Available online at BCREC Website: http://bcrec.undip.ac.id

Bulletin of Chemical Reaction Engineering & Catalysis, 4(2), 2009, 43-53

Surface Modification, Characterization and Photocatlytic Performance of Nano-Sized Titania modified with Silver and Bentonite clay

Neetu Divya1[1], Ajay Bansal[1]*, and Asim K Jana [2]

[1] *Department of Chemical Engineering*
National Institute of Technology, Jalandhar, 1440011, Punjab, INDIA
[2] *Department of Biotechnology*
National Institute of Technology, Jalandhar, 1440011, Punjab, INDIA

Received: 30 October 2009, Revised: 20 November 2009, Accepted: 21 November 2009

Abstract

In many textile industries dyes are used as coloring agents. Advanced oxidation processes are used for degrading or removing color from dye baths. Catalysts play a key role in these industries for the treatment of water. Solid catalysts are usually composed of metals that form supports onto the surface and create metal particles with high surface areas. TiO_2 composites containing transition metal ions (silver) and/or bentonite clay were prepared. Photocatalytic efficiencies have been investigated for the degradation of Orange G an azo dye. Various analytical techniques were used to characterize the surface properties of nano-sized titania modified using silver and/or bentonite clay. Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), X-ray diffraction (XRD) and FTIR analyses showed that TiO_2 (10 ± 2 nm) and Ag (2 to 3 nm) particles were supported on the surface of the bentonite clay and the size was in the range of 100 ± 2 nm. The modified catalysts P-25 TiO_2/Bentonite/Ag and P-25 TiO_2/Ag were found to be very active for the photocatalytic decomposition of Orange G. The percent decolorization in 60 min was 98% with both P-25 TiO_2/Ag and P-25 TiO_2/Bentonite/Ag modified catalysts. Whereas mineralization achieved in 9 hr were 68% and 71% with P-25 TiO_2/Bentonite/Ag and P-25 TiO_2/Ag catalyst respectively. © 2009 BCREC. All rights reserved.
.

Keywords: Decolorization; Mineralization; Orange G; Nano-composite catalyst; Catalyst-characterization

1. Introduction

In many textile industries dyes are used as coloring agents and large amount of water is consumed between 25-250 m^3 per ton of product depending on the operating processes [1].The effluent comes from these industries containing a large amount of organic compounds, that raises environmental concerns. Advanced oxidation processes are used for degrading and removing color from dye baths. The treated water can be reused. Photocatalytic reaction using semiconductors in the powder form can effectively degrade many organic pollutants, and even makes the compounds completely mineralized. Modifying the properties of one mate-

---

* Corresponding Author, E-mail: E-mail: drajaybansal@gmail.com
Tel: +91-181-2690301; Fax: +91-181-2690320.

rial by doping it with another type of material seems to be a popular approach [2, 3, 4, 5, 6].

Menesi et al. [2] prepared montmorillonite-TiO_2 composites containing various transition metal ions (silver, copper, or nickel). Photocatalytic efficiencies of composite catalysts were tested and found more efficient for the degradation of ethanol under UV-C ($\lambda = 254$ nm) than in visible light. Furthermore, these samples containing silver or copper ions were, in each case, about twice more efficient than P-25 TiO_2 (Degussa AG) used as a reference. In photooxidation by visible light, TiO_2/clay samples doped with silver or copper were also more efficient.

Li et al. [4] used the TiO_2 pillared bentonite catalyst to degrade 2,4-dichlorophenol and Orange II under UV light irradiation. It was found that the color and COD removal of the organic compound by P-25 TiO_2, Ti-pillared bentonite SCD (super critical drying) and Ti- pillared bentonite catalyst indicating that the degradation rate of the pollutant by P-25 TiO_2 was the fastest, while the photocatalytic efficiency of Ti-pilb. SCD was much better than that of Ti- pillared bentonite for this degradation under UV irradiation. Although the catalytic activity of Ti- pillared bentonite SCD was slightly lower than that of P-25 TiO_2.

Sun et al. [5] prepared titanium dioxide/bentonite clay nano-composite by acid-catalyzed sol–gel method for the cationic azo dye decomposition under UV irradiations. They observed that the doping metal ions can also be delivered to the surface of the support by ion exchange and significantly altered the optical characteristics of the TiO_2/clay composite.

Zhao et al. [7] coated nano-sized titanium dioxide (TiO_2) crystal particles onto the surface of palygorskite fibrous clay which had been modified by silver ions and apply various analytical techniques (TEM, XRD and XPS) to characterize the surface properties of titanium dioxide particles on the palygorskite. TiO_2 particles were supported on the surface of the palygorskite clays and found that their size was in the range of 3–6 nm. The titanium oxide coatings were found to be very active for the photocatalytic decomposition of methylene blue.

Arabatzis et al. [8] prepared silver modified titanium dioxide thin film to degrade methyl Orange. Doctor-blade procedure was used for the film preparation. It was found that the silver modified titanium dioxide thin film enhanced photocatalytic efficiency and degraded the organic pollutant three-times faster than the undoped original films (Degussa P-25). It was concluded that the enhancement is attributed to the action of Ag^+ cations, which attract the conduction band photoelectrons and prevent electron–hole recombination.

Bentonite is colloidal, alumino-silicate clay derived from weathered volcanic ash and largely composed of montmorillonite. It consists of an aggregate of flat platelets, has a high specific surface area, high plasticity, non-toxic and expands when wet. If used in combination with nano-sized titania makes it easier to separate the titania based photocatalysts [6].

