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Photocatalytic oxidation of congo red by NiO-Ag

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ABSTRACT

NiO-Ag catalyst was prepared by photodeposition method by applying uv radiation on a mixture of slurry nickel oxide with silver nitrate in a solution of water: acetone (1:1). The catalyst was investigated by XRD analysis and showed a successive deposition of silver metal only on NiO surface. FTIR analysis showed no deviation altering the absorption in the range 400-4000 cm^{-1}. The photocatalytic activity of NiO and NiO-Ag was examined by degradation of congo red dye and the later was more active photocataltically about two times. Weight of catalyst was studied and it was about 300 mg/ L. The reaction last 2.5 hours to get full decolorized solution.

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INTRODUCTION

Dyes (likes congo red) are not decomposed naturally, staying for a long time in environment and consuming more oxygen when decomposed by microorganisms. Dye are stable compounds and harmful for man when fall on skin or have it from contaminant water and they are allergic, irritated, skin reddish and most of them are classified as carcinogenic like congo red (S. Dawood and T. Kanti Sen, 2012), and it has been treated by adsorption (S. Dawood and T. Kanti Sen, 2012) (Dakhil Nasir, *et al*, 2012), ozone (M. Khadhraoui, *et al* 2009), microorganism (Amar A. *et al* 2010) or photocatalytic degradation (Amjed Mirza Oda, *et al* 2012).

Semiconductor oxides are one of the best photocatalyst since its ability to oxidation-reduction process by absorbing energy. This energy equal or more than band gab of semiconductor oxide, transfers electron from valence band to conduction band. This action of semiconductor can donate electron as reducing agent and accepts electron as oxidizing agent (D. Friedmann *et al* 2010) . The electron–hole pair remains separated, the valence band hole will oxidize the hydroxyl groups that are present in the aqueous environment to the highly oxidative hydroxyl radicals (•OH). Simultaneously, the conduction band electron will capture the electron scavengers (e.g. dissolved oxygen) creating the superoxide radical (•O) (M. Nan Chong *et al* 2009).

The important application of photocatalyst in treatment of waste water of industries. This pollution produces physical, chemical and biological problems and responsible of dangerous organic compounds inter environment (Y. Yang and J. Luan, 2012). In spite of many industries in charge of water pollution but plastic and textiles industries have the most risk (Amjed Mirza Oda *et al* 2012).

Decolorization process is the first step of water treatment contaminant with dyes and photocatalysis methods are one of the safe and modern important methods in this field (Y. Yang and J. Luan, 2012).

Deposition of metals on the photocatalyst surface improves its photocatalysis by changing surface area and photoconductivity. Metals work as sink of electrons so the recombination between electron-hole pairs is reduced. Metal added not more 5% of oxide and Ag metal is one of interest metal used for this purpose (P. Li *et al* 2012).

In this research, photodeposition of Ag on nickel oxide (NiO) was carried out successfully in simple mixture of acetone and water. Efficiency of NiO and NiO-Ag was compared by photocalytic degradation of congo red dye.

Experimental:

Catalyst preparation: NiO (BDH) added to a mixture of water and acetone (GCC) 50:50 and silver

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nitrate (BDH) was added which is represent 2.5% as Ag then the group was agitated by magnetic stirrer for one hour in the dark. The mixture was illuminated with 125 watt mercury lamp located above the solution with distance of 20 cm. and reaction go on for 4 hours. Solvents are evaporated at 80 C and catalyst was collected

Catalyst test:

The catalyst was tested by FTIR and XRD analysis.

Photocatalysis reaction:

NiO and NiO-Ag weighed approx. 0.1 gm. Each one per 100 ml of congo red dye solution and agitated (dark reaction) for 1 hour for adsorption. Cylindrical reactor with 5 watt lamp and cooling for heat dissipation with fixed volume (130 ml) was used for photoreaction as shown in figure (1). For interval time, samples were drawn by syringe and centrifuged doubly. The clear solution absorbance was measured by uv. vis. Spectrometer (2601) at 495 nm.

