SDS (sodium dodecyl sulphate, $CH_3(CH_2)_{11}OSO_3Na$ Merck, %99) and oleic acid ($C_{17}H_{33}COOH$) were used as surfactant. Ag doped Nano TiO_2 synthesis was realized by a high pressure and high temperature reactor (Berghof Pressure Digestion DAB- 3, Germany).

Tetraethylorthosilicate ($Si(OC_2H_5)_4$, Merck, 99%), ethanol (C_2H_5OH, Merck, 99%) and ethylene glycol monobutyl ether ($C_6H_{14}O_2$, Merck, 99%) was used for the coating solution. Ceramic pellets were used as coating material. Coating process was realized by a computer aided dip-coating device (Chemat Technology Dip Master 201, USA). A special designed circulating aquarium was used for the photocatalytic application.

2.2 Preparation of Ag doped nano TiO_2 photocatalysts

Silver-doped TiO_2 powders were prepared by the hydrothermal methods involving reduction agent. Initially, liquid 21 ml Titanium (IV) isopropoxide and 71 ml 2-propanol were mixed and added 9 ml glacial acetic acid during magnetic stirring. After the reaction was allowed to proceed for 2 h during stirring, the resulting solution was transparent. To produce Ag doped TiO_2 nanopowder, prepared solution obtained from $AgNO_3$ (5.8% wt) and different reducing agent, separately (0.125M ascorbic acid, 0.01 M sodium dodecyl sulphate (SDS), 0.04 M $NaBH_4$, Hydrazine, PEG-600 (see table 1.) in 4 ml deionized water was added drop –wisely to TiO_2 solution and stirred for 1 h. The solution was put into a high pressure and high temperature reactor for the hydrothermal synthesis (180 ˚C, 2h). pH of the solution ranged from 6.0-7.0 according to using the reduction agent after synthesis. Nanopowders were washed with 2-propanol and deionized water. Powders were centrifuged and dried in a vacuum sterilizer at 60 ºC for 5 h to obtain the Ag doped nano TiO_2 powders.

2.3 Coating of the ceramic pellets with Ag doped nano TiO_2 powder

3-Glycidoxypropyltrimethoxysilane (GLYMO) was first reacted with TEOS for 10 min. (GLYMO/TEOS: 1) then EtOH was added to this mixture. After stirring 10 min., the mixture was solved HCl and deionized water were added into the mixture. After stirring 10 min., dispersed Ag doped nano-TiO_2 (0, 25 g) was added to the solution and stirred for 10 min. Then, 2-butoxyethanol was added into the last solution and that solution was stirred for 24 h to obtain good dispersed coating solution. Finally, depending on the reduction agent between light brown to dark brown solution was obtained (see table 2). The ethanol, HCl, deionized water, 2-butoxyethanol to Tetraethylorthosilicate mol/mol ratios were 10.5, 0.05, 6.3 and 0.05, respectively. Ceramic pellet surfaces were coated with this solution using dip-coating apparatus at 12 inch /min. speed. The Ag doped nano-TiO_2 coated ceramic pellet were cured in the vacuum oven at 80 ºC for 1 h.

Table 1. The values calculated for the different samples synthesized by the hydrothermal method

Composition Name	**Titanium isopropoxide $Ti\{OCH(CH_3)_2\}_4$ (mL)**	**Propan-2-ol/Glasiyel acetic acid (mL)**	**$AgNO_3$/ 1 mL pure water**	**Reduction agent**
Undoped TiO_2[44]	21	71/9	**-**	**-**
A-1	21	71/9	1 gr	1 mL ascorbic acid /2ml SDS
H-1	21	71/9	1 gr	1 mL Hydrazine /2 ml SDS
P-1	21	71/9	1 gr	2 mL PEG-600
N-1	21	71/9	1 gr	2 mL $NaBH_4$/ 0.5 mL oleic acid

2.4 Characterization

X-Ray Diffractometer-XRD, (Rigaku D-Max 2200, Japan) was used for qualitative, quantative analysis and crystal size calculation. The crystalline size of the nano-TiO_2 was calculated from the X-ray diffraction peak according to the Scherer's equation: $d_{hkl} = k\lambda/[\beta\cos(2\theta)]$, where dhkl is the average crystalline size (nm), λ is the wavelength of the CuKα radiation applied (λ= 0.154 nm), θ is the Bragg's angle of diffraction, β is the full-width at half maximum intensity of the peak observed at $2\theta = 25.3^\circ$ and k is a constant usually applied as *ca.* 0.94. Scanning Electron Microscope-SEM, (JEOL JSM 5910-LV, Japan) was used for morphological and particle size. Energy-dispersive X-ray spectroscopy (EDS) (EOL JSM-5910 LV scanning electron microscope- EDS) was used for elemental analysis of the powder to regional integration. BET (Autosorp-1 MP/Kr) was used for synthesized nano-sized powder homogeneously 1g/m^2 surface area can be calculated. Transmission electron microscopy -TEM (Jeol TEM-2100) was used for synthesized nano-sized powder the purpose of displaying the atomic structure. UV-Visible Spectrophotometer (Agilent Technologies UV-Vis. Spect., USA) was used for the analysis of photocatalytic properties of synthesized Ag doped nano TiO_2 on indigo blue (İB) ($C_{16}H_{10}N_2O_2$).

