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Photocatalytic Degradation of Azo Dye (Methyl Red) In Water under Visible Light Using Ag-Ni/TiO_2 Sythesized by γ - Irradiation Method

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***Abstract*—** *Commercial TiO_2 (P25) co-doped with bimetallic silver and nickel nanoparticles (Ag-Ni/TiO_2) was prepared by γ-irradiation method. The properties of Ag-Ni/TiO_2 were characterized by X-Ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), energy dispersive X-ray spectroscopy techniques (EDX) and surface area measurement by Brunauer-Emmett-Teller (BET) method. The size of silver and nickel nanoparticles was determined by TEM to be of 1-2 nm.The photo-catalytic degradation of azo dye methyl red in the aqueous suspensions of TiO_2 and Ag-Ni/TiO_2 under visible light was carried out to evaluate the photo-catalytic activity. Results showed that Ag-Ni/TiO_2 was found to enhance photo-degradation efficiency of azo dye metyl red compared to commercial TiO_2. The results showed that Ag 3% (w/w) and Ni 1.5% (w/w) co-doped TiO_2 had the highest photoactivity among all studied samples under visible light. Thus, γ-irradiation method can be suitably applied to prepare photo-catalyst of Ag-Ni/$TiO_2$with highly photocatalytic activity.*

***Keywords*—TiO_2, silver, nickel, nanoparticles, photocatalytic,γ-irradiation.**

I. INTRODUCTION

Photocatalytic reactions at the surface of titanium dioxide have been attracting much attention in view of their practical applications to environmental treatment [1]. The material TiO_2 is a well-known photocatalyst for its high efficiency, low cost, physical and chemical stability, widespread availability, and noncorrosive property [2].NanoTiO_2 shows relatively high reactivity and chemical stability under ultraviolet light (<387nm), whose energy exceeds the band gap of 3.2 eV in the anatase crystalline phase. The development of photocatalysts with high reactivity under visible light (> 400 nm) should allow the main part of the solar spectrum, even under poor illumination of interior lighting, to be used [3]. Several approaches for nanoTiO_2modification have been reported [4]. These included dye sensitization, semiconductor coupling, impurity doping, use of coordination metal complexes, and metal deposition. A combination of two or more kinds of metals has been widely applied in various materials to enhance the performance and reliability of the materials. The incorporation of metals in the titanium dioxide crystal latticemay result in the formation of new energy levels between valence bandand conduction band, inducing a shift of light absorption towards the visible light region. Possible limitations are photocorrosion and reduce charge recombination at metal sites[5].

The use of Ag and Ni for bimetallic catalyst has been reported as the effective method to improve the efficiency of various reactions[6, 7]. Ag-Ni/cacbonnanotube for glucose oxidation[6]. Silver and nickel doped TiO_2 by sol-gel method applied against bacteria under UV and visible light irradiations[7].

Various methodsfor the synthesis of modified TiO_2photocatalyst included precipitation [8] , hydrothermal, solvothermal[9], chemical vapour deposition[10], and electrospinning[11] , radiolysis [12]. Among several methods for modified nanopowder TiO_2, radiolysis method usingγ-irradiation is advantageous because the experiment can be

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carried out at very mild conditions, ambient pressure and room temperature with high reproducibility and it is the unique method [13, 14, 15]. In addition, Zhang et al. (2010) [16] also synthesized Ag-Ni alloy nanoparticles by radiolytic method. So, in this study, we reportedthe preparation of Ag and Nico-doped on TiO_2 (Ag-Ni/TiO_2)byγ-irradiation method andstudied of its photoactivityof degradation of methyl redin water. The properties of the catalysts were characterized by X-ray diffraction(XRD), diffuse reflectance spectroscopy (DRS), surface area measurement by Brunauer-Emmett-Teller (BET) method, transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy techniques (EDX), X-ray photoelectron spectroscopy (XPS). The photocatalytic performance, reaction kinetic, and reusability of the catalysts were also investigated.

II. EXPERIMENTAL

2.1. Materials

Silver nitrate ($AgNO_3$)and nickel nitrate hexahydrate($Ni(NO_3)_2{\cdot}6H_2O$)were purchased from China used as dopant metal salts. Titanium dioxide, TiO_2 (Degussa P25)wasfrom Germany used as the supportand ethanol was from China. Methyl red from China was used as the model of organic pollutant for photocatalyticdegradation study.

2.2. Sample preparation

A series of TiO_2 samples was prepared by codoping with silver and nickel in the range of 0.75–3% (w/w) by γ-irradiation method. 2 g TiO_2 and 10 ml ethanol were added into 90 ml distilled water and stirred. The required amount of $AgNO_3$ and $NiNO_3$ were then added to the TiO_2 suspension mixture with variousmass ratios of Ag and Ni. The reduction of Ag^+ and Ni^{2+} was carried out by γ-irradiation on a γ- ^{60}Co sourceusing gamma chamber GC – 5000, BRIT, India at the Nuclear Research Institute, Da Lat, Vietnam with dose rate of 2.5 kGy/h and absorbed dose range from 15.8 to 46.5kGy measured by a dichromate dosimetry system [17] at room temperature and under atmospheric pressure. The TiO_2 doped with Ag and Ni photo-catalyst was separated by centrifugation, washed by distilled water and dried at 60ºC. The detailed parameters of experiments were listed in Table 1.