It is therefore interesting to investigate the photocatalytic activity of composite photocatalysts comprising of Ag, titania and bentonite. Keeping this in view catalysts such as P-25 TiO_2, P-25 TiO_2/Bentonite, P-25 TiO_2/Bentonite/Ag and P-25 TiO_2/Ag were prepared. The catalysts thus formed were used for the photocatalytic degradation of OG. The catalysts have also been characterization to record the surface modifications

2. Materials and Methods

2.1 Chemicals

The azo dye Orange G (OG) 90%, H_2O_2 (30% w/v), HCl (34%), Sodium hydroxide pellets purified (NaOH), ethanol (99.9%), HNO_3 (60-70%), ferrous ammonium sulphate ($NH_3(FeSO_4)_2.6H_2O$), potassium dichromate ($K_2Cr_2O_7$), silver sulphate ($AgSO_4$), mercury sulphate ($HgSO_4$), ferroin indicator, Sulphuric acid (H_2SO_4) were all purchased from S. D. Fine Chemicals Limited, Mumbai, India. $AgNO_3$ reagent used for catalyst modification was purchased from Qualigens Fine Chemicals Limited, Mumbai, India. P-25 TiO_2 (80% anatase, 20% rutile) with a specific surface of 50 m^2/g, was purchased from Evonic (Degussa), Germany. They were used without any further treatment.

2.2 Preparation of catalyst composite

2.2.1. P-25 TiO_2/Ag catalyst

Modification of catalyst was done using impregnation method. Impregnation occurs when metal attached to the oxides. The titania based photocatalyst employed was commercial titanium dioxide powder (Degussa P-25) with a BET surface area of 50 m^2/g and an average particle size of 10 ± 2 nm. Metal ion doped TiO_2 (Degussa P-25) was prepared using the following procedure. The doping was done using transition metal salt $AgNO_3$. 0.3120 g of $AgNO_3$ was dissolved in 30 ml of distilled water in a porcelain bowl. 7.9105 g of

TiO_2 was then added to the solution. The solution was stirred well and was allowed to stand for 24 hr. The contents were heated at 100 ± 5 °C to evaporate all the water. The dried solids were first ground and then calcined at 400 °C for 6 hr in a muffle furnace.

2.2.2. P-25 TiO_2/Bentonite catalyst

For the preparation of P-25 TiO_2/Bentonite catalyst acid- catalyzed sol-gel process was used. In a porcelain bowl 3 g of P-25 TiO_2 was mixed with 33 ml of ethanol and stand for 2 hr under continuous stirring. Then 1M HNO_3 was added drop wise under continuous stirring. 3 g bentonite clay saturated with water for half an hour was then mixed with P-25 TiO_2 solution and live for 2 hr under continuous stirring. The solution was stirred well and was allowed to stand for 24 hr (maturation period). The contents were heated at 100 ± 5 °C to evaporate all the water. The dried solids were first ground and then calcined at 500 °C for 3 hr in a muffle furnace. The scheme for preparation of composites catalyst was suggested in Figure 1.

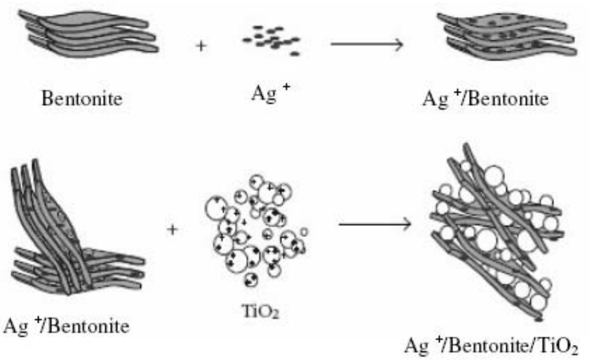


Figure 1. Schematic diagram for preparation of P-25 TiO_2/Bentonite/Ag composites

2.2.3. P-25 TiO_2/Bentonite/Ag catalyst

P-25 TiO_2/Bentonite/Ag catalyst was prepared by following procedure. In a porcelain bowl transparent solution of 0.5 g $AgNO_3$ was prepared and 10 ml ethanol was added drop wise. 3 g P-25 TiO_2 and 20 ml 1M HNO_3 (dropwise) was mixed simultaneously in $AgNO_3$ and ethanol mixture under continuous stirring. 3 g bentonite was added. The rest of the procedure was same as that for P-25 TiO_2/Bentonite catalyst. For different concentration of $AgNO_3$ similarly method was used. The composites preparation scheme was proposed in Figure 1.

2.3. Photocatalytic degradation of azo dye

Spectrophotometer was used for the measurement of decolorization. A calibration plot based on Beer–Lambert's law was established by relating the absorbance to the concentration. The measurement of maximum absorbance was taken for Orange G was 490 nm. The degradation studies are reported as 'η' called photodegradation efficiency and was discussed in previous article [10].

Chemical Oxygen Demand (COD) of the treated sample was measured by the dichromate titration method (APHA). The efficiency of dye mineralization was estimated using the following expressions [11]:

$$Mineralization\,\% = \left(1 - \frac{COD_t}{COD_i}\right) \times 100 \qquad (1)$$

Where CODt correspond to time t and CODi correspond to initial conditions. Eutech pH/lon 510, pH meter was used for the measurement of pH of solution.

Stock solution of the dye (1000 ppm) was prepared with double distilled water from which working solution (50 ppm) was prepared. Then solution pH value was adjusted to 3 using 0.1 N NaOH and 0.1N HCl. For homogeneous photocatalytic degradation, twenty milliliters of the working solution of the dye (50 ppm) was taken in a beaker then H_2O_2 was added. The zero time reading was taken and the solution was then subjected to irradiation. Aliquots were taken at regular intervals to analyze the percent degradation of the dye. In case of heterogeneous photocatalysts, TiO_2 based catalyst was added along with H_2O_2.The solution was then subjected for continuous stirring for 60 min in dark and the rest of the procedure was same as that for homogeneous photocatalysis. The decolorization and mineralization studies were carried out under pre-optimized conditions discussed elsewhere [10].

