

Photocatalytic degradation of Textile dye Acidblack-1 using silver impregnated nanosized titania

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Abstract:

Dyes were one of the most notorious contaminants in aquatic environments because of their huge volume of production from industries, slow biodegradation character, low decolouration character and toxicity. In order to remove poisonous dyes from wastewater, various methods such as adsorption, coagulation, precipitation, filtration, photocatalytic oxidation method, etc. had been used. Among them, Heterogeneous photocatalysis using semiconductor oxides is proved to be a useful treatment technique for the degradation of water pollutants over the last three decades. TiO_2 is the best semiconductor oxide, because it has the most efficient activity, the highest stability and the lowest cost. In the present study, we have successfully synthesized nanosized TiO_2 for the degradation of textile dye, Acid black-1. However it shows good absorption of UV light and poor absorption of visible light. In order to obtain titania as a visible light active photocatalyst with a decreased bandgap, transition metal – Ag is impregnated over nano titania. The as synthesised catalyst is characterized by XRD, UV-DRS and SEM techniques. Further, the photocatalyst is tested for their photocatalytic activity towards the degradation of Acid black-1. Optimization parameters such as effect of initial concentration, effect of catalyst and effect of pH are also carried out. The results shows that the metal impregnated titania catalyst is good compared to bare titania catalyst.

Keywords: *dyes, impregnation, nano titania, photocatalysis, silver, visible activity, semiconductor oxides*

1 INTRODUCTION

Increasing environmental pollution from industrial wastewater in developing countries is of major concern. The degradation of organic pollutants has become the focus of the research efforts in today's scientific world. Pollutants that are emitted from various sources pose severe ecological problems because the biodegradation of these pollutants is often very slow and conventional treatments are mostly ineffective and not environmentally compatible. Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger. Colour in textile effluents has become particularly identified with the dyeing of cotton products and the use of reactive azo dyes since up to 30% of the used dyestuffs remain in the spent dye-bath after the dyeing process [1].

The wastewaters containing organic dyes can cause a serious environmental problem since they are extremely resistant to microbial degradation, and thus can be unavoidably converted to toxic or carcinogenic compounds[2]. Various chemical and physical processes are currently used, which work by direct precipitation and separation of pollutants, or elimination by adsorption on activated carbon or similar

materials. Due to the large degree of aromatics present in dye molecules and the stability of modern dyes, conventional biological treatment methods are ineffective for decolouration and degradation. Furthermore, the majority of dyes is only adsorbed on the sludge and is not degraded. Chlorination and Ozonation are also being used for the removal of certain dyes but at slower rates as they have often high operating costs and limited effect on carbon content. Indeed, ultraviolet irradiation combined or not with oxidative agents such as ozone or hydrogen peroxide leads to a complete destruction of the pollutants, but the presence of intermediates arising from the photodegradation reaction could be more harmful than the pollutant itself [3].

However, the above mentioned processes are unable to completely eliminate the dye pollutants, since they mostly transfer the dye compounds from aqueous to another phase, leading to secondary pollution problems and posing a major drawback of such the treatment processes. But, photocatalytic degradation by semiconductors is a new, effective and rapid technique for the removal of pollutants from water. In this process, hydroxyl radicals ($\text{OH}\cdot$) are generated when the photocatalyst is illuminated in the presence of water and air, these ultra

reactive species associated with oxygen are able to achieve a complete mineralization of organic pollutants into carbon dioxide, water and other nontoxic products[4]. When semiconductors are excited by photons with energy equal to or higher than their band gap energy level, electrons receive energy from the photons and are thus promoted from VB to CB if the energy gain is higher than the band gap energy level [5-7].