2.3. Characterization of TiO_2 doped with Ag-Ni nanoparticles

The size of Ag and Ni nanoparticles doped on TiO_2 catalystwas characterized by TEM images on a JEM 1010, JEOL, Japan and XRD patterns were measured on D8 Advanced, Brucker, Germany using a Cu Kα (λ = 0.15418 nm). The specific surface areas of samples were determined by nitrogen adsorption at 77K using Quantachrome 1994-2010 instrument of Germany using BET method.The solid UV–vis DRS was carried out using JASCO V550 model UV-vis spectrometer. XPS analyses were obtained with a ULVAC PHI instrument, equipped with Al KαX-ray source. The morphology and the elemental content of the catalyst were investigated with SEM (Hitachi SEM S-4800) coupled with a Genesis 4000 EDX spectrometer.

2.4. Photocatalytic degradation activity

0.025 g of photocatalystswas added to 50 mL methyl red(10^{-5}M). The solution with the catalyst was stirred in the dark for 1hour for the solution to attain absorbed equilibrium.It was then irradiated using the 150 W halogen lamp (the visible light source) at a distance of 40 cm from the solution level and the temperature of the reactor was controlled at 30± 2°C. After period of time of 20, 40, 60, 80, 100 and 120 min, the aqueous suspension was filtered through centrifugation to remove catalyst particles. Each set of experiment was performed three times. MR concentration was estimated by colorimetric method using UV-vis spectrophotometer (Biochrom, Libra S32).

The photo-catalytic kinetic of methyl red degradation was described by the pseudo-first-order kinetic as follows:

$$v = -dC/dt = -kC \text{ (or } C = C_o e^{-kt}) \quad (1)$$

Where v is the reaction rate, C is the concentration of MR dye at certain reaction time, C_o is the initial concentration of MR, k is rate constant and t is reaction time.

After the integration of the equation (1), the model can be expressed by the following equation (2):

$$\ln(\frac{C_o}{C}) = kt \quad (2)$$

A plot of $\ln(\frac{C_o}{C})$ with time will yield a linear plot with slope k.

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III. RESULTS AND DISCUSSION

Table 1.Composition and absorbed dose for preparation of different Ag-Ni/TiO_2 samples

Sample name	Weight of precursor	V(H_2O): V (C_2H_5OH)	Dose (kGy)	Irradiation time (min)
Ag0.75-Ni1.5/TiO_2	m$AgNO_3$ =0.0236 g m$Ni(NO_3)_2.6H_2O$ = 0.1488 g	90 ml: 10 ml	23.3	1398
Ag1.5-Ni0.75/TiO_2	m$AgNO_3$ = 0.0472 g m$Ni(NO_3)_2.6H_2O$ = 0.0744 g	90 ml: 10 ml	15.8	948
Ag1.5-Ni1.5/TiO_2	m$AgNO_3$ = 0.0472 g m$Ni(NO_3)_2.6H_2O$ = 0.1488 g	90 ml: 10 ml	26.0	1560
Ag1.5-Ni3.0/TiO_2	m$AgNO_3$ = 0.0472 g m$Ni(NO_3)_2.6H_2O$ = 0.2976 g	90 ml: 10 ml	46.5	2790
Ag3.0-Ni1.5/TiO_2	m$AgNO_3$ = 0.0944 g m$Ni(NO_3)_2.6H_2O$ =0.1488 g	90 ml: 10 ml	31.6	1896

The absorbed doses presented in Table 1 were calculated based on the dose of ~1.67 kGy for reduction of 1 mM Ag^+[18], but in excess for 20% .

3.1. Characterization of catalysts

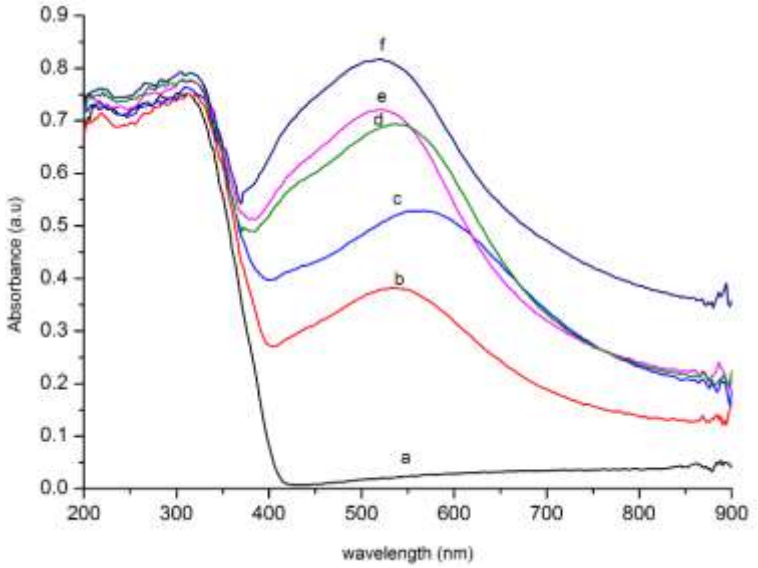

Fig.1:UV-vis Diffuse reflectance spectra (DRS) of pure TiO_2 and modified TiO_2: (a) Pure TiO_2; (b) Ag0.75-Ni1.5/TiO_2; (c) Ag1.5-Ni0.75/TiO_2; (d) Ag1.5-Ni3.0/TiO_2; (e) Ag1.5-Ni1.5/TiO_2; (f) Ag3.0-Ni1.5/TiO_2