3. Results and Discussion

3.1. Decolorization

The degradation of OG was investigated with different combination of P-25 TiO_2, bentonite and silver metal ion. The amount of silver metal ion was varied from 0.3120 to 0.9360 g for doping. Whereas the amount of bentonite considered was 1 and 3 g. The developed modified catalyst-combinations are P-25 TiO_2/Bentonite, P-25 TiO_2/Bentonite/Ag, and P-25 TiO_2/Ag. The decolorization of OG under 60 min UV irradiation was observed as 96%, 95%, 98% and 98% for P-25 TiO_2, P-25 TiO_2/Bentonite, P-25 TiO_2/Bentonite/Ag and P-25 TiO_2/Ag catalysts respectively [Figure 2].

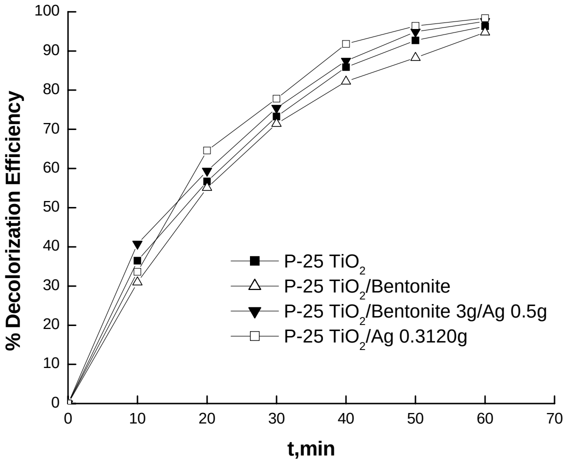


Figure 2. Percent decolorization of OG with different modified catalysts

The doses of Ag were varied to find out the optimum dose of Ag. As such Ag was varied from 0.312 g to 0.936 g. The decolorization efficiencies under 60 min UV irradiation were observed 82%, 98%, 88% and 86% for P-25 TiO_2/Bentonite/Ag 0.312 g, P-25 TiO_2/Bentonite/Ag 0.5 g, P-25 TiO_2/Bentonite/Ag 0.624 g and P-25 TiO_2/Bentonite/Ag 0.936 g catalysts, respectively [Figure 3].

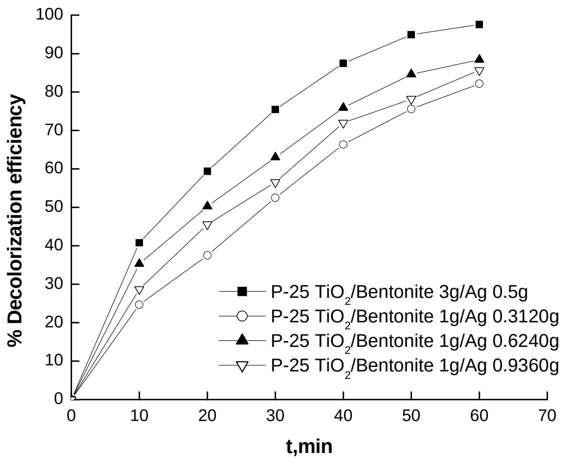


Figure 3. Percent decolorization of OG with different modified catalysts with different doses of Ag

With an increase in Ag concentration the decolorization efficiency increased up to 0.5 g Ag but above it the efficiency decreased. Probably it happened due to shading of the available photocatalyst surface (i.e. P-25 TiO_2 and Bentonite) by the silver layer [8].

The decolorization efficiency using P-25 TiO_2/Bentonite was 95%, which was a little less than 96% that was obtained with the catalyst with out bentonite (i.e. P-25 TiO_2). It could be for the reason that some of the photoactive surface of P-25 TiO_2 particles might not be exposed to radiations as TiO_2 particles might have been trapped between bentonite layers [Figure 2.]. It was, however found that the combination of P-25 TiO_2/bentonite/Ag and P-25 TiO_2/Ag catalyst efficiently decolorized OG to 98% [Tables 1 and 2].

Table 1. Percent decolorization of OG with different modified catalysts

Catalysts	**Catalysts compositions, g**	**% Decolorization efficiency (60 min)**	**% Mineralization efficiency (9 hr)**
P-25 TiO_2	Pure	96	56
P-25 TiO_2/Bentonite	3:3	95	35
P-25 TiO_2/Bentonite /Ag 0.5 g	3:3:0.5	98	68
P-25 TiO_2/Ag	7.1905: 0.312	98	71

3.2. Mineralization

For the mineralization studies percent COD removal was recorded at different time intervals. The mineralization efficiency was observed to be 56%, 35%, 68% and 71% with P-25 TiO_2, P-25 TiO_2/Bentonite, P-25 TiO_2/Bentonite/Ag and P-25 TiO_2/Ag catalysts, respectively [Figure 4.]. Further with variation of silver ion doses the COD removal was observed as 33%, 68%, 13% and 25% for P-25 TiO_2/Bentonite/Ag 0.312 g, P-25 TiO_2/Bentonite/Ag 0.5 g, P-25 TiO_2/Bentonite/Ag 0.624 g and P-25 TiO_2/Bentonite/Ag 0.936 g catalysts, respectively [Figure 5.].The results show that the P-25 TiO_2/Ag catalyst resulted in better mineralization efficiency in terms of COD removal when compared with the other combinations of photocatalysts [Figure 4.]. However, where the separation of catalysts from process solution is critical and economic factor (inexpensive catalysts) is

Table 2. Decolorization and Mineralization efficiency of P-25 TiO$_2$/Bentonite/Ag modified catalysts with different doses of silver salt

Catalysts	Catalysts compositions, g	% Decolorization efficiency (60min)	% Mineralization efficiency (9 hr)
P-25 TiO$_2$/Bentonite/Ag 0.5 g	3:3:0.5	98	68
P-25 TiO$_2$/Bentonite/Ag 0.312 g	3:1:0.312	82	33
P-25 TiO$_2$/Bentonite/Ag 0.624 g	3:1:0.624	88	13
P-25 TiO$_2$/Bentonite/Ag 0.936 g	3:1:0.936	86	25

more important then P-25 TiO$_2$/Bentonite/Ag 0.5 g modified catalysts can be considered as an alternative to P-25 TiO$_2$/Ag photocatalyst.