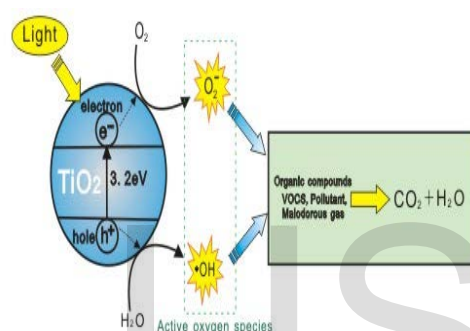


Fig.1: Mechanism of semiconductor oxide catalyst

The photo-generated electrons and holes can recombine in bulk or on surface of the semiconductor within a very short time, releasing energy in the form of heat or photons. Electrons and holes that migrate to the surface of the semiconductor without recombination can, respectively, reduce and oxidize the reactants adsorbed by the semiconductor [8,9]. The reduction and oxidation reactions are the basic mechanisms of photocatalytic hydrogen production and

photocatalytic water/air purification, respectively. The band gap of TiO_2 is about 3.2 eV and only UV light can be utilized. Since the UV light only accounts for about 4% of the solar radiation energy while the visible light contributes about 50%, this inability to utilize visible light limits the efficiency of solar photocatalytic process of dye degradations [10]. Among the several methods to overcome the limits, lowering the band-gap by doping metal or non-metal onto semiconductor metal oxide surface or inter-lattice structure promotes the photocatalysts into visible active. Azo dyes are extensively used in both textile, leather industries and also for many biotechnology applications. But, these dyes are carcinogenic in nature and hence their degradation becomes significant. The structure of the azo dye acidblack-1 which was selected for our study is shown in Fig.2.

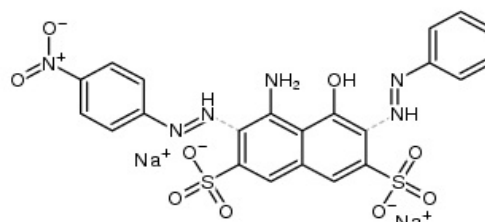
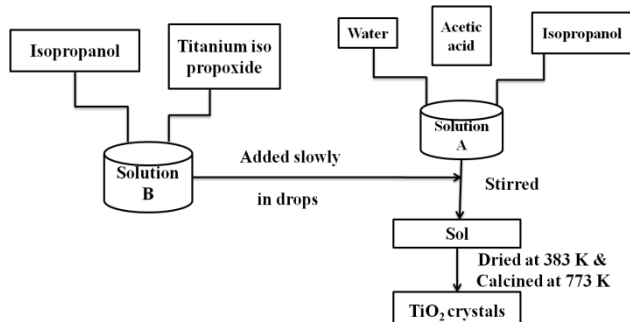


Fig.2. Structure of Acid black-1

2 EXPERIMENTAL METHODS

2.1 Synthesis of Nanosized Titania

Sol- gel process was adopted for the synthesis of nano sized titania (Scheme. 1).



Scheme.1. Flow chart showing the synthesis of nanosized titania

34 mL of TIP and 80 mL of isopropanol were mixed to get solution A. Solution B was prepared by mixing of 120 mL of isopropanol, 30 mL of glacial acetic acid and 10 mL of H₂O. Solution A and solution B were mixed and stirred overnight. The sol obtained was aged to get TiO₂ gel. The gel was dried overnight at 383 K and calcined at 773 K for 3 hrs and ground to get fine powders of TiO₂ [11].

2.2 Synthesis of Silver impregnated titania

The metal doped catalysts were prepared by simple wet impregnation method. To 10 g of as-synthesised titania, different concentration of aqueous solutions of silver nitrate were added, stirred overnight, dried and calcined at 773 K for 3 hrs to get Ag/TiO₂. Then the catalysts were reduced by passing H₂ at 523 K for 2 hrs.

2.3 Characterization

X- ray diffraction (XRD) patterns were recorded on a Rigaku diffractometer using CuK α ($\lambda = 0.154\text{nm}$) radiation in 2 theta range of 0.6 to 10 ° with a step of 0.01° and integration time of 1 sec. The UV-vis diffuse reflectance spectra were taken at room temperature with a JASCO U-650 spectrophotometer in the wavelength range 200-800 nm. ESEM Quanta 200 was used in the SEM analysis and High resolution TEM images were obtained with a JEOL JEM 2000EX2 microscope operated at 200 kV.