The UV-visible spectral of the pure TiO_2 and modified TiO_2 by Ag and Ni in the range of 200 to 900 nmwere shown in Fig. 1. It was found that the absorbance of Ag-Ni/TiO_2 in the visible region was always higher than that for pure TiO_2. The absorption peak of Ag-Ni/TiO_2 shifted towards the visible region. The visible-light photo absorption of Ag3.0-Ni1.5/TiO_2 was the highest among studied samples. The absorption of the modified TiO_2 samples in the range of 510−570 nm was probably due to Ag and Ni nanoparticles which absorbed in this spectral range.

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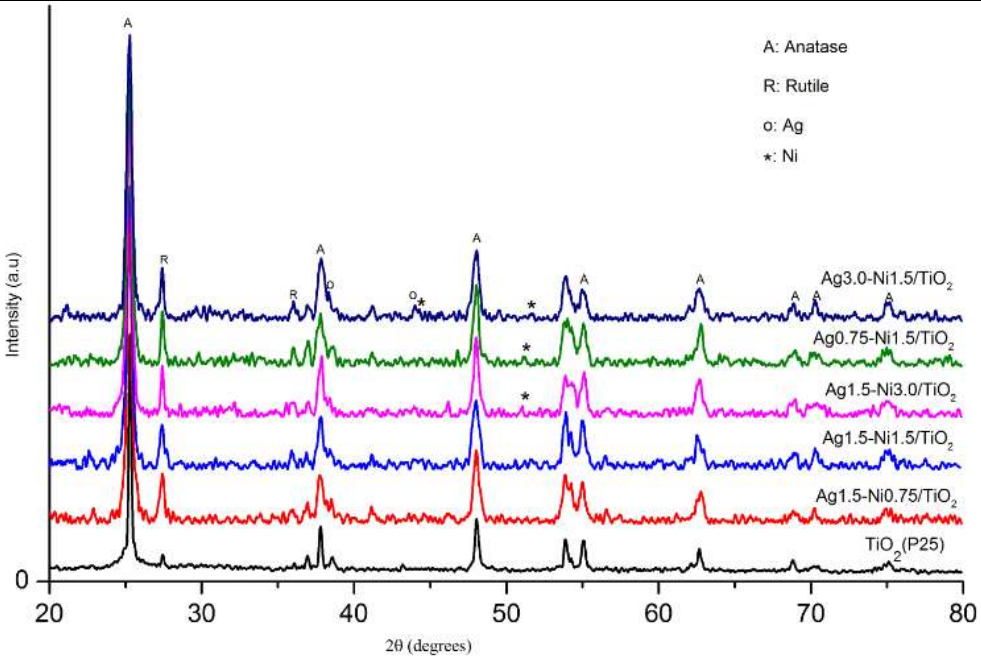

Fig. 2.XRD patterns of TiO_2 (P25) and$Ag-Ni/TiO_2$with various content of Ag and Ni.

Fig. 2 showed the typical XRD patterns of the pure TiO_2 (P25), and TiO_2 doped with various content of Ag and Ni. It is clearly from Fig. 2 that original TiO_2 powder exhibits typical pattern that indicate for the phases of anatase and rutile. The XRD pattern of $Ag3.0-Ni1.5/TiO_2$ consisted of peaks at 25.2 º; 37.6º; 48.0º; 53.9º; 55.1º; 62.4º; 68.7º; 70.2º and 75.1º correspond to the crystal planes [101], [004], [200], [105], [211], [204], [220], [220] and [215] respectively; this is indicate for phase anatase of TiO_2, whereas rutile crystallites structure has peaks at 27.4º and 36.1º correspond to the crystal planes [110] and [101].Peaks at 2θ values of 38.1º, 44.1º that reflect the cubic Ag phase which can be attributed to the crystal planes of metallic silver [111] and [200], respectively.Peaks at 2θ values of 44.5º and 51.7ºthat indicated for crystal planes of metallic nickel [111] and [200]. All peaks for Ag and Ni were weak because of the low content of silver and nickel.