3.3 Catalysts Characterization

3.3.1 SEM analysis

The structures of P-25 TiO$_2$, P-25 TiO$_2$/Bentonite,P-25 TiO$_2$/Bentonite/Ag, P-25 TiO$_2$/Ag were observed by scanning electron microscope JSM 6100 (JEOL) operated at 20 kV at SAIF, Panjab University, Chandigarh. The observed structures of catalysts are shown in Figure 6. Scattered clusters of P-25 TiO$_2$ at x25000 magnification were observed as shown in Figure 6a. The SEM picture, Figure 6b, for bentonite at x30000 magnification showed layered structure of bentonite. SEM picture, Figure 6c, at x4300 magnification, corresponding to modified catalysts of P-25 TiO$_2$/Bentonite clearly shows the deposition of TiO$_2$ particles on bentonite. Whereas, Fig 6d. corresponding to P-25 TiO$_2$/Bentonite/Ag at x4000 magnification shows the Ag and P-25 TiO$_2$ particles on the surface of bentonite. Similarly, Figure 6e indicates Ag particles deposition on P-25 TiO$_2$ at x25000 magnification . However, SEM micrographs shown in Figure 6 (a, b, c, d, e) do not clearly display the particle size of modified catalyst. For observing the size of fine particles of silver, TiO$_2$ and bentonite the TEM analysis of the modified catalysts was performed.

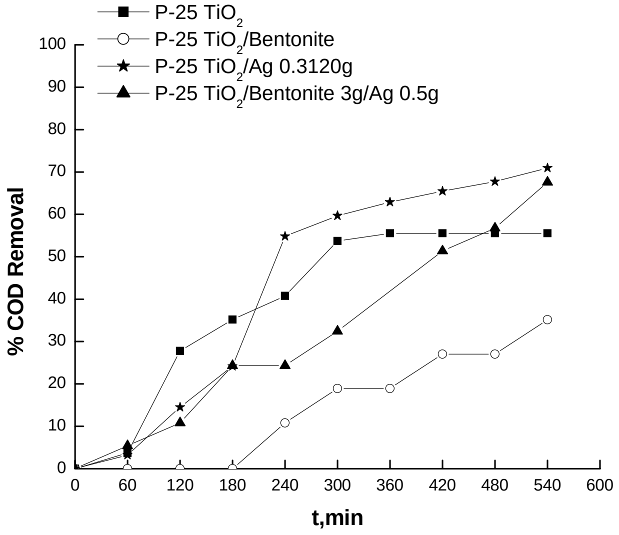


Figure 4. Percent COD Removal of OG with different modified catalysts

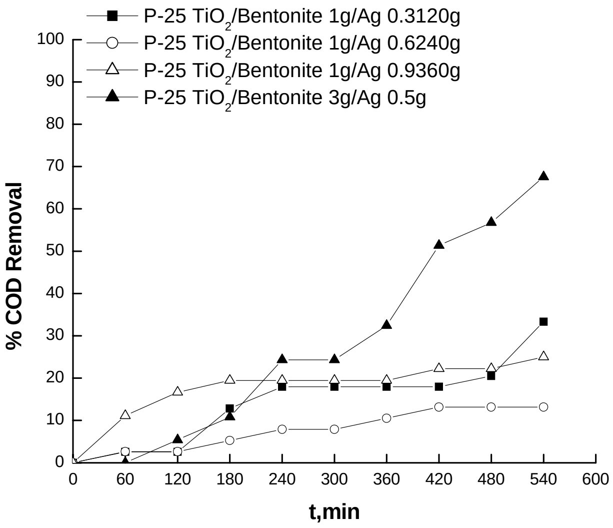


Figure 5. Percent COD Removal of OG [Modified P-25 with Bentonite and different doses of Ag

3.3.2 TEM analysis

The catalysts morphology was analyzed using transmission electron microscope. The particle size of P-25 TiO$_2$, P-25 TiO$_2$/Bentonite, P-25 TiO$_2$/Bentonite/Ag and P-25 TiO$_2$/Ag catalysts were analyzed by transmission electron microscope operated at 100 kV. Transmission electron microscopy (TEM) has the advantage of giving a real space image for the distribution of particles, their surface and shape. Samples were placed onto a carbon-coated copper grid having 400 holes. The sample was analyzed to see the particles that remained adhered to the grid. The TEM studies were performed using a Hitachi 7500 at SAIF, Panjab University, Chandigarh. It was observed that the mean particle sizes were as P-25 TiO_2 10 ± 2 nm [Figure 7a. at x300000], Bentonite 100 ± 2 nm [Figure 7b. at x120000], deposited Ag particle size 1 to 2 nm at direct magnification [Figure 7d. at x500000]. These images clearly indicated that a modified silver doped titania based clay photocatalyst of nano-size was obtained. Nano-sized particles are well known to exhibit different physical and chemical properties than bulk materials. When

