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Green and eco-friendly synthesis of Co_3O_4 and Ag-Co_3O_4: Characterization and photo-catalytic activity

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Abstract: In this study, Co_3O_4 and Ag-Co_3O_4 were synthesized by a novel and green method using leaves extract of *Helianthus annuus* from cobalt nitrate and silver nitrate. The synthesized particles were characterized using X-ray powder diffraction, thermal gravimetric analyses, scanning electron microscopy, particle size analyses and UV-Visible spectroscopy. The photo catalytic activities of synthesized Co_3O_4 and Ag-Co_3O_4 were appraised by degrading methyl orange dye and after 120 minutes of reaction a degradation of 53 and 87% was achieved using 100 mg/L (50 mL) solution of methyl orange and 0.1 g Co_3O_4 and Ag-Co_3O_4 as catalyst respectively. This green synthesis of Ag-Co_3O_4 proves to be an eco-benign, environmental benign, simple and effective approach for degradation of dyes in aqueous medium.

Keywords: green synthesis; *Helianthus annuus,* Ag-Co_3O_4; photo degradation; methyl orange

1 Introduction

Cobalt oxide, a p-type semiconductor, has been largely researched due to its remarkable magnetic, electrical and catalytic properties and its broad range of applications in capacitors, energy storage, field emission materials, gas sensing, magnetic semiconductors, lithium-ion batteries and heterogeneous catalysis. Co_3O_4 has spinel crystal structure in which Co^{3+} and Co^{2+} occupy octahedral 16d and tetrahedral 8a sites respectively. It has a direct optical band gap of 2.13 to 3.95 eV [1-7]. Several methods such as irradiation-assisted chemical reaction, reduction reactions, sequential injection, thermal decomposition, chemical vapor deposition, sonochemical route, sol-gel, co-precipitation, mechano-chemical processing, combustion, chemical spray pyrolysis etc. for the synthesis of cobalt oxide have been reported. However, these synthetic methods are largely associated with several drawbacks due to the use of prolonged reaction time, high temperature complex synthesis steps, expensive equipment and high cost of synthesis. Furthermore, almost all of mentioned methods are environmentally un-friendly [8-18]. Hence, an alternative method for elimination or minimization of drawback associated with mentioned methods is offered by green chemistry. Green chemistry has been accepted as an inventive means for minimization of hazardous and toxic chemicals during synthesis of metal oxides particles. Green chemistry is associated with use of environmentally friendly materials which have many advantages in terms of compatibility and eco-friendliness. Green synthesis employing plants and microorganisms extracts as reducing and stabilizing agents has gained much attention in recent years due to the use of mild experimental conditions of temperature, pH and pressure [19,20]. Plant extracts are easy to handle, non-toxic and can be processed using easy protocols. The phytochemicals such as flavonoids, saponin, phenolic acids and tannins present in plant extract are bioactive compounds and are good chelating and reducing agents for synthesis of nanoparticles which can donate hydrogen and quench singlet oxygen. The plant assisted green synthesis is more appropriate in comparison to physico-chemical methods due to redox activities of phytochemicals [21-27]. Co_3O_4 is one of the oxides which has been synthesized by green method extensively using various types of plants. Diallo et al. [28] have reported the biosynthesis of cobalt oxide using natural extract of *Aspalathus linearis* as chelating agent. Siadat [29] has used fruits of extract of Piper longum fruit for biosynthesis of Co nanoparticles. Vijayanandan and Balakrishnan [30]

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have used *Aspergillus nidulans* fungus for biosynthesis of cobalt oxide nanoparticles. Khalil and his co-workers [31] have reported the *Sageretia thea* (Osbeck.) assisted green synthesis of Co_3O_4 nanoparticles.

Herein, we report the green synthesis of Co_3O_4 and Ag-Co_3O_4 using leaves extract of *Helianthus annuus* (Sun flower). The prepared particles were employed as catalysts for aqueous phase photo degradation of methyl orange.

2 Experimental

2.1 Green synthesis of Co_3O_4

Co_3O_4 was synthesized by green method using leaves extract of *Helianthus annuus* (Sun flower). Frist the leaves extract was prepared. For this purpose, fresh leaves were plucked from *Helianthus annuus* and dried in shade. About 15 g of dried leaves were washed with distilled water followed by a 3 h reflux in distilled water. Then the leaves were filtered off after cooling the mixture and the filtrate collected was used for synthesis of Co_3O_4 in next step. For synthesis of Co_3O_4, the leaves extract (50 mL) was dropped to a 0.5 M cobalt nitrate solution. The stirring of reaction mixture resulted in precipitation of Co particles. The paste obtained was washed with ethanol followed by washing with water and drying at 100°C for 12 h. The obtained powder was than calcined at 500°C for 3 h to get Co_3O_4.