Table.2:θºvalues of [101] plane and [200] plane of TiO_2after doping by Ag and Ni with different content

Ag content , %(w/w)	0.0 (TiO_2)	0.75	1.5	1.5	1.5	3.0
Ni content, %(w/w)	0.0 (TiO_2)	1.5	0.75	1.5	3.0	1.5
2θº [101] plane	25.5	25.37	25.34	25.21	25.42	25.22
2θº[200] plane	48.29	48.16	48.13	47.98	48.17	48.02

In addition, from the results of XRD inTable 2, it can be seen that the position of TiO_2 plane [101] and [200] change the angle by doping with Ag and Ni. According to Bragg's law: $n\lambda=2d\sin\theta$[19], can be drawn that the lesser is the value of sinθ,the larger is the d spacing. Opposite, the larger is the value of sinθ, the lesser is the d spacing. So we can conclude that the value of d spacing change with Ag and Ni doping, which implies that nickel and silver ions diffused into the lattice of TiO_2.

Table.3:Sample, BET surface area of pure TiO_2 and Ag-Ni doped TiO_2 samples

Sample	BET surface area (m^2/g)
TiO_2	69.417
$Ag0.75-Ni1.5/TiO_2$	53.083
$Ag1.5-Ni0.75/TiO_2$	55.991
$Ag1.5-Ni1.5/TiO_2$	56.200
$Ag1.5-Ni3.0/TiO_2$	53.747
$Ag3.0-Ni1.5/TiO_2$	51.800

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The surface areas of pure TiO_2 and Ag-Ni/$TiO_2$with various content of Ag and Ni were determined by the nitrogen gas adsorption method and shown in Table 3. Theresults in Table 3 showed that the surface area of Ag-Ni/TiO_2samples decreased compared to that of TiO_2.

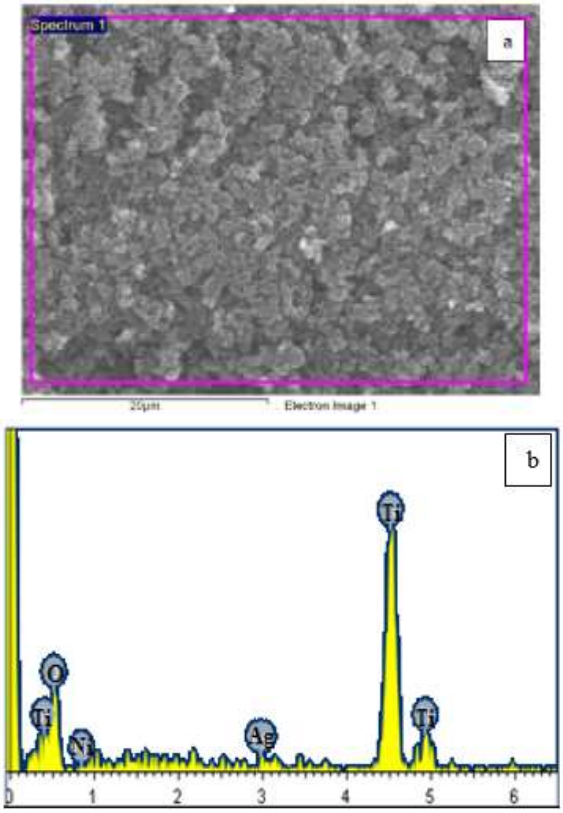

Fig. 3:SEM image (a) and EDX diagram (b) of Ag3.0-Ni1.5/TiO_2 catalyst

The SEM micrograph and EDX spectrum of Ag3.0-Ni1.5/TiO_2 catalyst were shown in Fig. 3. The SEM micrograph showed catalyst particles with spherical morphology. The composition of the Ag3.0-Ni1.5/TiO_2 catalyst was determinedby EDX analysis. The EDX spectrum was recorded in the binding energy region of 0 - 6 eV which was shown in Fig. 3b. The existence of Ag and Ni atoms on the TiO_2 was confirmed.