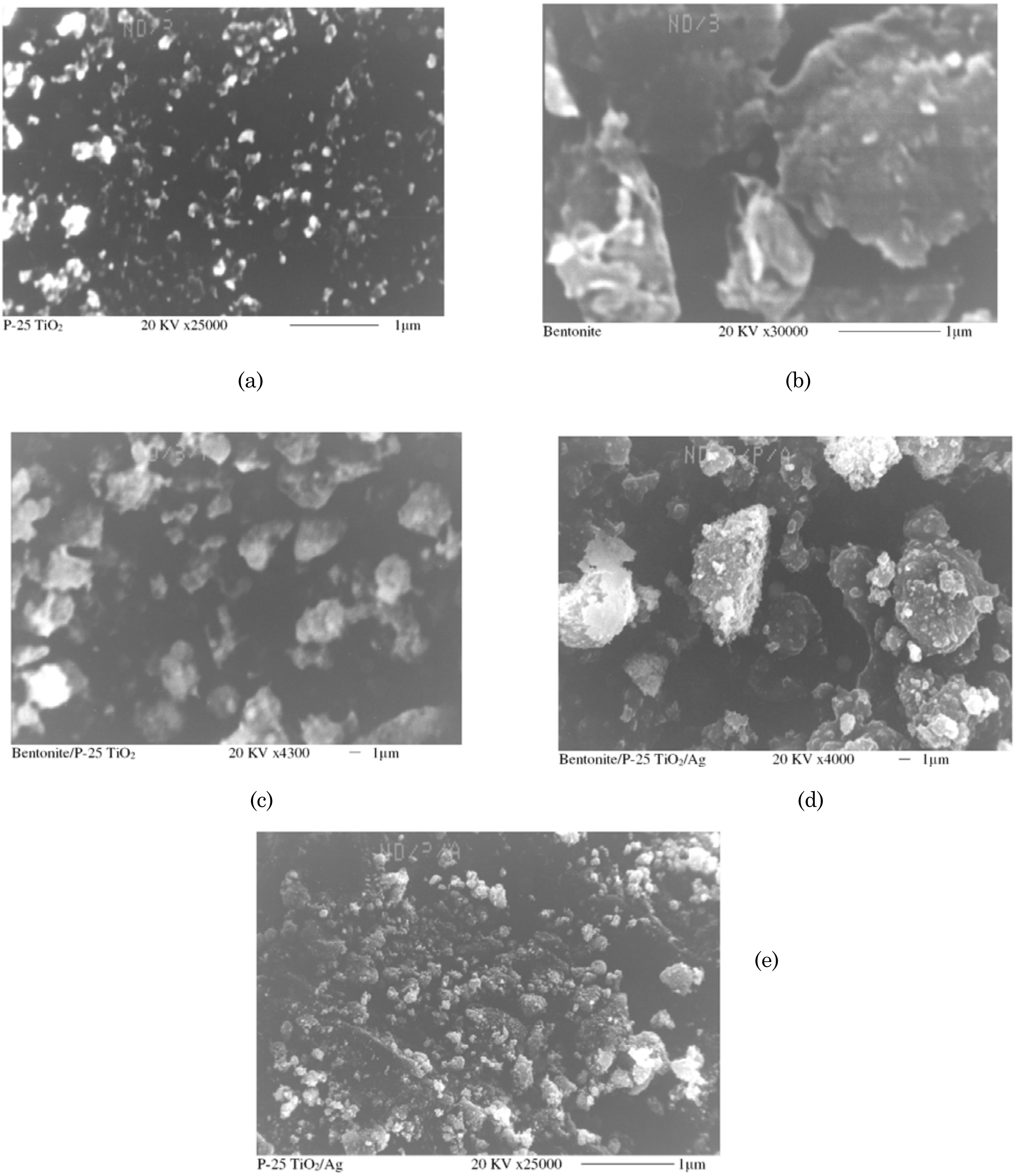
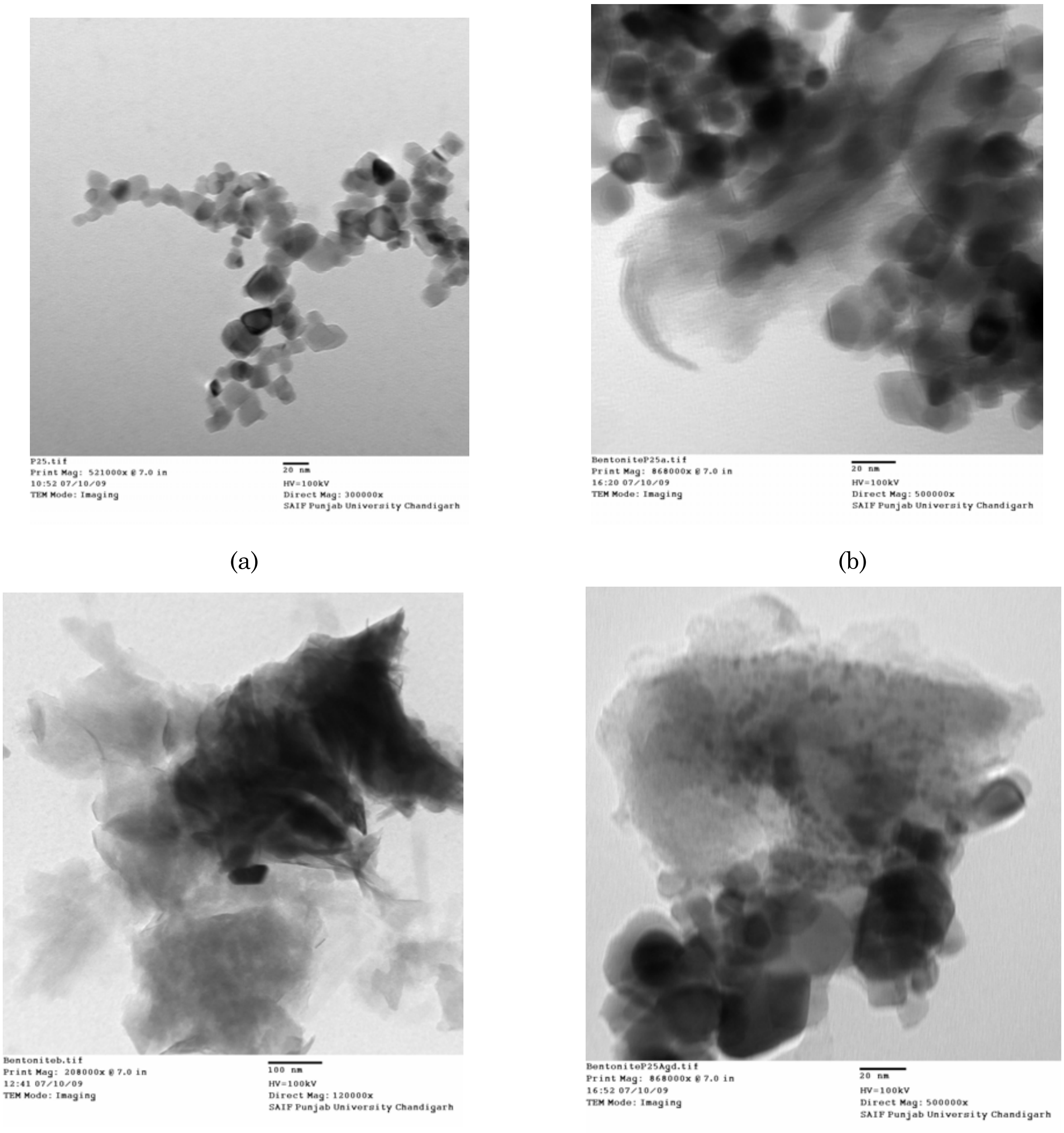