2.5 Photocatalytic study

The photocatalytic activity of the Ag doped nano TiO_2 photocatalysts was determined by the degradation of indigo blue dye solution. Under UV (365 nm) light irradiation at room temperature in the photo reactor. The coated ceramic pellets was immersed into indigo blue dye solution with a concentration of 0.002 g/2L at pH 6.0 the indigo blue dye solution was circulated into at the ambient temperature. Four 8 W UV lamps with a primary wavelength at 365 nm were used in the photocatalytic system. An aliquot of 3 ml was taken out from reaction mixture at definite time intervals and the absorbance was measured at 672 nm. The change of indigo blue dye concentration was measured by UV-vis spectrophotometer. It was observed that the absorbance of the reaction mixture decreases with increasing time interval, which indicates that the concentration of indigo blue decreases with increasing time of exposure.

3. Results and discussion

3.1 Characterization of Ag doped nano TiO_2 photocatalysts

In this section; the crystalline phase of hydrothermally synthesized Ag doped nano TiO_2 A-1, H-1, P-1 and N-1samples were analysed by XRD. Figure 1(A),1(B),1(C) and 1(D) shows XRD pattern of the Ag doped nano TiO_2 powders prepared by hydrothermal method at 180ºC for 120 min. The XRD pattern of the Ag doped nano TiO_2 was compared with JCPDS PDF-021-1272 data files and all the sharp peaks observed in the XRD pattern belong to anatase phase of TiO_2 and silver peaks. The other crystalline forms of TiO_2, rutile and brookite, have not been detected. As shown in Figure 1, the most intense (101) peak was observed at $2\theta= 25.30^\circ$, meaning the interference-free reflection of the typical tetragonal anatase structure. Strong diffractions peaks at 25.00˚ and 48.00˚ further support TiO_2 in the anatase phase [55]. The 2θ at 25.40˚ confirms the TiO_2 anatase structure [56].The other peak was observed at 200(2θ =48.06˚), 004(2θ =37.80˚), 105(2θ =54.16˚) and 204(2θ =62.70˚). The experimental XRD pattern agrees with the JCPDS card no: PDF-021-1272 standards. In addition; the peak of elemental Ag was appeared 37, 90˚ (111); 64, 06˚ (220) and 77, 20˚ (311). The result agrees with JCPDS card no: 04-0783. It suggesting that all powders were successfully prepared by standards hydrothermal method involving reduction agents. According to this result; it is obvious that the all powders have structure of anatase TiO_2 and contain elemental silver. The average crystalline size of the Ag doped nano TiO_2 powders were measured by applying Debye-Scherrer equation (1). The crystallite sizes all the prepared powders were between 10 and 13 (Table 2.). Table 2 shows some physical characteristics of synthesized Ag doped nano TiO_2 crystallines.

$$D_p = \frac{0.94\lambda}{\beta_{1/2}\cos\theta} \tag{1}$$

D_p is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size λ is the X-ray wavelength; $\beta_{1/2}$ is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. This quantity is also sometimes denoted as $\Delta\ (2\theta)$; θ is the Bragg angle. Table 2 shows the crystal size values of different composition powders synthesized by hydrothermal method. According to this; the synthesized all powders is lower than the commercial TiO_2 calculated value of 60.86 nm crystal size. The Ag crystal size value was found to between 12 and 23 nm. It is very very-well know that the photocatalytic effect of a catalyst is dependent on the crystallite size and surface area. The smaller particles, the larger will be its specific surface area and the higher photocatalytic activity. Surface area of the samples has a role to monitor the efficiency of dye degradation. These results have proven that the method used for the appropriate particle size by hydrothermal method. P-1 has the smallest particle size of powders (TiO_2/Ag - 10/12 nm see Table 2).