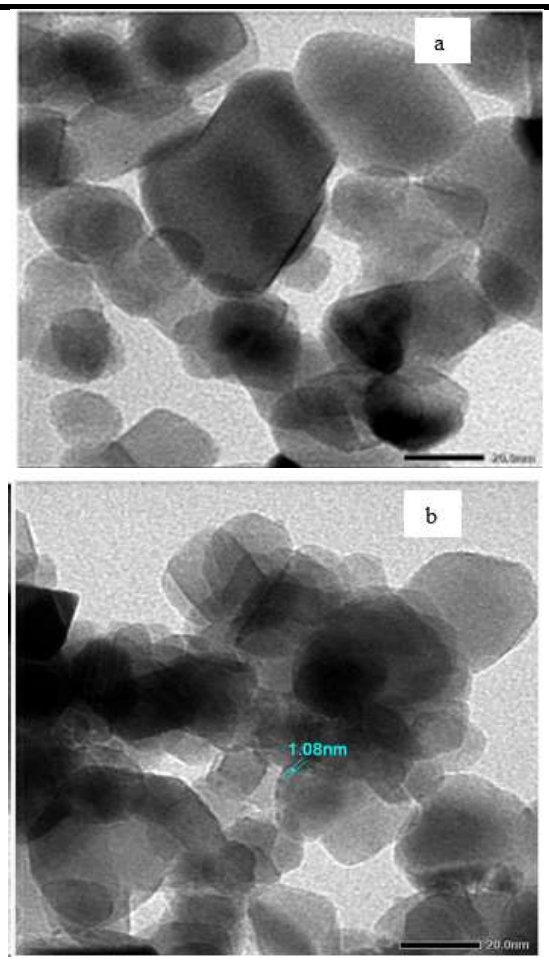

Fig. 4:TEM images of TiO_2 (P25) (a) and Ag 3.0-Ni1.5/TiO_2 (b) photocatalyst

The morphology and metal distribution of the catalysts were then examined by TEM images. Fig. 4 showed the TEM images of TiO_2 (P25) and Ag3.0-Ni1.5/TiO_2. TEM image of TiO_2in Fig. 4a indicated that the TiO_2 particles have not agglomerated. The average size of particles of TiO_2 was estimated to be 10 – 40 nm. TEM image of Ag3.0-Ni1.5/TiO_2 in Fig. 4b indicated that Ag and Ni nanoparticles with size of about 1-2 nm were dispersed on the surface of TiO_2.The size of TiO_2 particles was almost unchanged for TiO_2 and Ag3.0-Ni1.5/TiO_2sample.

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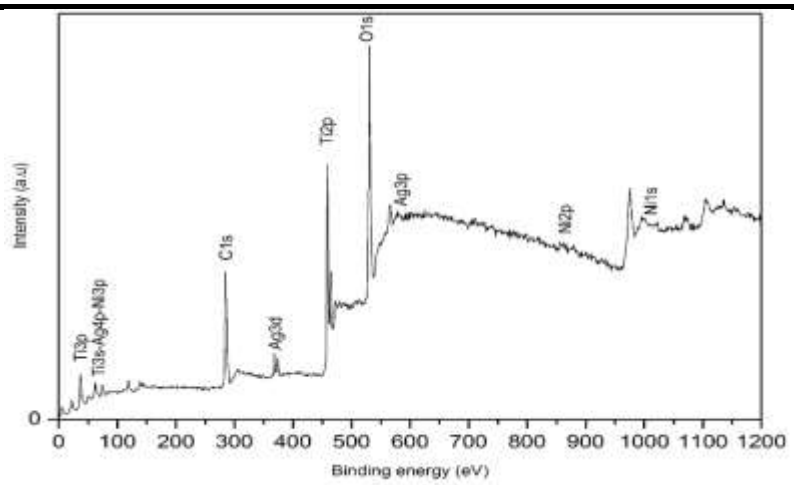

Fig. 5: XPS full survey of Ag3.0-Ni1.5/TiO_2

XPS analysis of silver and nickel co-doped TiO_2 sample (Ag3.0-Ni1.5/TiO_2) was performed and shown in Fig. 5. The XPS full spectrum showed the presence of different elements on the surface of the catalyst. XPS analysis of Ag3.0-Ti1.5/TiO_2 sample detected peaks of Ti, O, C, Ni and Ag. The presence of C was attributed to carbon contamination existed on the sample rack.

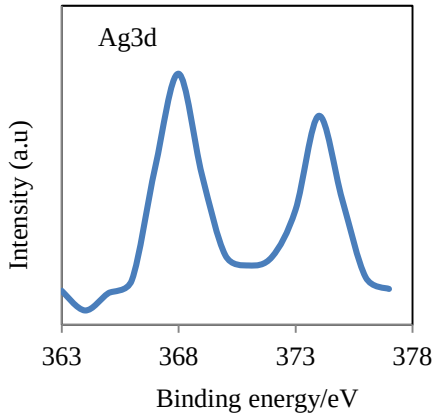

Fig. 6: XPS survey for Ag3d

Fig. 6 showed that the catalyst exhibited their Ag3d level two peaks (at around 368 and 374 eV), which indicated for the Ag 3d5/2 and 3d3/2. The binding energy of peak Ag 3d5/2 maximum at 368.1 eV was close to the value reported for metallic Ag(0) [12].

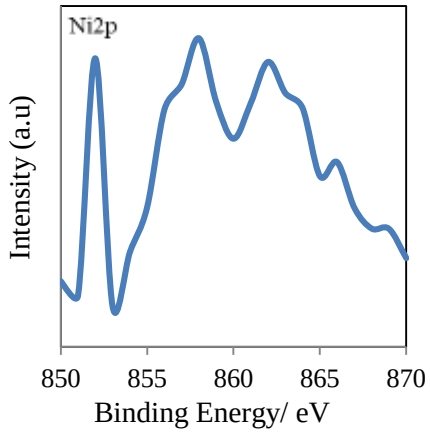

Fig. 7: XPS survey for Ni2p

The Ni 2p3/2regions of the Ag3.0-Ti1.5/TiO_2catalystshowed severalpeaks in the range of 850–870 eV (Fig. 7). The first peak at 852.1 eV resulted for metallic nickelNi(0)[20]. The second peak at 858.1 eV was attributed to Ni^{2+} ions within the composite oxide structure [21], whereas the peak at 862 eV was assigned to its corresponding shake-up satellite lines. The detection of metallic nickel Ni(0) clearly indicated a reduction of the ion Ni^{2+}on the surface of the catalyst.