Figure 6. SEM analysis of (a) P-25 TiO_2 (b) Bentonite (c) P-25 TiO_2/Bentonite (d)P-25 TiO_2/Bentonite/Ag (e) P-25 TiO_2/Ag



(a) (b)

(c) (d)

Figure 7. TEM analysis of (a) P-25 TiO_2 (b) Bentonite (c) P-25 TiO_2/Bentonite (d)P-25 TiO_2/Bentonite/Ag

nano-sized particles are used as catalyst, catalytic activity is expected to be enhanced due to the increased surface area. It was confirmed that silver is present in/on the bentonite and that the crystal structures of the bentonite and P-25 TiO_2 were not changed by the silver doping.

3.3.3 XRD analysis

The phase composition of photocatalyst was studied using powder XRD technique. The patterns were recorded on an Philips PW-1710 X-ray diffractometer using Cu-Kα (1.54060 Å) radiation at SAIF, Panjab University, Chandigarh. Diffraction patterns were taken over the 2θ range 20–100°. The crystallite size is determined from XRD pattern, using Sherrer formula $t = (0.9\lambda/\beta \cos \theta)$, where t is in nm, λ the wavelength of X-ray in Å (1.54060 Å), β full width half maxima (FWHM) in radians and θ is the Bragg angle. Based on the full width half maxima of X-ray diffraction pattern, the mean crystallite size is estimated to be 10 ± 2 nm. The commercial catalyst (Degussa P-25 TiO_2) used in the present study was pure anatase phase

[Figure 8]. The results show that no phase change was observed and even the modified bentonite clay photocatalytic had TiO_2 mainly in anatase form. The XRD spectrum of P-25 TiO_2/Ag showed no significant differences from that of the P-25 TiO_2, except the intensity of the basal plane peak are smaller than seen for the P-25 TiO_2. Since the concentration of silver in the P-25 TiO_2/Ag sample is very low (0.3120 g) characteristic Ag peaks were not seen. This implies that the crystal structure of P-25 TiO_2 was not changed by the silver ion.

The reflection at dA=0.3526 nm characteristic of anatase, was observed at $2\theta=25.24°$. According to JCPDS 21-1272, anatase presents the following diffraction pattern: a major intensity signal associated with the reflection (110) located at$2\theta=25.28°$ (relative intensity 100%), as well as other important signals at 37.8° (20%), 48.05° (35%), 53.89° (20%), 55.06° (20%), and 62.69° (14%) were observed [7]. All these signals were present in our modified catalysts. Thus the XRD spectra confirmed the crystalline nature of the titanium dioxide and modified catalysts, with anatase being the main crystalline phase present.

3.3.4 FTIR analysis

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantify some components of an unknown mixture. FTIR studies of modified catalysts were carried out in the 450–4000 cm^{-1} frequency range, in the transmission, mode using Perkin-Elmer-Spectrum RX-I (SAIF, Panjab University, Chandigarh) [Figure 9].