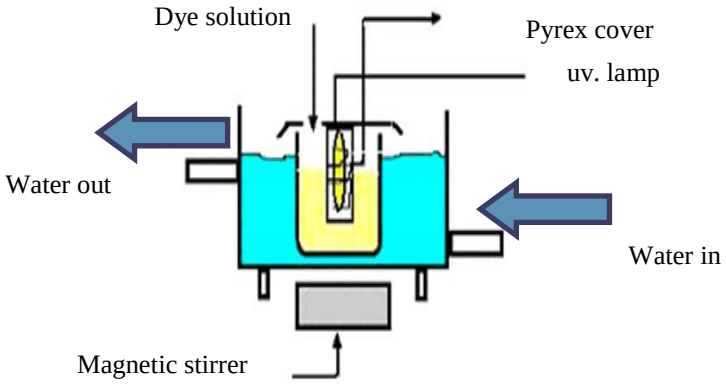

Fig. 1: Photocalytic oxidation reactor.

RESULTS AND DISCUSSION

XRD analysis:

The catalyst characterized by XRD technique and figure (2) shows the diffraction spectrum of NiO after silver photodeposition on its surface.

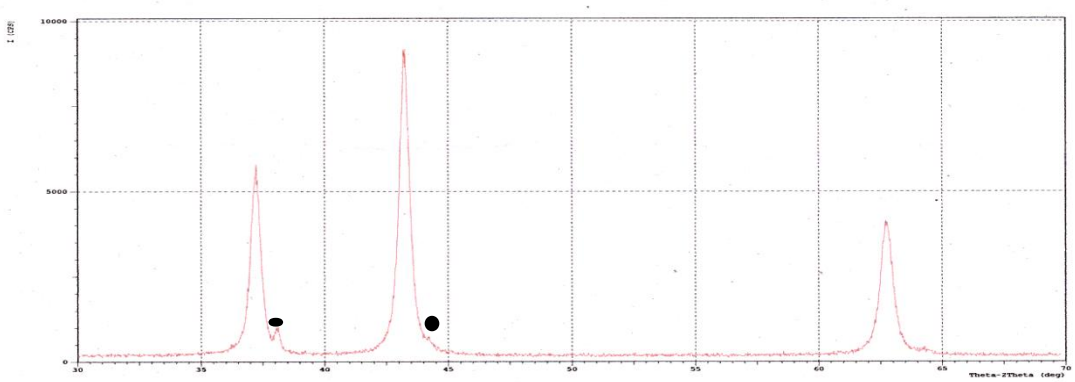

Fig. 2: the diffraction spectrum of NiO after silver photodeposition (the black balls refer to Ag metal peak and peaks without labeling belong to NiO).

2 theta angles 37, 43 and 62.8 are belong to rock salt crystal of NiO (JCPDS, No. 04-0835) and no angle deviation was noticed. The new angle at 2 theta= 38^o belong to silver metal and usually silver has another angle = 44^o appeared very weak (JCPDS 040783) and merged with 2 theta= 43^o of NiO, thus silver appears as one phase deposits on NiO surface and no any silver oxides are formed.

Crystal NiO parameters were calculated from face center cube law according to the equation: (Richard J. D. Tilley 2006) (C. Kittel 1976)

$$1/ d^2=(h^2+ k^2 +l^2)/ a^2 \quad (1)$$

Where (a)is crystal parameter, (h,k,l) are Miller indices and (d) is space between crystal levels. Table (1) shows (d) and (a) of this work compared with original NiO.

Table 1: values of d and a parameter according to specific 2theta

2theta	hkl	d A^o	a A^o
43.28	200	2.086	4.173 *
43.23	200	2.090	4.181 **

*(M. Nieuwenhuizen *et al* 2004)
** this work.