3.2. Photocatalytic degradation of methyl red

3.2.1.Effect of dopant content

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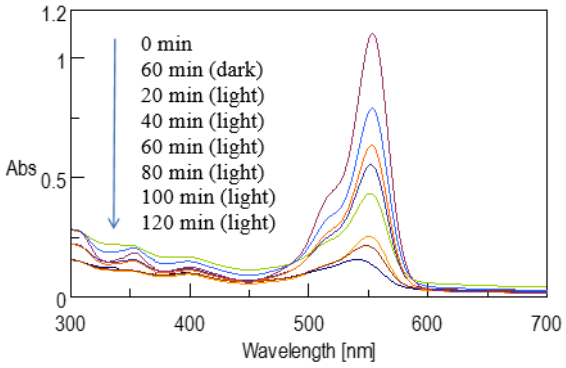

Fig. 8:Absorption spectra of MR at different time interval degraded by the Ag1.0-Ni0.75/TiO₂catalyst under visible light.

Fig.8 showed the absorption spectra of MR before and after irradiating under the visible light for different time interval using Ag1.0-Ni0.75/TiO_2 as a photocatalyst. The intensity of the peak was found to decrease with increasing irradiation time during photocatalytic degradation of MR. It proves that the concentration of MR decreased with increasing degradation time.

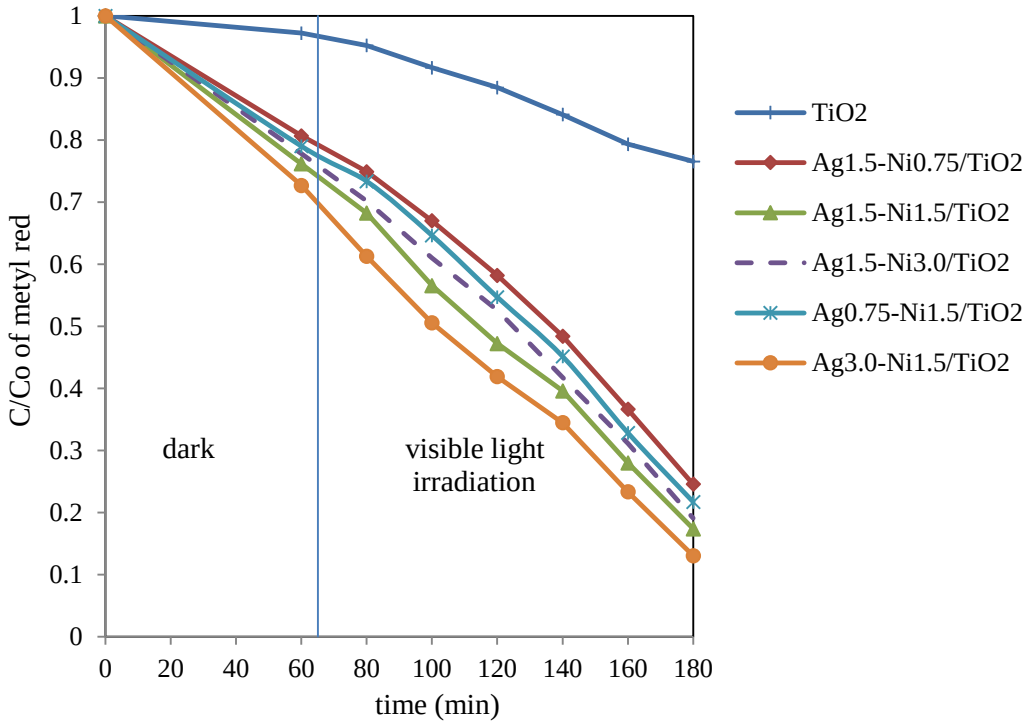

Fig.9: Degradation of MR under visible irradiation by TiO_2 and Ag-Ni/TiO_2 with different dopant (Ag and Ni) content. The initial concentration of MR: 1×10^{-5}M, amount of catalyst: 0.5 g/L.

Photocatalytic degradation of MR by pure TiO_2 and Ag and Ni co-doped on TiO_2 catalysts with various dopant concentrations under visible light was presented in Fig. 9. The effect of dopant on the percentage of methyl red degradation was studied with different amount of Ag and Ni varying from 0.75 to 3.0 % (w/w), with MR solution concentration of 10^{-5}M and amount of catalyst of 0.5 g/L. All the Ag-Ni/TiO_2 samples showed higher photocatalytic activity than that of commercial TiO_2 (Degussa P25) under visible light irradiation. Thus modified TiO_2 by Ag and Ni nanoparticles resulted in higher photocatalytic activity. Among catalysts, the sample containing 3% Ag and 1,5% Ni (w/w) performanced the highest photodegradation efficiency.