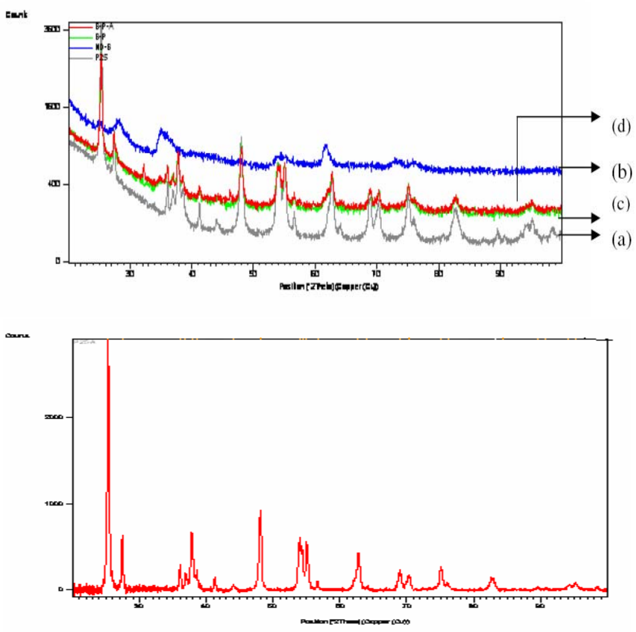
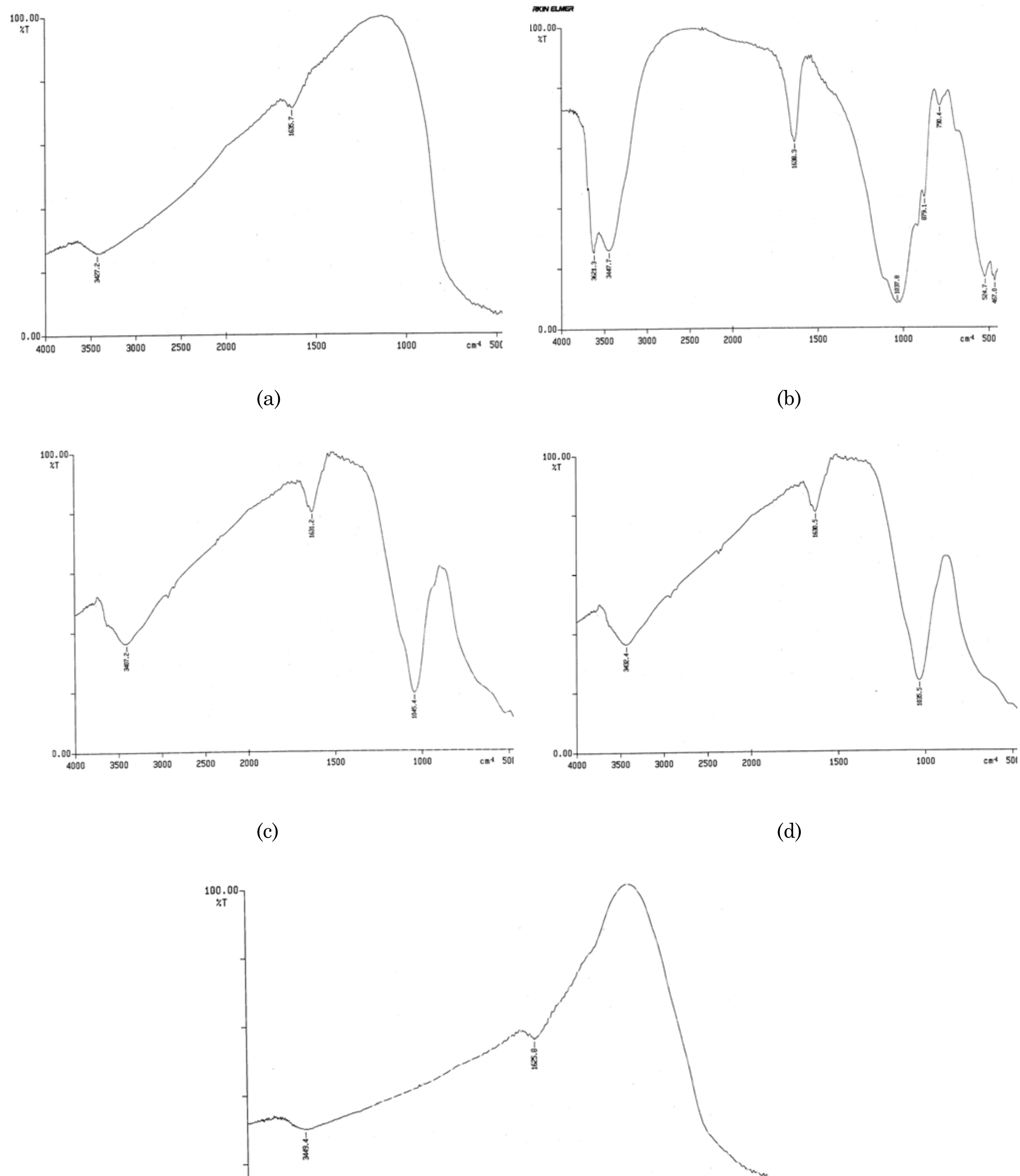


Figure 8. XRD analysis of (a) P-25 TiO_2 (b) Bentonite (c) P-25 TiO_2/Bentonite (d) P-25 TiO_2/ Bentonite/Ag (e) P-25 TiO_2/Ag

Peaks of 3427.2 cm^{-1} 3447.7 cm^{-1}, 3407.2 cm^{-1}, 3432.4 cm^{-1} and 3449.4 cm^{-1} wavenumbers are present in P-25 TiO_2, betonite, P-25 TiO_2/betonite, P-25 TiO_2/betonite/Ag and P-25 TiO_2/Ag catalysts respectively fall in the region 3550–3450 cm^{-1} and conform that the OH stretch functional group was present in the calatysts. If the peaks occur between 3670 and 3550 cm^{-1}, the compound probably contains a non-hydrogen-bonded hydroxyl group. For wavenumbers 3400–3200 cm^{-1} and 3550–3450 cm^{-1} regions, the compound contains the normal "polymeric" OH stretch and dimeric OH stretch bend, often an alcohol or phenol with a sterically hindered OH group. This spectral feature is also exhibited by certain inorganics and minerals, and is indicative of a "free" OH group, either on the surface, or embedded within a crystal lattice, and free from interactions with other ions or groups [12]. 3621.3 cm^{-1} peak of bentonite in the 3670-3550 cm^{-1} range confirms this type of OH functional group.

Molecules containing NO_2 groups, such as nitro compounds, nitrates, and nitramines, commonly exhibit asymmetric and symmetric stretching vibrations of the NO_2 group at 1660 to 1500 cm^{-1} region. Peaks of 1635.7 cm^{-1}, 1638.3 cm^{-1}, 1631.2 cm^{-1}, 1630.5 cm^{-1} and 1625.8 cm^{-1} are present in P-25 TiO_2, bentonite, P-25 TiO_2/bentonite, P-25 TiO_2/ bentonite/Ag and P-25 TiO_2/Ag modified catalysts found in the region of 1660 to 1500 cm^{-1}, respectively, which conform the presence of NO_2 group. Silicon-oxy absorptions occur within a crowded and highly overlapped region of the spectrum, mainly between 1350 and 950 cm^{-1} [12]. 1037.8 cm^{-1}, 1045.4 cm^{-1} and 1035.5 cm^{-1} peaks are found in that region are present in bentonite, P-25 TiO_2/ bentonite and P-25 TiO_2/bentonite/Ag catalyst combination. Peaks of C-H group 879.1 cm^{-1} and 524.7 cm^{-1} were present in bentonite. Corresponding to 790.4 cm^{-1} wavenumber ONO group was detected in bentonite. Frequencies and the functional groups present in the different modified catalysts are tabulated in Table 3.