2.4 Photocatalytic Studies

The study was primarily done in a multi UV lamp photoreactor [Heber HML-

COMPACT-SW-LW-44] fitted with 4 nos. of 8-W fluorescent black light [SANKYO DENKI F8T5/BLB with dimensions 28.7 cm x 1.55 cm] with a maximum spectral intensity at 352 nm and UV output power of 1.4 Watt. The light intensity of the lamp was measured by using Luxmeter [Luxtron lx-101] and it was found to be 1775 lux/lamp. The photocatalytic activity experiments were carried out by taking 100 mg of photocatalysts and 100 mL of different concentrations of Acidblack-1 dye solutions in a cylindrical shape glass reactor. Air was passed through the solution for thorough mixing of dye solution and photocatalyst. The photo decolourization studies were done for a time period of 4 hours, including the first 30 minutes during which the lamp was switched off for adsorption desorption equilibrium. Samples of 3 ml volume were withdrawn from the suspensions at different time intervals and the catalysts were separated from the solution by centrifuging with the speed up to 2000 rpm by using Remi R8C laboratory centrifuge. The very small amount of photocatalyst retained in the centrifuge tube was transferred back to the original solution mixture. The quantitative determination of Acidblack-1 was performed by measuring its absorbance at 617 nm with Elico SL 164 double beam UV-Visible spectrophotometer.

The degree of decolorisation (T) at different intervals was calculated from decrease in absorbance value of the dye solution at its λ_{\max} using the following formula,

$$T = [(C_0 - C_t) / C_0] \times 100$$

where, C_0 and C_t are the concentration values of the dye solution before and after irradiation respectively at regular intervals (30,60,90,.....mins).

3 RESULTS AND DISCUSSION

3.1 Characterization of Catalysts

3.1.1 X-Ray Diffraction Studies

To obtain information regarding the phase information and crystallite size, X-ray diffraction measurements were performed for the synthesised TiO_2 and impregnated TiO_2 photocatalysts and the XRD patterns are shown in Figure 3. All the titania and metal impregnated titania catalysts exhibited similar XRD patterns. XRD patterns of metal impregnated titania showed mostly anatase peaks for catalysts calcined at lower temperatures and changed of rutile phase for the catalysts calcined at higher temperatures. The brookite

phases were not detected for all the catalysts.

The peaks located at 25.4°, 37.8°, 48.0°, 54.5° corresponds to the (101), (004), (200), (105 and 211) planes of the anatase phase (JCPDS 21-1272), and the peaks located at 54.4° corresponds to the (211) planes of the rutile phase (JCPDS 21-1276). However the intensity of the rutile peak was found to be negligible which confirmed the presence of anatase [12].

The particle size was calculated using the Debye Scherer equation,

$$D = \frac{k \times \lambda}{\beta \times \cos \theta}$$

where,

- d = diameter of the crystal
 λ = wavelength of the X-ray radiation ($\lambda = 0.15418$ nm)
 K = Constant
 θ = Characteristic X-ray diffraction peak
 β = Full width at half maximum in radians

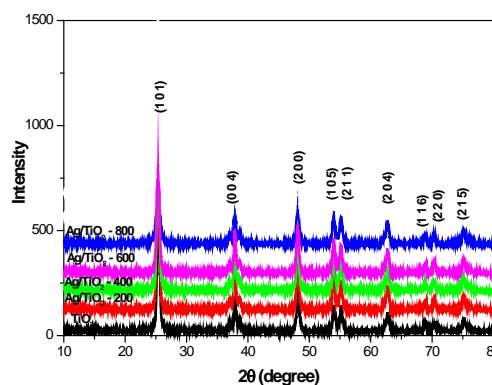


Fig.3. X-Ray Diffraction patterns of TiO₂ and impregnated TiO₂ catalysts

The average crystalline size of synthesised titania and impregnated catalysts were found to be in the nanometer range as shown in Table 1.