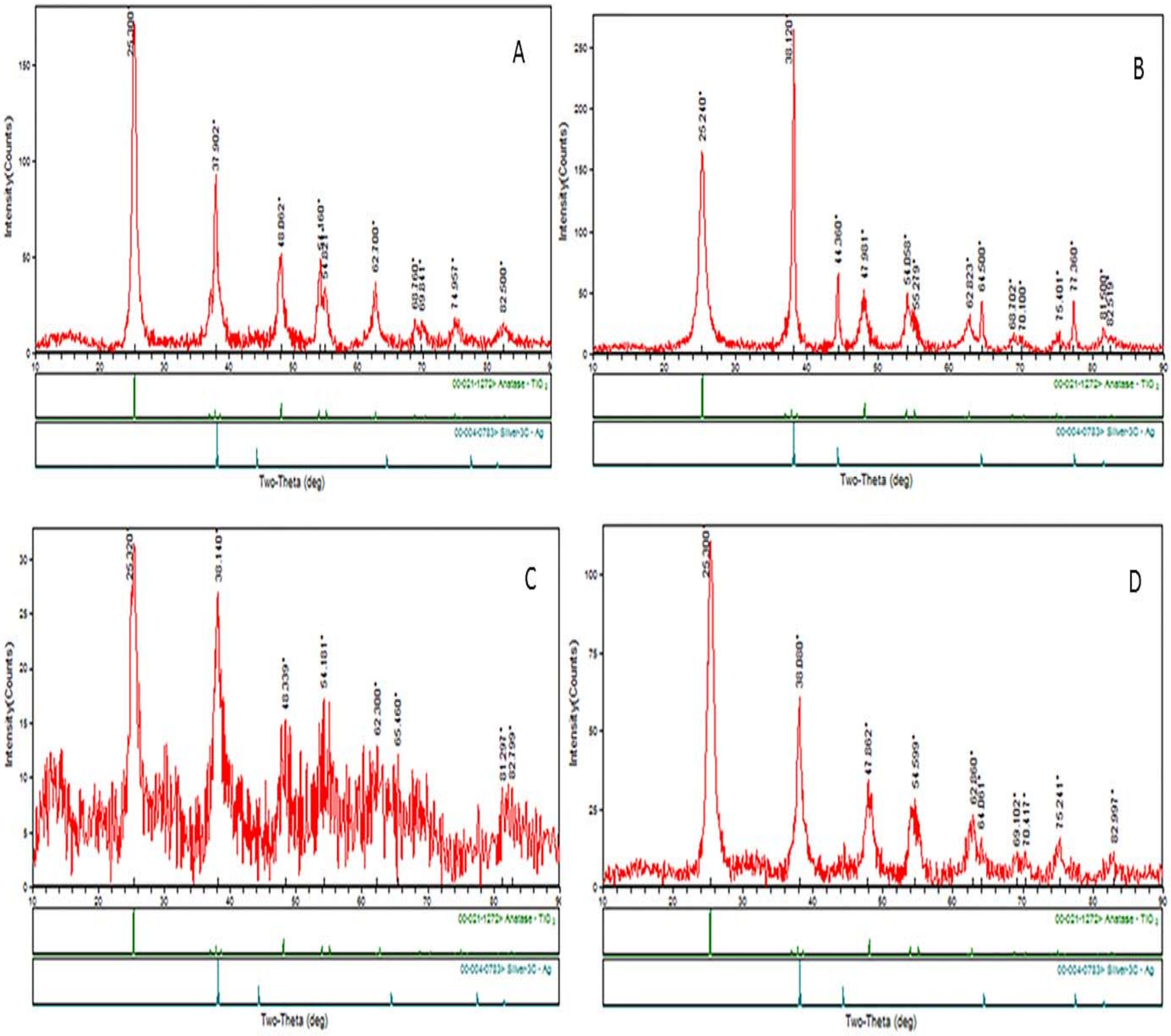

Figure 1. Powder XRD patterns of hydrothermally synthesized the Ag doped nano TiO_2 crystallines (A) A-1 (B) H-1 (C) P-1 (D) N-1

Liquid nitrogen absorption- desorption experimental results are presented in Table 2. BET surface area was dependent on reduction agent. It can be seen that SBET increased with using PEG-600 reduction agent. BET consequences is seen that a linear relationship between surface area and particle size (see Table 2). Silver doped nano TiO_2 join to form together with the surfactant caused the formation of anatase in the formation of smaller particle size and higher surface area.

Table 2. Some physical characteristics of synthesized Ag doped nano TiO_2 crystallines

Photocatalyst name	**Ag content (%wt)**	**Reduction agent**	**Sample colour**	**Crystallite size (nm) TiO_2/Ag**	**BET surface area analysis(m^2/g)**
Undoped TiO_2 [44]	-	-	-	10	65.0
Degussa P25-TiO_2	-	-	-	26	56
A-1	5,8	Ascorbic acid	brown	13/19	166.98
H-1	5,8	Hydrazine	grey	11/23	165.85
P-1	5,8	PEG-600	dark brown	10/12	175.11
N-1	5,8	sodium borohydride	black	11/15	135.40

The morphology of the synthesized Ag doped nano TiO_2 nanoparticles was studied by SEM. When the surface microstructures of the Ag doped nano TiO_2 was investigated by SEM, we observed that while A-1 and H-1 powders have striped structure, P-1 and N-1 powder have a spherical structure (Figure. 2(A), 2(B), 2(C), 2(D)). Sedimentation and agglomeration of TiO_2 particle have also been reported [57].The Agglomeration is occurred when the Ag doped powder TiO_2 is become damp from air. The main causes of agglomeration are small and mild particles and the variable electrical charges in the atmosphere. Doped metal concentration, surfactant and the applied method of synthesis may cause agglomeration. SDS, PEG and oleic acid surfactant is used to protect the resulting Ag nano metal particles undergo agglomeration. The surfactants are used to remain as small particles by wrapping the Ag metal. Although the same amount of transition metal ion is used, different reduction agents and surface active agents used for reduction causes a difference in the SEM images (figure 2). Our study not only the amount of silver added to achieve better global structure of the diversity of the surfactant and reduction agent used shows that important. Therefore, if it is desired to obtain a better global form, P-1 formulation that PEG (600) must be used. P-1 powder is quite nano metric size. So; it exhibits high performance coatings for photocatalytic applications.