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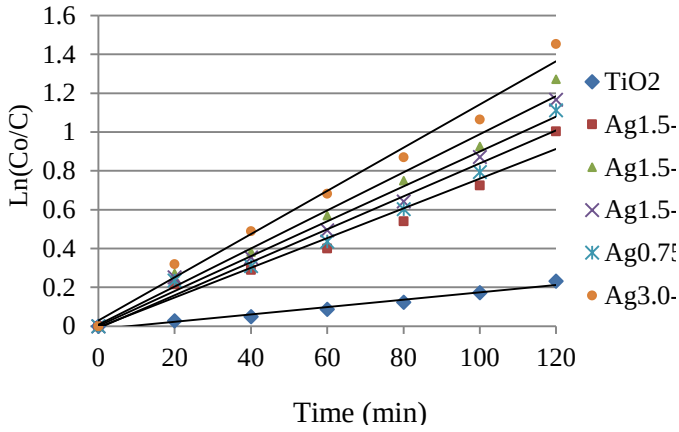

Fig.10: Ln(C_o/C) versus irradiation time for MR under visible light by TiO_2 and Ag-Ni/TiO_2 catalysts with initial concentration of MR: 10^{-5}M, amount of catalyst: 0.5 g/L.

As a result, the photodegradation kinetics fitted well with the pseudo first-order model that showed in Fig. 10. Degradation rate constants calculated from the results in Fig. 10 were of 0.0019; 0.0077; 0.0085; 0.009; 0.0098 and 0.0111 min^{-1} for TiO_2, Ag1.5-Ni0.75/TiO_2, Ag0.75-Ni1.5/TiO_2, Ag1.5-Ni3.0/TiO_2, Ag1.5-Ni1.5/TiO_2 and Ag3.0-Ni1.5/TiO_2, respectively. The sample with 3 % Ag (w/w) and 1.5 % Ni (w/w) doped on TiO_2exhibited the highest rate constant.

3.2.2. Effect of pH

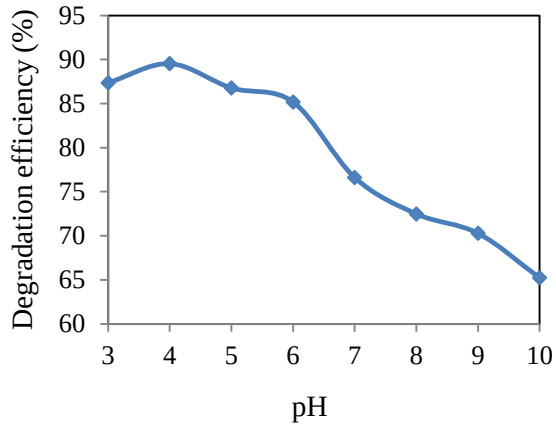

Fig. 11: The effect of pH on photodegradation of MR (amount of catalyst: 2.0 g/L; irradiation time: 60 min; MB initial concentration: 10^{-5}M;)

The pH of a dye solution is an important parameter that affects the rate of degradation. The effect of pH on photo catalytic degradation of MR was investigated with content of catalyst (Ag3.0-Ni1.5/TiO_2) of 0.5 g/L, concentration of MR of10^{-5} M,irradiation time of 60 min andthe range of pH from 3 to 10. PH was adjusted by 1N HNO_3 and 1N NaOH. Fig. 11 showed the degradation efficiency of MR at different pH values.The results clearly showed that photo catalytic degradation of the MR dye increased to pH 4 and then decreased significantly to pH 10. The maximum MR degradation of 89.18% was observed at pH 4. This may be explained that the higher degradation extent of MR occurred in acidic medium rather than alkaline. Hence, at acidic pH values,the particle surfaces of catalysts are positively charged and at basic pH values, they are negatively charged [22]. In acidic environment, the adsorption of anionic dye molecules on the surface of the catalyst particle increased.Moreover,in acidic pHthe photo excited electrons in the photo catalyst could be fast abstracted from the surface by the numerous protons of the medium [23].

3.2.3. Effect of catalytic content

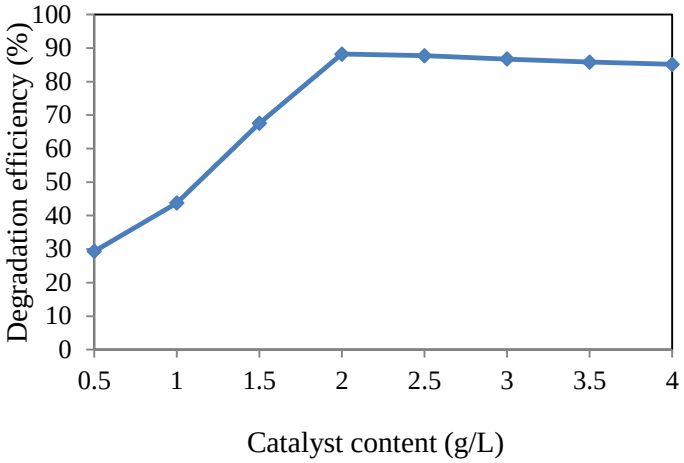

Fig. 12: Degradation at different content of Ag3.0-Ni1.5/TiO_2 catalyst (MR initial concentration: 10^{-5}M; pH: 4; irradiation time: 60 min).