2.2 Green synthesis of Ag-Co_3O_4

The deposition of Ag on Co_3O_4 was accomplished by green method using leaves extract of *Helianthus annuus* (Sun flower). In a typical experiment, 50 mL leaves extract was added drop wise to a solution containing a calculated amount of already prepared Co_3O_4 and $AgNO_3$. Then the reaction mixture was stirred for 2 h followed by filtration. The precipitate obtained was washed with ethanol and water and then dried at 80°C for 12 h.

2.3 Characterization

The prepared Co_3O_4 and Ag-Co_3O_4 were characterized by XRD, TGA, SEM and particle size analyses. The crystalline phases of Co_3O_4 and Ag-Co_3O_4 were confirmed using JDX-3532 Japan X-Ray Diffractometer. Thermal stability of Co_3O_4 and Ag-Co_3O_4 were examined using Perkin Elmer 6300 USA TGA Analyzer. The morphologies of prepared particles were studied by JSM-5910 Japan Scanning Electron Microscope. The particle size distribution of prepared catalysts was measured with Analysette 22 Compact, Fritsch, Germany particle size analyzer. UV-Visible spectra of prepared particles were recorded using Perkin Elmer USA UV-Visible spectrophotometer.

2.4 Photo catalytic degradation experiment

The synthesized Co_3O_4 and Ag-Co_3O_4 were tested as catalysts for degrading the methyl orange using a Pyrex glass batch reactor. For this purpose, a 50 mL solution of 100 mg/L was taken in bath reactor and 0.1 g of prepared catalyst was added to dye solution, followed by stirring for 15 min in dark to get adsorption equilibrium. Afterward, the reaction mixture was stirred in visible light. A 100 W incandescent light bulb was used for irradiation of reaction mixture. A sample of 0.5 mL was pipped out after regular interval of time. The visible spectrum of each sample was measured by a UV–visible spectrophotometer.

2.5 Reaction kinetics

The reaction kinetics is described by Eley–Rideal (E-R) mechanism in present study. According to this mechanism dye molecule reacts with adsorbed oxygen at the surface of catalyst. It is suggested that irradiation of catalyst generates an electron-hole pair between conduction and valence band. The oxygen adsorbed at the surface of catalyst is converted to superoxide anion (O_2^-) by reaction with electron which produce OH radical on protonation. Similarly, water reacts with hole and produces OH radical. These OH radicals are strong oxidizing species, which degrade the dye molecule into inorganic molecules [32-36].

The kinetics expression for proposed mechanism is given by Eq. 1, which changes to Eq. 2 on considering constant partial pressure of oxygen.

$$-\frac{d[MO]}{dt}=k_r O_{2(ad)}[MO] \tag{1}$$

$$-\frac{d[MO]}{dt}=k[MO] \tag{2}$$

On integration, we get Eq. 3 which is a straight-line pseudo first order kinetics equation.

$$\mathrm{In}\frac{MO_o}{MO_t}=kt \tag{3}$$

3 Results and discussion

3.1 Characterization

Crystalline structures and phase purity of prepared Co_3O_4 and Ag-Co_3O_4 were investigated with X-rays diffraction spectroscopy and XRD patterns of Co_3O_4 and Ag-Co_3O_4 are given in Figure 1. These patterns are dominated with sharp peaks indicating the crystalline nature of synthesized material. The dominant peaks at 2θ 19°, 31°, 37°, 38°, 44° and 59° correspond (1 1 1), (2 2 0), (3 1 1), (2 2 2), (4 0 0) and (5 1 1) planes of face centered cubic (FCC) spinel crystalline phase of Co_3O_4 respectively (JCPDS 073–1701) [33-36]. In the XRD pattern of Ag-Co_3O_4 (spectrum b), peaks at 2θ 38° and 44° has been pronounced and an additional peak at 2θ 65° (2 2 0) appeared. These peaks correspond to face centered cubic phase of Ag (JCPDS No. 87–0597) [8,41-43]. Goudarzi et al. [8] have assigned peaks at 2θ 38° and 44° to (1 1 1) and (2 0 0) planes of Ag respectively. Absence of any other peak in XRD pattern indicates the purity of prepared products.

Thermal stability of the prepared Co_3O_4 and Ag-Co_3O_4 was studied by thermal gravimetric analysis (TGA) over temperature range 30-600°C (Figure 2). There was no significant loss in the weight of sample with temperature which shows the stable nature of prepared particles. A 4% weight loss in Ag-Co_3O_4 over 150°C (Figure 2b) is due to evaporation of moisture. Similarly, a 30% loss in weight of both samples over 300°C is due to decomposition of unwashed plant material.