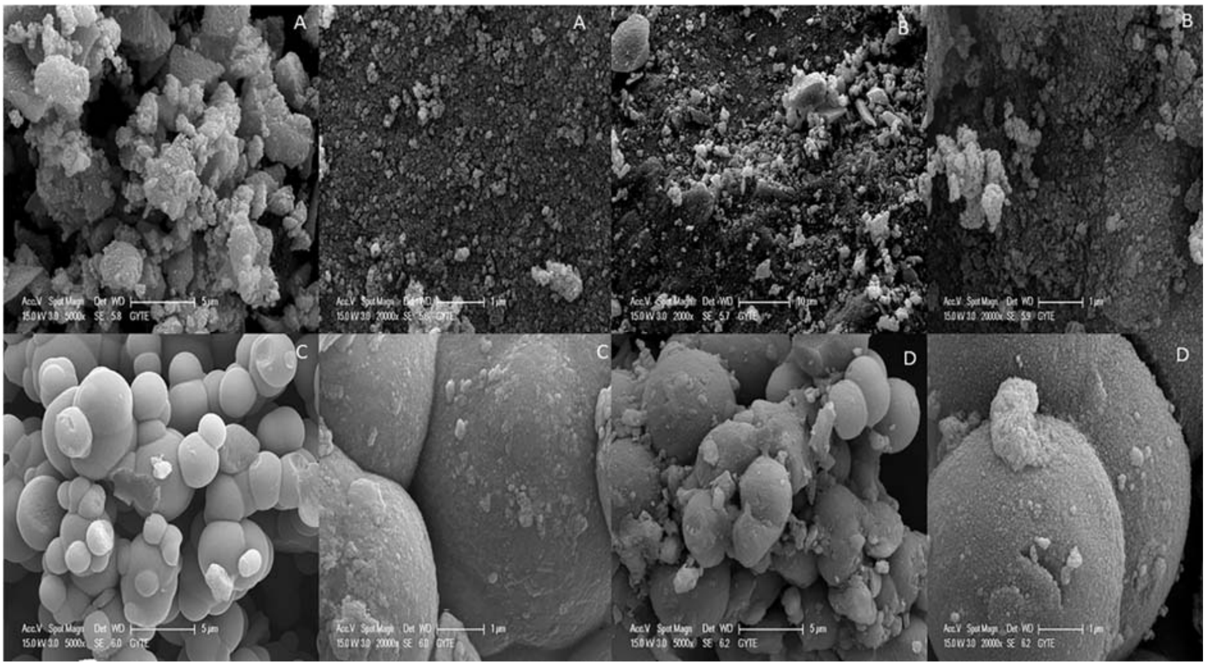

Figure 2. SEM images of the Ag doped nano TiO2 crystallines (A) A-1 5 µm and 1 µm (B) H-1 10 µm and 1 µm (C) P-1 5 µm and 1 µm (D) N-1 5 µm and 1 µm

The surface composition of Ag doped nano TiO2 nanoparticles was qualitatively determined by EDS. EDS analysis was conducted in a selected area via SEM images. EDS analaysis was show that high-intensity Ti, O and Ag peaks are achieved (Figure 3.). Figure 3(C) it showed that P-1 nano powders weight (%) and atomic concentration ratios of Ti plus O to Ag were 96.78/3.21 and 99.26/0.74, respectively. Therefore, it can be assumed that Ag nanoparticles are doped of the TiO2 nanoparticles.

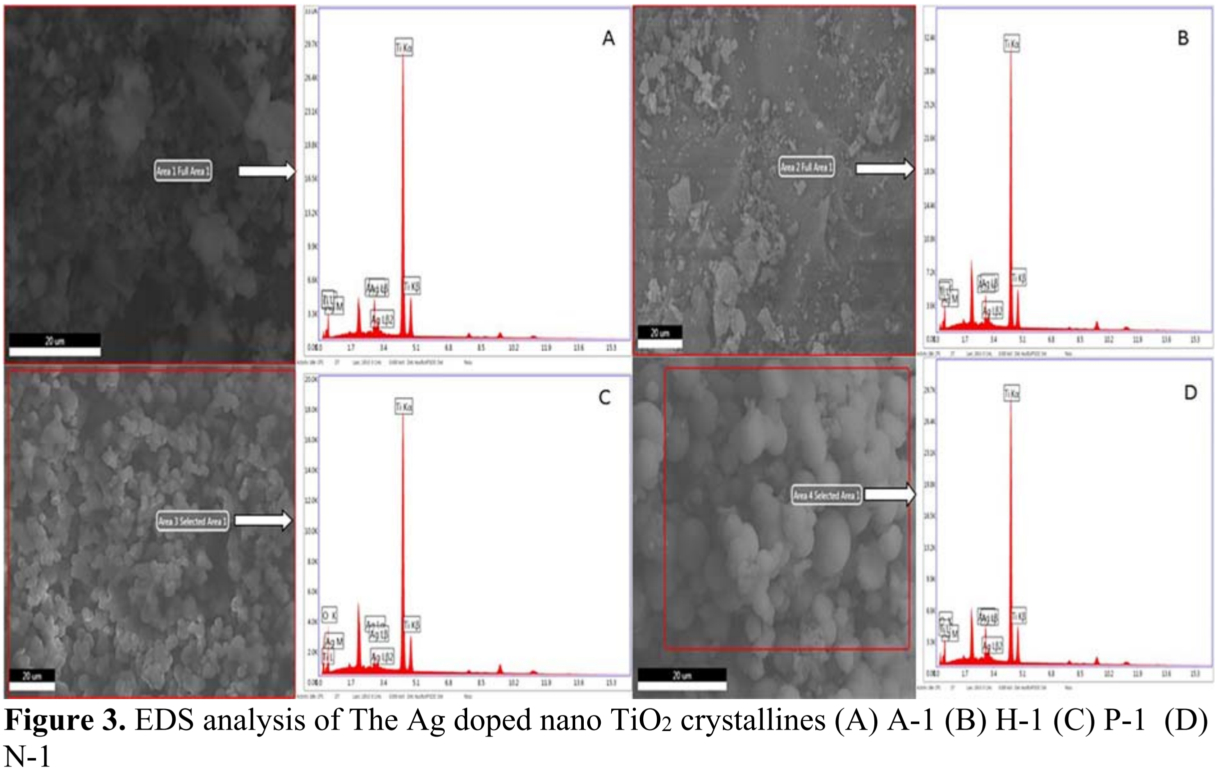

Figure 3. EDS analysis of The Ag doped nano TiO2 crystallines (A) A-1 (B) H-1 (C) P-1 (D) N-1

TEM analysis of the P-1 powder in terms of whether the model is examined. Figure 4 shows TEM images of Ag doped P-1 powder. We have been observed that P-1 powder synthesized by hydrothermal method have the particle size of 20-40 nm. This shows us that it is compatible with theoretically calculated XRD results and Ag doped nano TiO_2 structure shows that the crystal structure.