Table 1

CRYSTALLITE SIZE AND BANDGAP OF CATALYSTS

S.No	Catalyst	Crystalline Size (nm)	Band gap (eV)
1	Synthesised TiO ₂	31	3.2
2	Ag/TiO ₂ (200°C)	39	3.3
3	Ag/TiO ₂ (400°C)	22	3.3
4	Ag/TiO ₂ (600°C)	21	3.2
5	Ag/TiO ₂ (800°C)	20	2.9

3.1.2 UV- Diffuse Reflectance Spectroscopic analysis

UV-Visible DRS spectra taken for all the doped catalysts calcined at different temperatures are shown in Fig. 4. The band gap energy values [E_g] were calculated from the cut-off wavelength using the relation $E_g = hc / \lambda$ and the values are given in Table 1.

The TiO_2 samples exhibited strong absorption in the UV region with a sharp absorption edge located at about 400 nm. E_g value decreased slightly with the impregnation of Ag over TiO_2 .

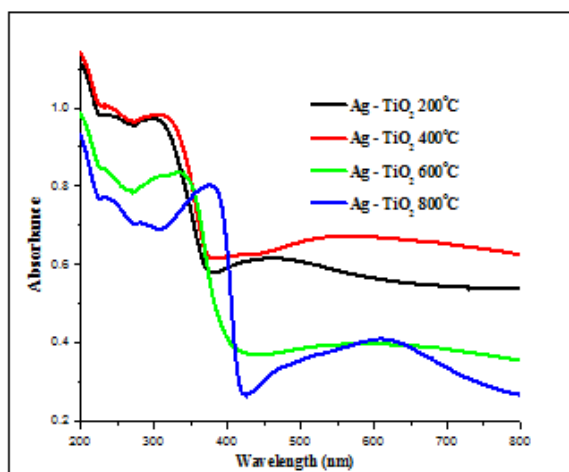


Fig.4. UV-DRS of Ag - TiO_2 at different calcinations temperatures

The band gap value decreased slightly with the impregnation of Ag over TiO_2 with a minute change in the absorption edge. However, a surface plasmon absorption of the Ag nano particles is seen around 400-600 nm which confirms the presence of Ag on the TiO_2 surface [13].

3.1.3 Scanning Electron Microscopy and Transmission Electron Microscopy

SEM and TEM images of the most active photocatalyst namely Ag/ TiO_2 (400°C) catalyst are shown in Figure 5 (a) and (b). The average size of the Ag/ TiO_2 (400°C) particle was calculated and found to be around 20 nm.

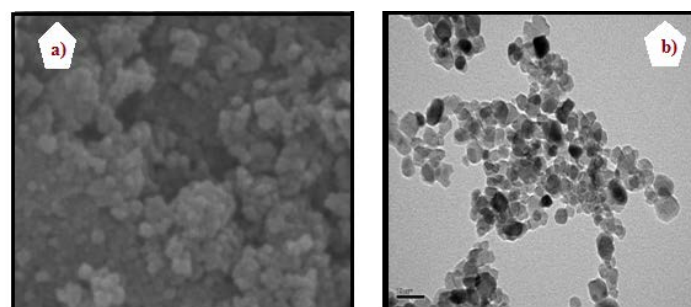


Fig.5. SEM and TEM images of Ag/ TiO_2 calcined at 400°C

3.2. Photo Decolourisation Studies

3.2.1 Effect of Parameters on Percentage Decolourisation

The efficiency of the photo catalytic system are highly dependent on the number of operational parameters that govern the photo degradation of the organic molecules. Hence the effect of dye concentration, catalyst amount and time on stream were studied and optimised for Amido black-10B using synthesised titania catalyst.

3.2.2 Calibration Curve Of Amido Black-10b

Different concentration of Amido black-10B dye solution was prepared and their absorbance (λ_{\max}) values were measured at 617 nm. Calibration graphs (absorbance vs concentration) was constructed for AB-10B.