Crystalline size was calculated from Scherrer's equation (Richard J. D. Tilley 2006)

$$D = 0.94\ \lambda/B\ Cos\theta \quad (2)$$

θ: diffraction angle, λ: wave length of x-ray beam, B: full width at half maximum of peak.

Table 2: shows the crystalline size of NiO and Ag in specific angles.

Material	2theta	Crystalline size, nm
NiO	37.26	13.90
	43.23	9.60
Ag	38.00	30.00

When the particles considered globular and the ratio of area to volume equal 6, the surface area can be calculated and found 80 m^2/gm. According to equation (3) (M.V. Shankar *et al* 2004):

$$\text{Surface area } (m^2/gm) = 6/(D * \text{density}) \quad (3)$$

So theoretical density calculated from equation (4) (Richard J. D. Tilley 2006) and the volume of crystal shown in table (2).

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$$d_{th} = M_w * z * 1.66/ V_o \quad (4)$$

d_{th}: theoretical density, M_w: molecular weight of crystal unit, z: No. of atoms in the crystal unit and V_o: volume of crystal unit ($V_o = a^3$). Density and volume of unit crystal are listed in table (2). 1

Table 2: density and volume of NiO crystal.

2theta	hkl	V	Density
43.28	200	72.668	6.85 *
43.23	200	73.07	6.78

* (M. Nieuwenhuizen *et al* 2004)

FTIR of catalyst:

FTIR analysis of NiO showed strong absorption in 400-600 cm^{-1} (M.V. Shankar *et al* 2004) and no change was noticed after NiO doping with Ag. There are several shoulders in NiO spectrum and these disappeared after doping this may be according to Ag occupying on NiO surface. FTIR spectrum of NiO and NiO-Ag showed in figure (3).

Photcatalytic Activity:

Efficiency of photodecolorization was investigated by using aqueous solution of congo red dye (25 ppm). Dye decolorization was examined at 495 nm (λ max) and during 25 min the photoreaction carried out in the presence of uv. Light and agitation and it obvious that NiO degraded 25% of dye concentration while NiO-Ag degraded 45% of dye concentration in same conditions. Decolorization process was doubled in presence of NiO-Ag more than NiO alone and this made Ag a good sensitizer and enhances photoreaction by separation of electron and hole on oxide surface and Ag work as a sink of electrons (D. Friedmann *et al* 2010) (P. Li *et al* 2012). The result was showed in figure (4) of NiO and NiO-Ag efficiency.

Effect of catalyst loading:

Catalyst loading was studied, where catalyst weight increases the decolorization increases. In low loading, the efficiency of light absorption by catalyst particles is low while in high loading there is high scattering of light and accumulation of particles made light absorbed by close particles which is shielded the penetration of light to particles inside and these work as filter of light (M.V. Shankar *et al* 2004) (Amjed Mirza Oda *et al* 2013) The optimum weight was 300 mg/ 100 of dye solution. The effect of catalyst loading was showed in figure (5).