The effect of catalyst content (Ag3.0-Ni1.5/TiO_2) on the degradation efficiency of MR was investigated with different catalytic content varying from 0.5 to 4.0 g/L, at dye solution concentration: 10^{-5}M for 60 min and pH at 4.The results were shown in Fig.12. The degradation efficiency significantly increased up to 2 g/L of catalytic content. When catalytic content was more than 2.0 g/L, the degradation efficiency of dye was found to bealmost unchanged. Therefore, an optimum catalytic dose of 2 g/L was selected for further experiment.

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3.2.4. Effect of irradiation time

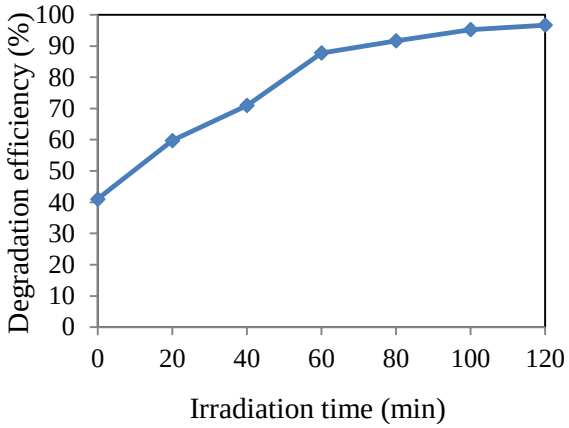

Fig. 13: The effect of irradiation time on photodegradation of MR (catalyst content: 2.0 g/L;pH: 4; MR initial concentration: 10^{-5}M).

In order to study the effect of irradiation duration on the degradation efficiency on MR, the experiments were carried out with Ag3.0-Ni1.5/TiO_2 catalyst amount of 2.0 g/L; pH of dye solution at 4, initial concentration of MR of 10^{-5}M and irradiation time of the dye solution in the range from 0 to 120 min. The results in Fig. 13 indicated that the degradation percentage increased with the increase of irradiation time. At the irradiation time of 120 min, the percent degradation of MR achieved 96.7%.

3.2.5. Reuse of the photocatalyst

To determine the ability of reuse of Ag-Ni/TiO_2as a photocatalytic, reuse experiment of the photocatalytic activity of Ag3.0-Ni1.5/TiO_2 catalyst was performed. After degradation of MR, the photocatalyst was then washed with distilled water and dried. Then the catalyst was reused for degradation of MR solution. The results in Fig. 14 showed that after four times of reuse, the catalyst was still active with a slight decrease in the degradation efficiency from 96.7% (first cycle) to 89.1% (fifth cycle). Hence, it can be confirmed that the photocalytic activity of Ag-Ni/TiO2 catalyst was almost stable during degradation of MR.

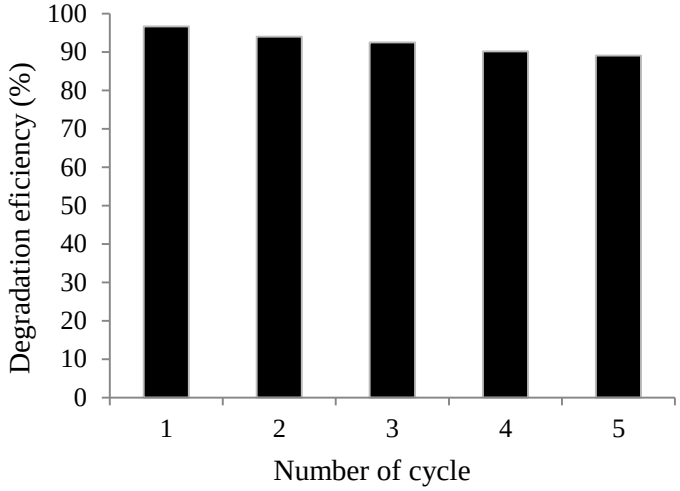

Fig. 14: Regeneration of Ag3.0-Ni1.5/TiO_2photocatalyston degradation MR (amount of catalyst: 2.0 g/L; pH: 4; MR initial concentration: 10^{-5}M; irradiation time: 120 min).

IV. CONCLUSION

Co-doping Ag and Ni nanoparticles on $TiO_2$with different amount of Ag and Niwas carried out byγ-irradiation method. The presence of Ag and Ni in the crystal lattice of TiO_2 was confirmed. The size of Ag and Ni nanoparticles on the surface of TiO_2 was of 1-2 nm. Ag-Ni/TiO_2photocatalysts displayed higher photocatalytic activity for pure TiO_2. Among all synthesized catalysts, the TiO_2 modified with 3.0%Ag (w/w) and 1.5%Ni (w/w) exhibited the highest photocatalytic activity under visible light. In addition, the Ag 3.0-Ni 1.5/TiO_2photocatalystcan be reused many times with almost unchangeof photocatalyticactivity. Thus, Co-doping $TiO_2$with silver and nickel by γ-irradiation can besuitably usedas photocatalyt for degradation of organic pollutants in water.

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