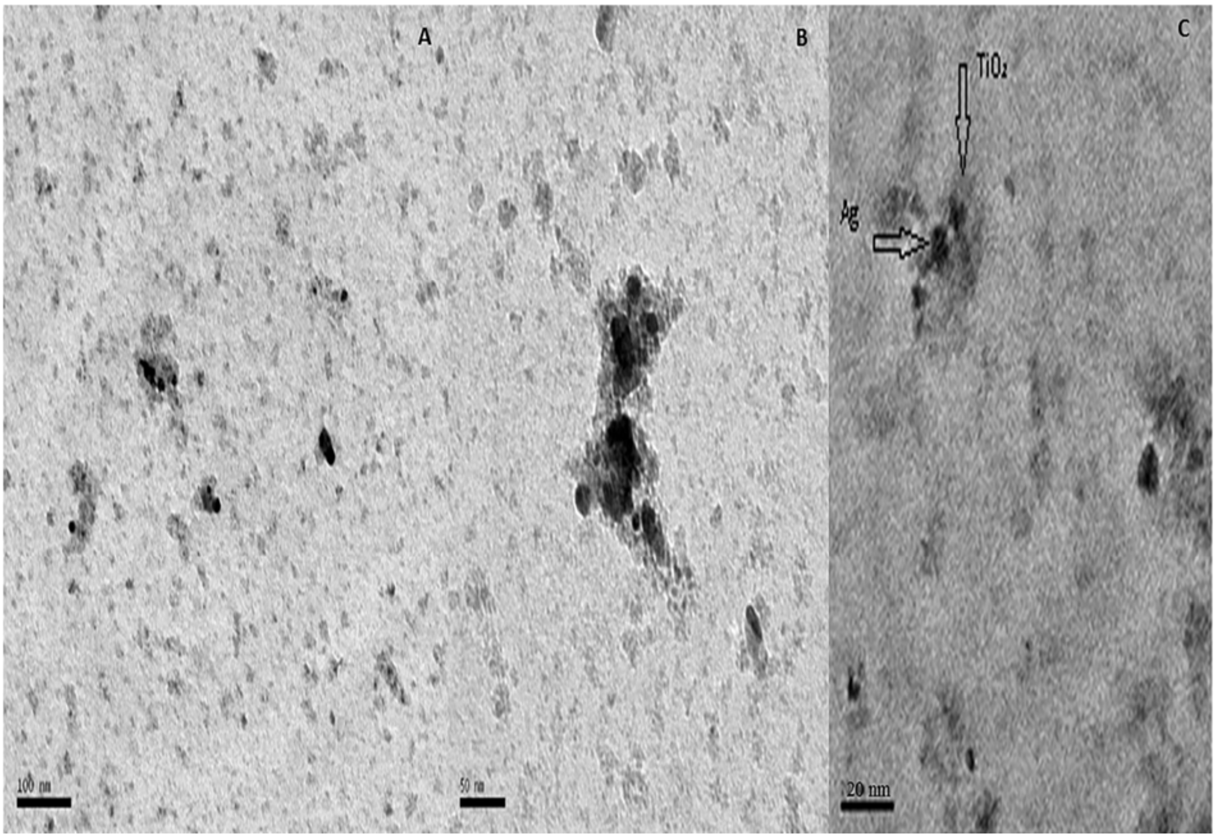

Figure 4. TEM images of P-1 Powder A) 100 nm B) 50 nm C) 20 nm

All results indicate that the P-1 powder is the best powder for photocatalytic effect. Shrinkage of the nanoscale in studies to increase the photocatalytic activity for photocatalytic applications of this powder is then selected. However; it is very difficult for the powder-type photocatalysts to be separate from the purified water and reused. A functional coating instead of the materials to be added directly to the solution of the photocatalytic powder for photocatalytic applications is preferred. Water separation of suspended dust Ag doped nanoTiO_2 is difficult. In this case, another problem arises. Hence; the coating of ceramic pellets are preferred. When the nano-dimensions is observed that P-1 powders has the best nano-sized. P-1 powder, ceramic pellets coated with the dip coating method and the photocatalytic activity was investigated.

3.2 Characterization of coated of the ceramic pellets with Ag doped nano TiO_2 powder

Figure 5 shows that SEM images of the before and after coating. When the coating of ceramic pellets examined before and after coating the image is observed that surface substantial uniformly coated with the Ag doped nano TiO_2.