(a)

(b)

(c)

(d)

(e)

Fig 9. FTIR analysis (a) P-25 TiO_2 (b) Bentonite (c) P-25 TiO_2/Bentonite (d) Bentonite/P-25 TiO_2/Ag (e) P-25 TiO_2/Ag

Table 3. Presences of various functional groups in modified catalysts using FTIR analysis

Catalysts	Peaks found (Wavenumber,cm^{-1})	Group(s) present
P-25 TiO_2	3427.2	O-H
	1635.7	Asymmetric and symmetric stretching vibrations of the NO_2 group
Bentonite	3621.3	O-H
	3447.7	O-H
	1638.3	Asymmetric and symmetric stretching vibrations of the NO_2 group
	1037.8	Si-O-Si
	879.1	C-H
	790.4	ONO bend
	524.7	C-H
	467.0	Not found
P-25 TiO_2/Bentonite	3407.2	O-H
	1631.2	Asymmetric and symmetric stretching vibrations of the NO_2 group
	1045.4	Si-O-Si
P-25 TiO_2/Bentonite/Ag	3432.4	O-H
	1630.5	Asymmetric and symmetric stretching vibrations of the NO_2 group
	1035.5	Si-O-Si
P-25 TiO_2/Ag	3449.4	O-H
	1625.8	Asymmetric and symmetric stretching vibrations of the NO_2 group

4. Conclusions

The decolorization efficiency was maximum with the P-25 TiO_2/Ag combinations (i.e. 98%) under 60 min UV irradiation. Further 71% dye mineralization in terms of COD removal was achieved with P-25 TiO_2/Ag catalyst under 9 hr UV irradiations. However, with P-25 TiO_2/Bentonite/Ag combination a moderate decolorization and mineralization efficiency was noticed and was 98% (60 min UV irradiation) and 68% (9 hr UV irradiation) respectively.

The SEM pictures show that bentonite consists of an aggregate of flat platelets and nano-sized particles of silver and P-25 TiO_2 is deposited on the surface of bentonote. It was observed by TEM analysis that the transition metal particles and nano-sized titania catalysts were supported on the surface of bentonite clay. Their mean particle size was 10 ± 2 nm P-25 TiO_2, 100 ± 2 nm bentonite and deposited silver 1 to 2 nm. XRD studies support the above result and anatase phase was observed. It suggests that even after modifications there was no significant change in the P-25 TiO_2 structure. From FTIR analysis different peaks were found indicating the presence of OH, Si-O-Si, CH and NO_2 functional groups in modified photocatalysts r.

References

[1] Lucas, Marco S.; Peres, Jose A. 2007. Degradation of Reactive Black 5 by Fenton/UV-C and ferrioxalate/H_2O_2/Solar light processes. *Dyes and Pigments* 74: 622-629.

[2] Menesi, Judit; Kekesi, Renata; Kor osi, Laszlo; Zollmer, Volker; Richardt, Andre; and Dekany, I. 2008. The Effect of TransitionMetal Doping on the Photooxidation Process of Titania-Clay Composites International *Journal of Photoenergy*. 1-9. doi:10.1155/2008/846304

[3] Pernyeszi, T.; Dekany, I. 2004. Photocatalytic degradation of hydrocarbons by bentonite and TiO_2 in aqueous suspensions containing surfactants. *Colloids and Surfaces A: Physicochem. Eng. Aspects* 230: 191–199.

[4] Li, Jingyi; Chen, Chuncheng; Zhao, Jincai; Zhu, Huaiyong; Ding, Z. 2002 Photodegradation of dye pollutants on TiO_2 pillared bentonites under UV light irradiation. *Science in China (Series B)* 45(4): 445-448.

[5] Sun, Zhenshi; Chen, Yingxu; Ke, Qiang; Yang, Ye; Yuan, J. 2002. Photocatalytic degradation of cationic azo dye by TiO_2/bentonite nanocomposite. *Journal of Photochemistry and Photobiology A: Chemistry* 149: 169–174.

[6] Ding, Z.; Zhu, H.Y.; Lu, G.Q.; and Greenfield, P.F. 1999. Photocatalytic Properties of Titania Pillared Clays by Different Drying Methods. *Journal of Colloid and Interface Science* 209: 193–199.

[7] Zhao, Difang; Zhou, Jie; Liu, N. 2007. Surface characteristics and photoactivity of silver-modified palygorskite clays coated with nanosized titanium dioxide particles. *Materials Characterization* 58: 249–255.

[8] Arabatzis, I. M.; Stergiopoulos, T.; Bernard, M.C.; Labou,D.; Neophytides, S.G.; Falaras, P. 2003. Silver-modified titanium dioxide thin films for efficient photodegradation of methyl orange. *Applied Catalysis B: Environmental*

42:187–201.

[9] APHA, AWWA, WEF, 1995. *Standard methods for the examination of water and wastewater*, Greenberg.

[10] Divya, N.; Bansal, A.; Jana, A.K. 2009. Degradation of acidic Orange G dye using UV-H_2O_2 in batch photoreactor. International *Journal of Biological and Chemical Science* 3 (1): 54-62.

[11] Aleboyeh, A.; Olya, M. E.; Aleboyeh, H. 2008. Electrical energy determination for an azo dye decolorization and mineralization by UV/H_2O_2 advanced oxidation process. *Journal of Chemical Engineering* 137: 518–524.

[12] Coates, J. 2000. *Interpretation of Infrared Spectra, A Practical Approach*, Encyclopedia of Analytical Chemistry,Chichester

.