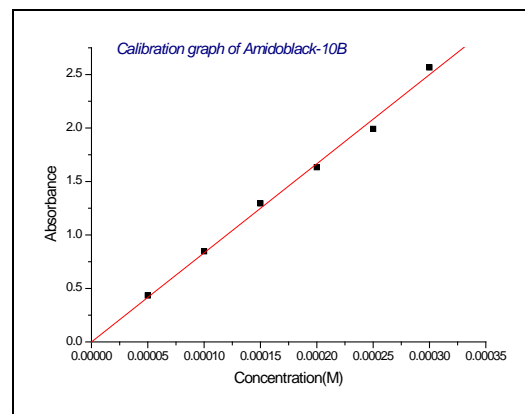


Fig. 6. Calibration curve of Amido black-10B

It shows that Amido black-10B obeys Beer Lambert's law which confirms that the dye molecules can be used for further photodegradation studies. The graph was found to be linear upto 2.5×10^{-4} M for Amido black-10B.

3.2.3. Effect Of Initial Dye Concentration

Different concentrations of Amido black-10B were taken in the multilamp photoreactor and their decolourisation was followed using UV-Visible spectrophotometer. The effect of initial concentration of Amido black-10B on % decolourisation is shown in Fig. 7(a & b).

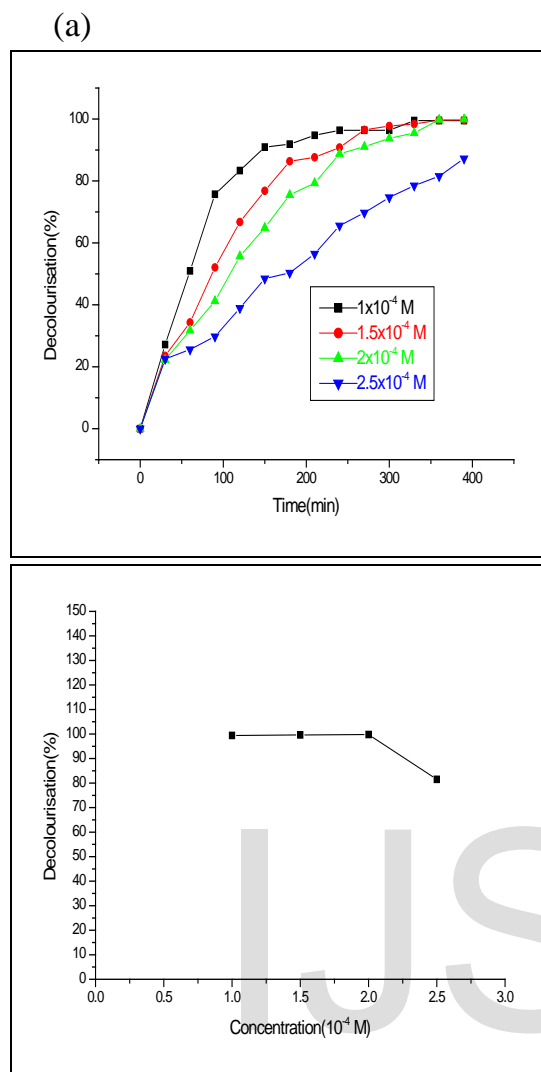


Fig.7. Effect of initial concentration of dye (AB-10B) on % degradation

It shows that % decolourisation of Amido black-10B increased with increase in initial concentration of dye from 1×10^{-4} M to 2×10^{-4} M and reached a maximum of 100% decolourisation at 5:30 hrs. However further increase in concentration to

2.5×10^{-4} M resulted in decrease in % decolourisation to 81% (Fig. 7. b). The initial increase in % decolourisation with increase in concentration may be due to the increase in adsorption of dye substrate molecules on the active sites of titania. Further increase in concentration resulted in decrease in % decolourisation. This may be due to non-availability of active sites of titania and poor penetration of light [14].

Hence, the optimised concentration was found to be **2×10^{-4} M** (Amido black-10B).