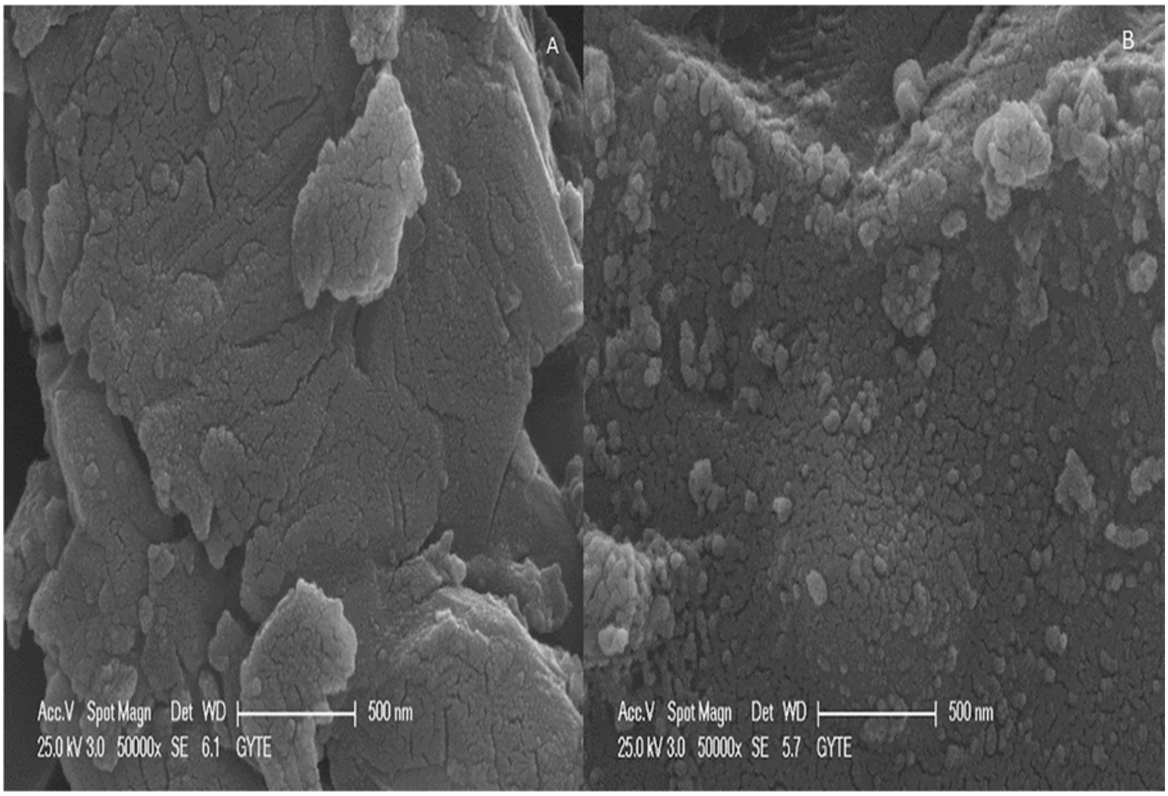

Figure 5. SEM images of the ceramic pellets (A) before coating (B) after coating

Figure 6 shows that EDS results of the before and after coating of the ceramic pellets. Besides the basic elements forming after coating ceramic beads is seen high intensity at the Ti, O and Ag elements. EDS results indicate that the surface of the ceramic pellets coated with nano Ag doped anatase TiO_2 form.

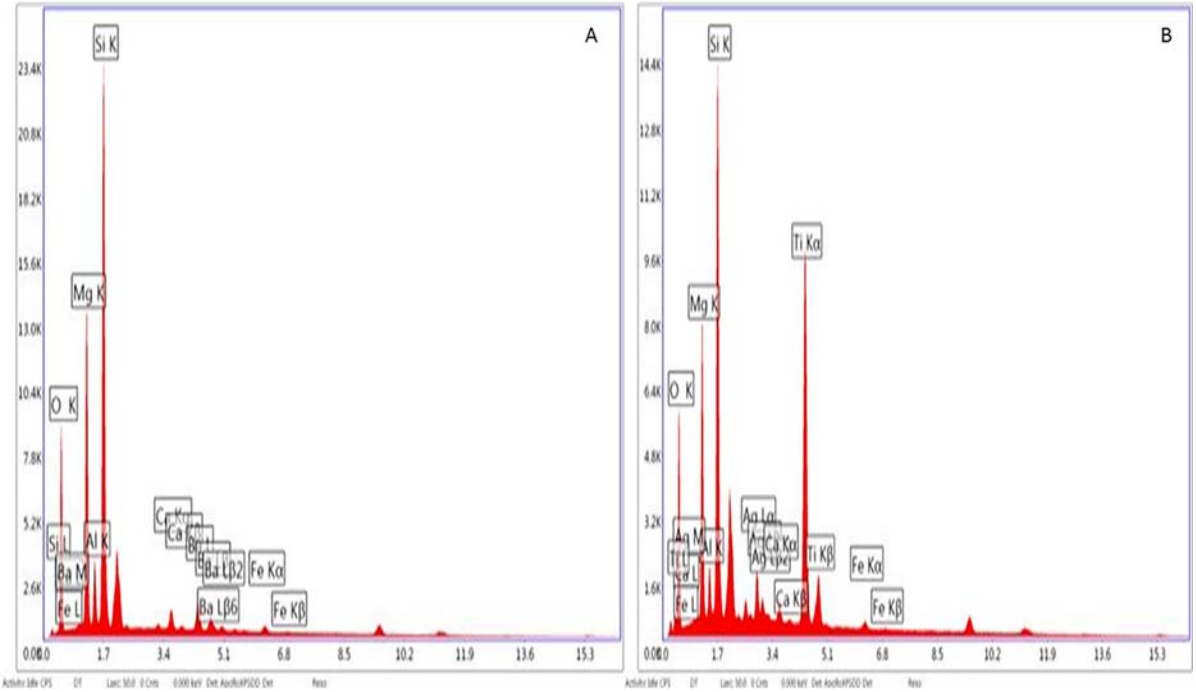

Figure 6. EDS Results of The Ceramic pellets (A) before coating (B) after coating

3.3 Photocatalytic degradation of indigo blue dye

The photocatalytic properties of the ceramic pellets coating with Ag doped nano TiO_2 were evaluated by examination of indigo blue dye degradation under UV light irritation. Firstly indigo blue solution was prepared (0.002 g indigo blue/2 L pure water). The coated ceramic pellets was immersed into indigo blue dye solution with a concentration 1 ppm at pH 6.0 the indigo blue dye solution was circulated into at the ambient temperature. Prepared solution was circulated in the aquarium glass under 8 W UV light. An aliquot of 3 ml was taken out from reaction mixture at definite time intervals and the absorbance was measured at 672 nm. The efficiency of decolourisation of the indigo blue solution with the prepared coated the ceramic pellets with Ag doped nano TiO_2 catalyst under UV irradiation is shown in Figure 7. It shows that the intensity of the maximum adsorption peak at 672 nm decreases rapidly as the irradiation time increases, which indicates the photo degradation of the IB dye. Approximately %75 of IB is degraded catalytically after 150 min. As new peak not appears during the reaction, degradation has been successful. It could be explained that the Ag particles doped on the TiO_2 surface can act as electron–hole separation centres [58, 59]. When a metal oxide photocatalyst is illuminated by light with an energy higher than its band gap, electron/hole pairs are generated. Some of these pairs can migrate to the surface weathered, after generating species such as the hydroxyl ($OH^{\bullet}$) and the superoxide radical ($^{\bullet}O_2^-$) by reaction with water and oxygen, they degrade adsorbed organic molecule [21, 60, 61].