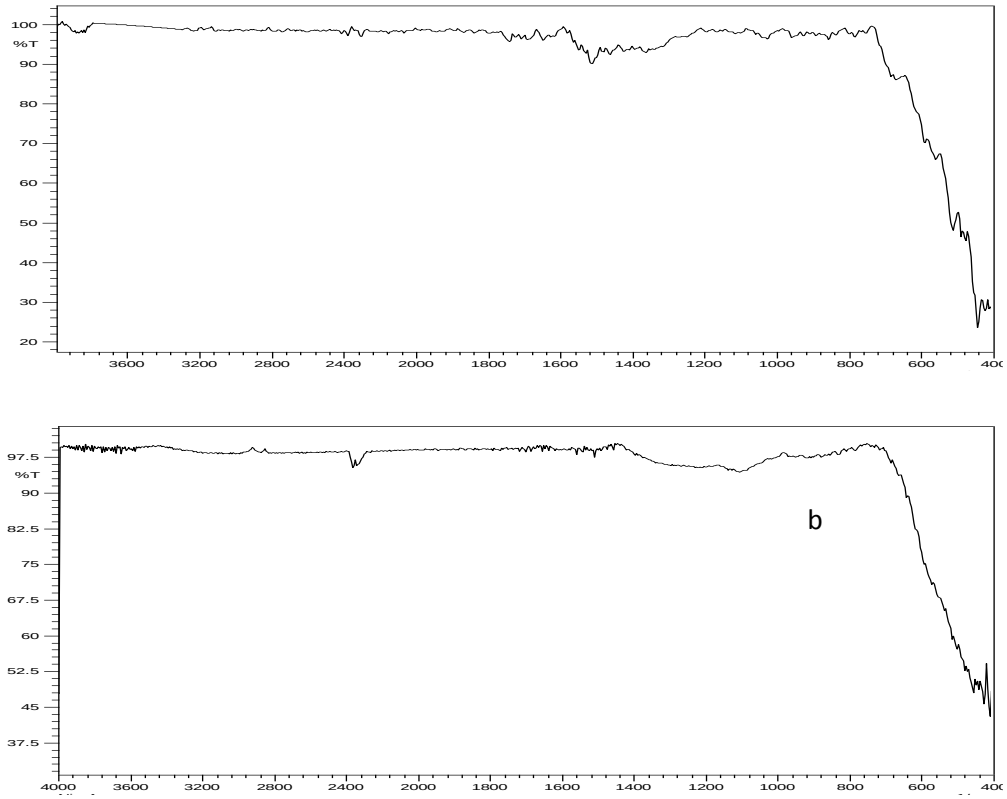

Fig. 3: FTIR spectrum of NiO (a) and NiO-Ag (b).

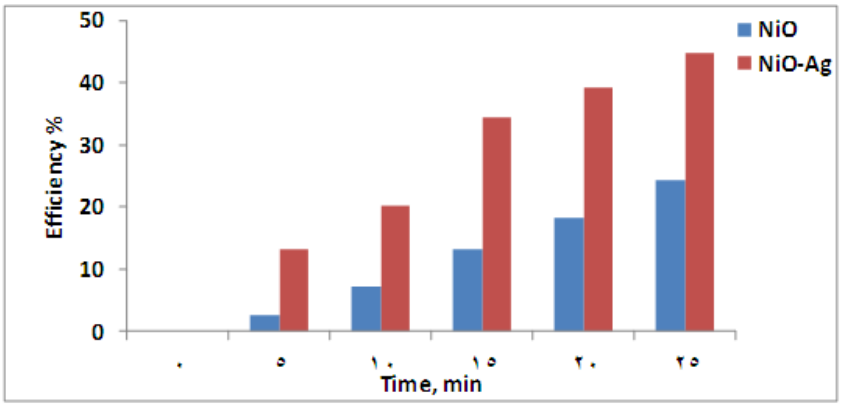

Fig. 4: NiO and NiO-Ag efficiency of congo red decolorization.

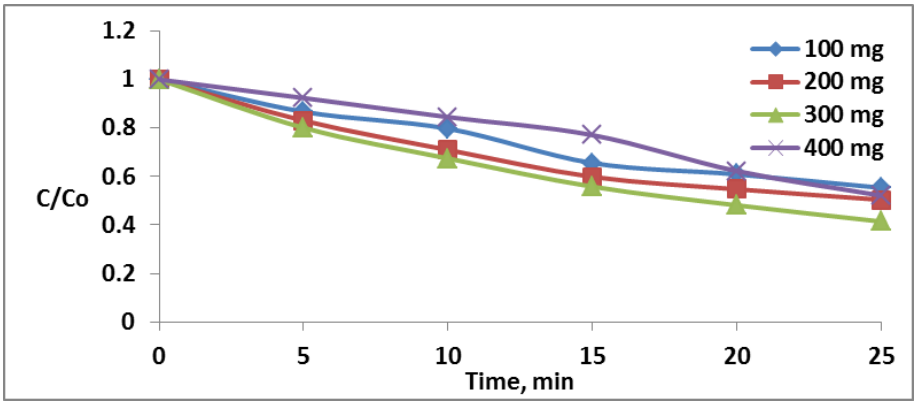

Fig. 5: effect of catalyst loading on photodecolorization of congo red solution.