3.2.4. Effect Of Catalyst Amount

Effect of catalyst weight on % decolourisation of AB-10B is shown in Fig.6. The catalyst weight was varied from 25 mg to 400 mg for AB-10B. The effect of catalyst weight on % decolourisation of AB-10B is shown in Fig 8. a.

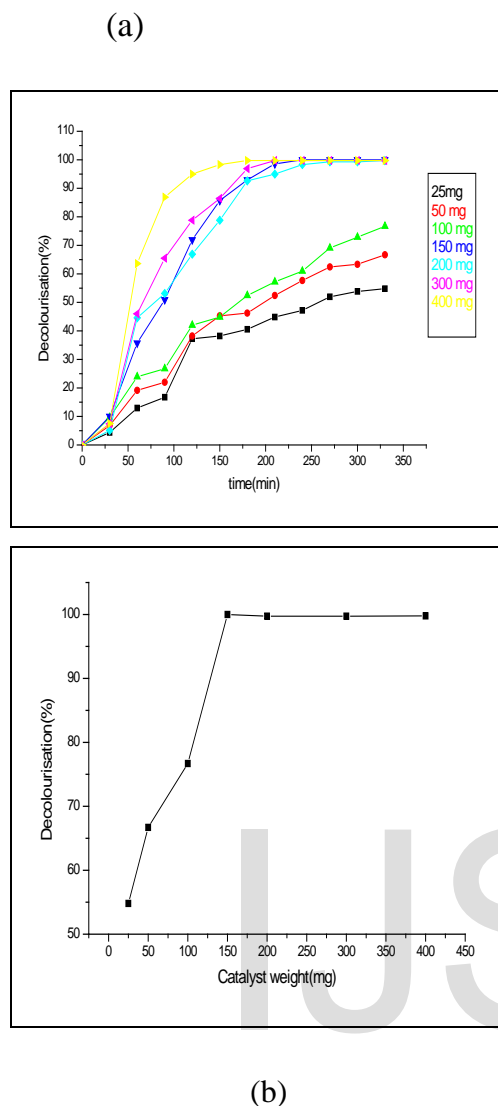


Fig.8. Effect of weight of the catalyst (AB-10B) on % degradation

The 100% decolourisation at 5½ hours was observed over the catalyst range of 150 mg to 400 mg. On decreasing the catalyst weight further resulted in significant decrease in % decolourisation to 75% (Fig.8. b).

In Acidblack-1, the increase in % decolourisation with increase in catalyst weight is due to

increase in number of active sites [15]. Since 100% decolourisation was observed over the catalyst weight of 150 mg itself, the optimised catalyst weight was found to be 150 mg.

3.2.5. Effect Of pH

With the optimum concentration and catalyst weight, pH was varied from 2 to 11. Amidoblack-10B was decolourised to the maximum extent at its natural pH – 4.