The morphology of prepared Co_3O_4 and Ag-Co_3O_4 was studied by scanning electron microscopy and the obtained micrographs are given in Figure 3. The scanning

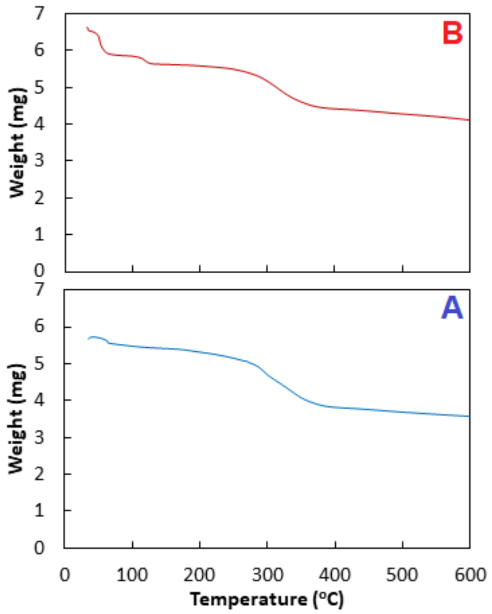

Figure 2: Thermal gravimetric analyses of prepared particles (a) Co_3O_4 and (b) Ag-Co_3O_4.

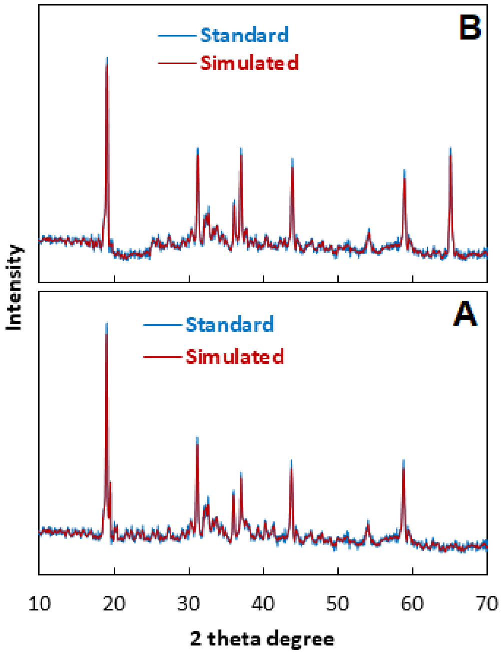

Figure 1: X-rays diffraction patterns of prepared particles (a) Co_3O_4 and (b) Ag-Co_3O_4.

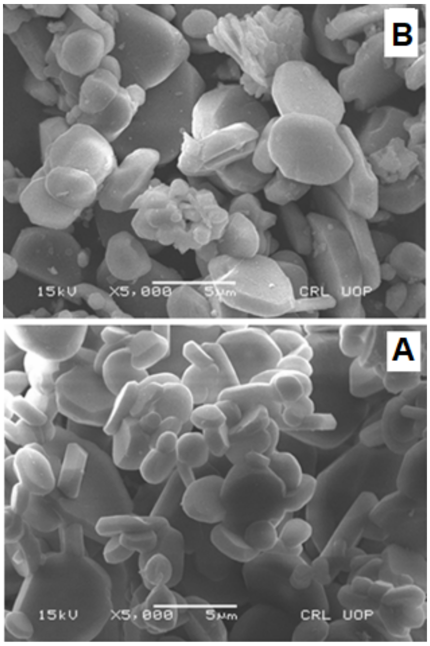

Figure 3: Scanning electron micrographs of prepared particles (a) Co_3O_4 and (b) Ag-Co_3O_4.

electron micrographs show that particles are plate shaped, heterogeneous, non-agglomerated and dispersed in nature.

Particle sizes determined by wet method of analysis were in the range of 1-20 µm, however 84% of the particles were in range of 2-5 µm. The overall distribution of particle size given in Figure 4.

UV-Visible spectrum of Co_3O_4 (Figure 5a) shows an absorption band at 360 nm which can be assigned to plasma resonance band of Co_3O_4. This absorption band arises due to electro-magnetic field induced oscillation of the electrons in conduction band. The distinguishing feature of the Co_3O_4 is to exhibit a surface plasmon absorption band in the regions of 350–550 nm. The absorption band in UV-Visible spectrum of Ag-Co_3O_4 (Figure 5b) at λ_{max} is due to surface plasmon resonance property of silver [21,44-47].