The electron transfer from the TiO_2 conduction band to metallic silver particles at the interface is thermodynamically possible because the Fermi level of TiO_2 is higher than that of the silver metals [34]. This causes the formation of the Schottky barrier at Ag doped TiO_2 contact region which improves the charge separation and thus enhances the photocatalytic activity of TiO_2. Under UV irradiation, IB is activated into its excited state, injecting an electron into the conduction of TiO_2. The injected electron on the TiO_2 particle reacts with adsorbed O_2 to produced active oxygen radicals. In this mechanism, the TiO_2 acts only as an electron-transfer and the oxygen as an electron acceptor. The Ag particles on the TiO_2 surface can act as electron traps enhancing the electron–hole separation. The proposed photocatalytic degradation mechanisms of indigo blue using Ag doped nano TiO_2 as photocatalyst as following equations [33];

$$\text{Ag-TiO}_2 + h\nu \rightarrow \text{Ag-TiO}_2\,(e_{CB}^-) + \text{Ag-TiO}_2\,(h_{VB}^+) \qquad (1)$$

$$\text{IB} + \text{hv} \rightarrow \text{IC}^* \qquad (2)$$

$$\text{IB}^* + \text{Ag- TiO}_2 \rightarrow \text{IC}^+ + \text{Ag-TiO}_2\,(e_{CB0}^-) \qquad (3)$$

$$(O_2)_{ads} + \text{Ag-TiO}_2\,(e_{CB}^-) \rightarrow O_2^{\bullet} \qquad (4)$$

$$(H_2O \leftrightarrow H^+ + OH^-)_{ads} + \text{Ag} - \text{TiO}_2\,(h_{VB}^+) \rightarrow H + OH^{\bullet} \qquad (5)$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet} \qquad (6)$$

$$2\,HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \qquad (7)$$

$$H_2O_2 + e^- \rightarrow OH^{\bullet} + OH^- \qquad (8)$$

$$\text{IB} + OH^{\bullet} \rightarrow \text{IB}^{\bullet} + H_2O \qquad (9)$$

$$IB + Ag\text{-}TiO_2\,(h^+) \rightarrow IB^{+\bullet} \rightarrow \text{degradation products} \qquad (10)$$

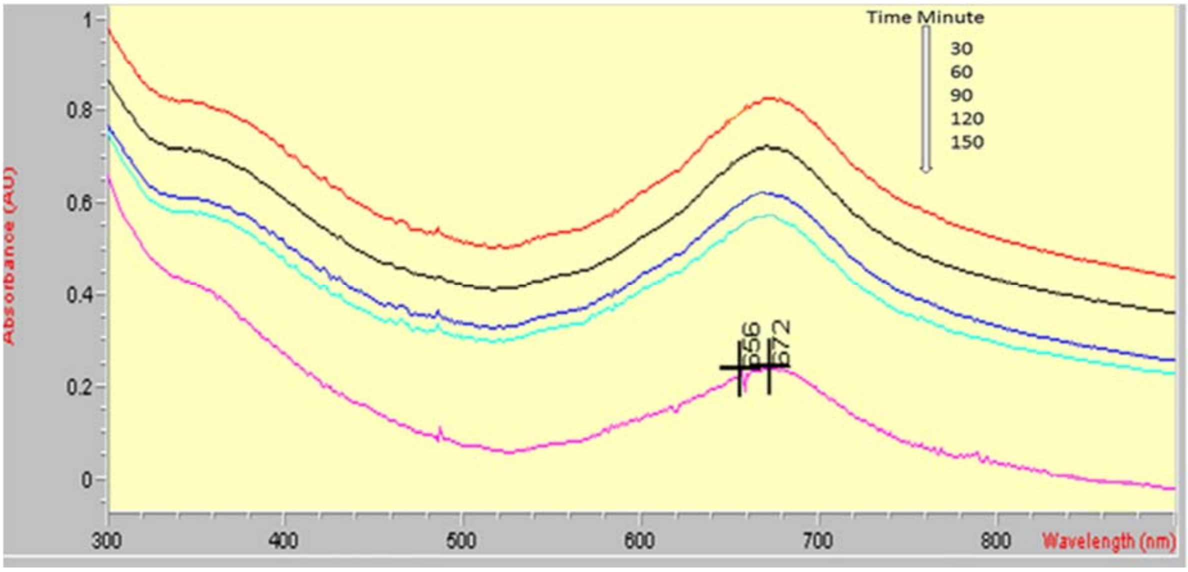

Figure 7. Change in Uv-Vis absorbance spectra of degradation of indigo blue dye (IB) in Ag doped TiO_2 with irradiation time

When Ag/ TiO_2 is exposed to UV light irradiation, the electrons below the Fermi level of the Ag's will be excited to the surface Plasmon states, leaving positive charges (h^+) below the E_f. Thus, with the contact of Ag on the TiO_2, the energetic electrons from Ag will be excited to the CB of TiO_2, As the CB is TiO_2 an electron acceptor, it is readily accepts the electrons and forms superoxide anion radicals ($^{\bullet}O_2^-$) and followed by the protonation that yields $^{\bullet}HO_2$ radicals. This $^{\bullet}HO_2$ radicals easily combines with the trapped electrons resulting H_2O_2 and finally forming a photo degradation active species $^{\bullet}OH$ radicals. Moreover Schottky barrier was formed at the interface of Ag doped nano TiO_2 because the Fermi level of TiO_2 is higher than that of Ag which will hinder the transfer of electron from the Ag to TiO_2. However, it is proven that electrons are able to transfer from the Ag to TiO_2 due to its strong electron oscillating collectively on the SPR excitation. These lead to interbant excitation giving sufficient energy to the electrons to overcome the Schottky barrier at the interface. Thus it triggers the energetic electrons to be transfer to the CB of TiO_2 and lead to the enriched formation of $^{\bullet}OH$ radicals thus enhancing the photocatalytic oxidation and occur degradation products.