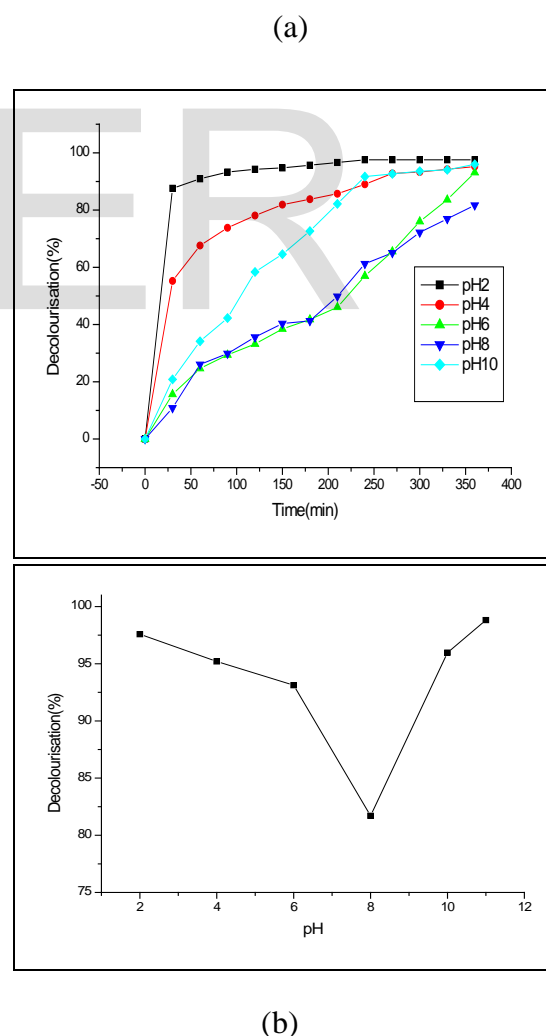


Fig. 9. Effect of pH on % degradation of dye (AB-10B)

The interesting observation was made when pH of the solution was changed from pH-2 to 10. The Fig. 7 shows that both at higher and lower pH values decrease in absorbance value was observed. It may be due to structural changes in dye. (i.e) At low pH -2, SO_3^-Na^+ groups present in dyes were converted into SO_3^-H^+ groups making the dye insoluble and hence settled down at the bottom of the vessel whereas at high pH-10 abstraction of proton from the phenolic group of AB-10B took place and resulted in breaking of azo group. Hence the optimised pH for decolourisation was found to be 4 (natural pH).

3.2.6 Photodecolourisation studies of Acid black-1

Fig. 10 shows the photodegradation studies of acidblack-1 using bare titania catalyst in the presence of dark, light and with the presence of light with the catalyst respectively. In dark, the decolourisation of acidblack-1 is very minimum that is 4%. In the presence of light alone, it is decolourised to 10%. But in the presence of both light and catalyst, that is in the photocatalytic

reaction the decolourisation of acidblack-1 is very high about 83%. This shows that the photocatalytic reaction decolourised the dye very quickly.

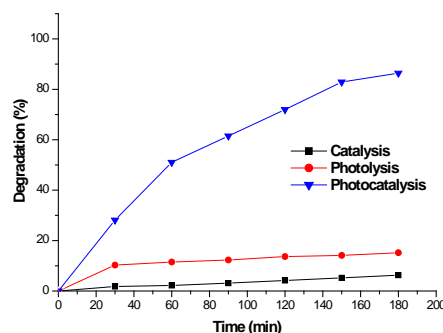


Fig. 10. Photolytic, Catalytic and Photocatalytic reaction of Acidblack-1

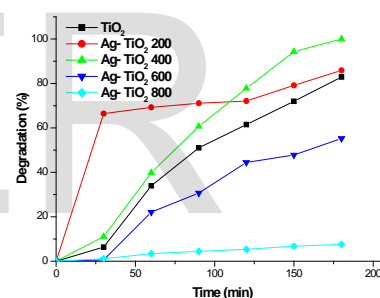


Fig. 11. Photocatalytic degradation of Acidblack-1 using Ag/TiO₂ catalysts

Fig.11. shows the decolourisation of acidblack-1 with different silver catalysts. The decolourisation shows that the silver catalysts are active compare to bare titania catalyst. Silver catalysts were prepared under various calcination temperatures. Hence, when the calcination temperatures go beyond 500°C, the active anatase phase of

titania may be converted to the inactive rutile phase. This may be the reason for the higher activity of silver catalysts calcined at 200°C and 400°C.

4. CONCLUSIONS

Bare titania and silver metal impregnated titania catalysts were successfully synthesised by sol-gel method and characterized by XRD, UV-DRS, SEM and TEM techniques. XRD confirmed the phase formation. UV-DRS study showed reduction in the bandgap and surface Plasmon resonance of silver impregnated catalysts. SEM and TEM images showed the morphology of the silver catalyst. Impregnation of silver over titania increased the efficiency of catalysts. Among the silver catalysts, Ag/TiO₂ (400°C) catalyst performed well in the decolourisation of Acidblack-1.

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