Photocatalysis reaction considered a pseudo-first order reaction in dilute concentration according to equation (M.V. Shankar *et al* 2004) (S. Sakthivel *et al* 2003):

$$\ln(Co/C) = -kt \quad (5)$$

where C_o and C are concentration at t=0 and after t of time respectively. k is apparent constant of reaction. Figure (6) showed the kinetic results at different weight of catalyst.

Figure (7) shows the effect of catalyst loading on apparent constant of reaction and so the optimum weight of catalyst to give higher constant of reaction.

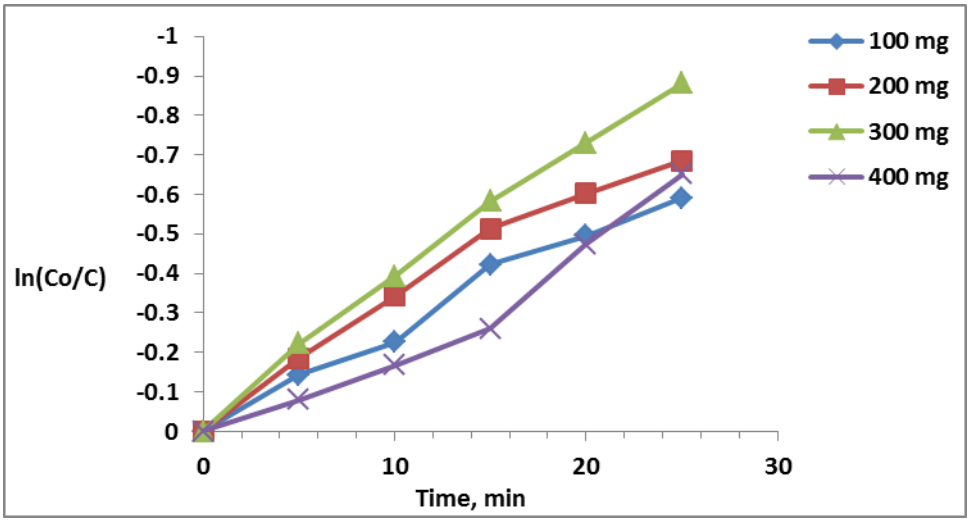

Fig. 6: relationship of $\ln(C_o/C)$ with time

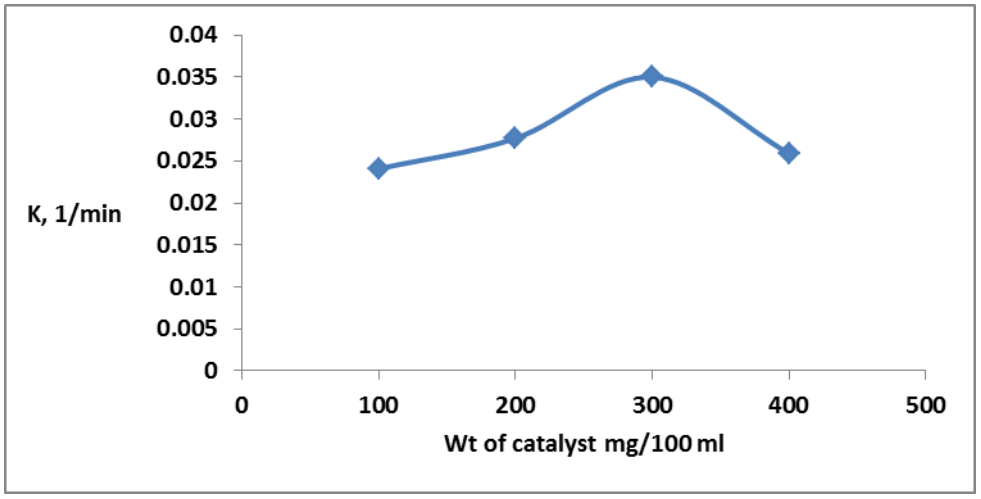

Fig. 7: effect of catalyst loading on the apparent constant of reaction.