Additionally, the photocatalytic degradation kinetic was investigated; the linear simulation of degradation of dye concentration can be accounted for by a pseudo first-order, called the Langmuir–Hinshelwood (L–H) model [62, 63]. In the presence of Ag doped TiO_2, the concentration of İB in suspension decreased rapidly with irradiation time (figure 8(A)). The efficiency of degradation was calculated from Eq. (2) as follows and shows figure 8(B):

$$C/C_0=A/A_0 \qquad (2)$$

Where A_0 and A are the initial and final absorbance at 672 nm for İB. The data could be satisfactorily described by the first-order kinetic equation;

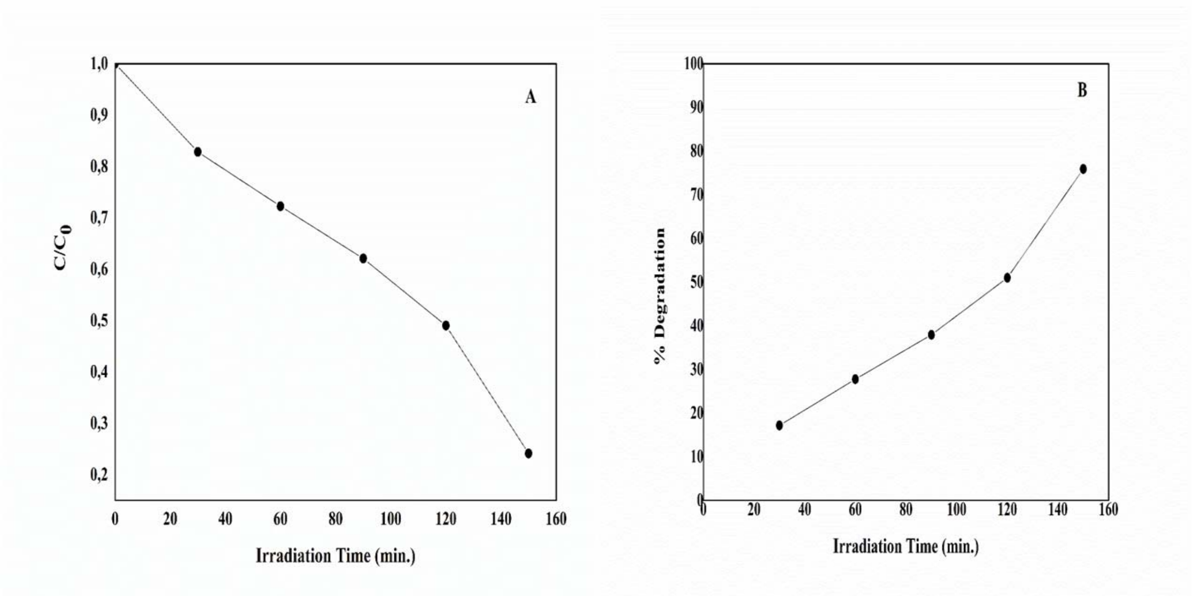

Figure 8. (A) Plots of C/C$_0$ versus irradiation time for photodegradations of İB (B) Photocatalytic activity of Ag doped nano TiO$_2$ under UV light irradiation

$$\ln(C/C_0) = -k_{app}t \qquad (3)$$

Where k_{app} is the apparent rate constant, C and C$_0$ are the concentrations of İB at time t = t and t =0, respectively. The kinetic analysis was performed to understand the İB degradation procedure, and the rate constant of İB degradation (k) over the samples under the simulated UV irradiation was obtained. The rates were corrected for dye decay rate of under simulated UV illumination with catalyst. The determined rate constant in the presence of TiO$_2$, 30 min, 60 min, 90 min, 120 min and 150 min is 6.27×10^{-3} min^{-1}, 5.42×10^{-3} min^{-1}, 5.30×10^{-3} min^{-1}, 15.94×10^{-3} min^{-1} and 9.48×10^{-3} min^{-1} respectively, indicating the Ag-TiO$_2$ (150 min) shows the highest catalytic activity with rate constant (k) of 9.48×10^{-3} min^{-1}.

4. Conclusion

Pure Ag doped nano TiO$_2$ powders with an 10/13 nm crystallite size was prepared by hydrothermal method at 180 ºC in 120 min using sodium borohydride, PEG-600, Hydrazine and ascorbic acid as reducing agents. The structure of the powders was characterized with XRD, SEM, EDS, BET and TEM. The result showed that the best structure powder were obtained from PEG-600 used as both a surfactant and reducing agents. The Ag doped nano TiO$_2$ existed in the anatase phase. Ag doped nano TiO$_2$ photocatalysts were coated to the ceramic pellets by dip coating technique. The photocatalytic activity of the ceramic pellets coated with Ag doped nano TiO$_2$ was evaluated in the photodegradation of İB as a model organic pollutant. The maximum photodegradation of İB achieved in this study was %75 after irradiation time of 150 min. The kinetics of the photodegradation in the presence of the catalysts follows a first – order rate model. Thus the present study has brought to light a novel method for the reduction of pollutants in future.

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