Effect of reaction time:

Time is important factor for catalyst action. The full decolorization of congo red solution last 2.5 hours and that appeared from uv. visible spectrum where congo red has two bands at 495 and 350 nm and both of them are decreasing as time of reaction increases. Figure (8) showed the uv. visible spectrum of congo red at dark reaction and after photoreaction.

Conclusion:

A successive photodeposition of silver on NiO by simple procedure. Photocatalytic oxidation increases by silver doping. Silver is a good photosensitizer to promote the photoactivity of NiO. Congo red solution decolorized completely after 3 hours.

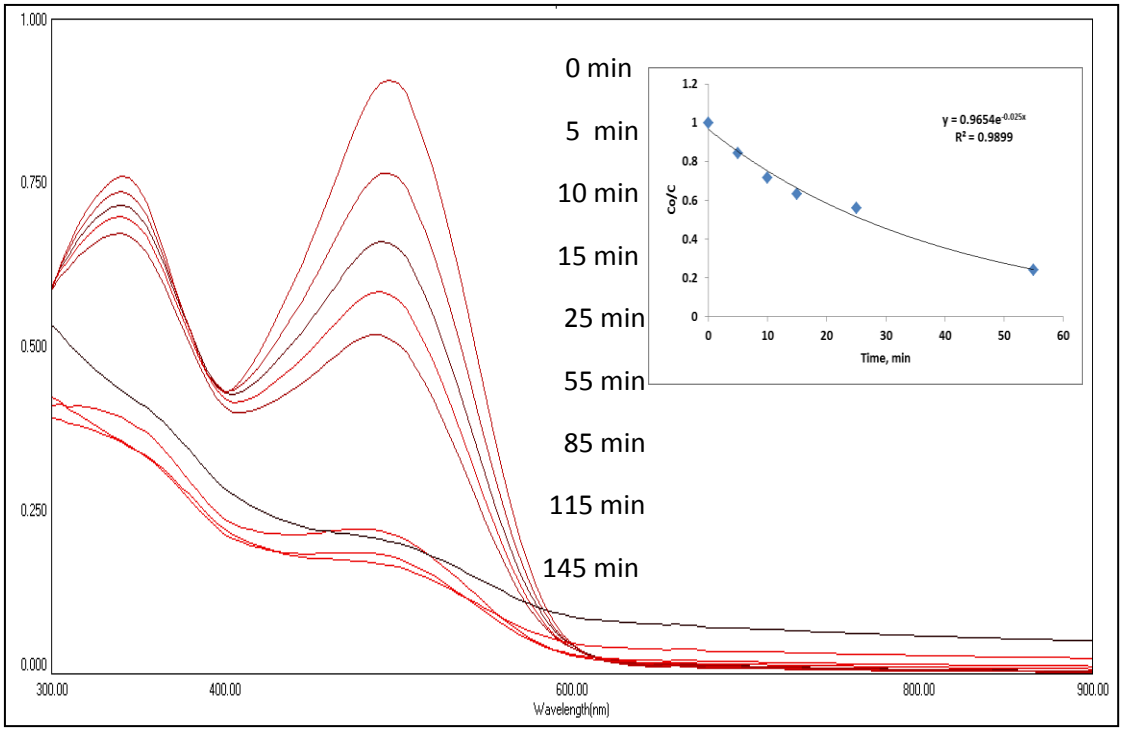

Fig. 8: The uv. visible spectrum of congo red at dark reaction and after photoreaction progress. (figure inside is C_o/C against time and fitted for 55 min only, where k= 0.025 min^{-1})

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