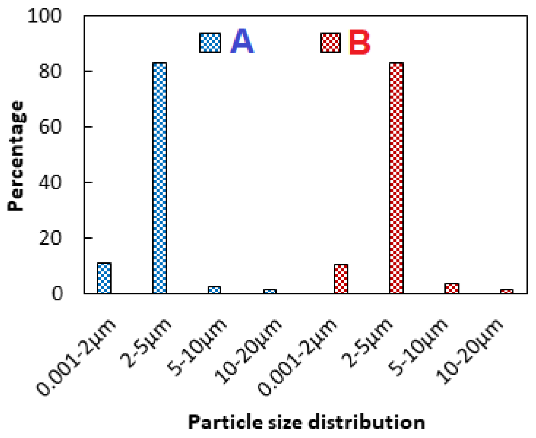

Figure 4: Particles size distribution of prepared particles (a) Co_3O_4 and (b) Ag-Co_3O_4.

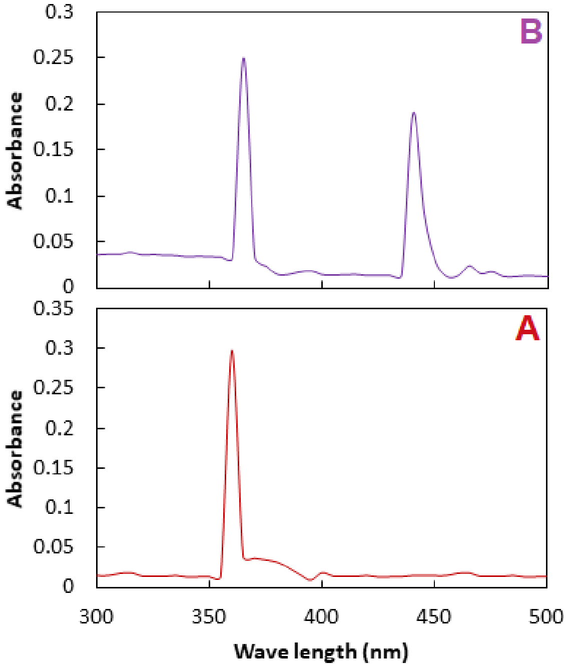

Figure 5: UV-Visible spectra of prepared particles (a) Co_3O_4 and (b) Ag-Co_3O_4.

3.2 Photocatalytic activity

Photo-catalytic degradation of methyl orange was studied over Ag-Co_3O_4 as catalyst under irradiation of visible light. It was found that 87% and 100% of 50 mL (100 mg/L) methyl orange degraded in 120 minutes of reaction time over 0.1 g of Ag-Co_3O_4 as catalyst at 40°C and 50°C respectively. The visible spectrum of treated dye solution is given in Figure 6. The absorbanve at λ_{max} (480 nm) reduced with increase in reaction time, which indicates that methyl orange degraded through photo catalytic treatment. The effect of Ag on photo catalytic activity of Co_3O_4 was studied by catalytic treatment of dye solution over Co_3O_4 and Ag-Co_3O_4 separately. It was found that declorization achieved with Co_3O_4 and Ag-Co_3O_4 were 53% and 87% respectively. These results indicate that Ag-Co_3O_4 is an efficient catalyt for aqueous phase degradation of methyl orange. The comparison of photo catalytic activity of Co_3O_4 and Ag-Co_3O_4 is given in Figure 7. The photo catalytic activities of Co_3O_4 and Ag-Co_3O_4 for degradation of methyl orange can also be expressed in terms of TON (number of moles of methyl orange degraded per unit mass of catalyst) and TOF (number of moles of methyl orange degraded per unit mass of catalyst per unit time) as given in Figure 8. It was noted that there was no significant loss in TOF of both Co_3O_4 and Ag-Co_3O_4 which indicates that Co_3O_4 and Ag-Co_3O_4 do not lose their catalytic efficiency during

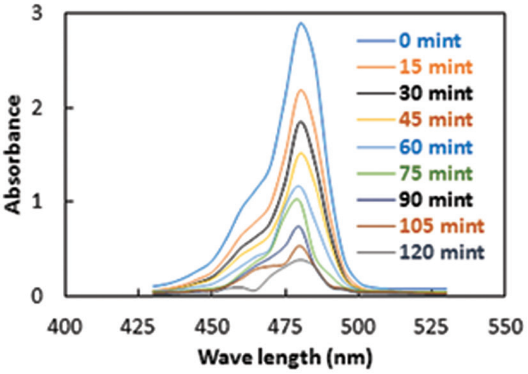

Figure 6: Visible spectra of solution of methyl orange treated with Ag-Co_3O_4 catalyst at different time intervals.

degradation reaction. The dye degradation is mainly due to the generation of electron and hole on catalyst surface under irradiation. These electron and hole produce OH radicals through a series of reactions. The OH radicals are strong oxidizing species, which degrade the dye molecule into inorganic molecules. The deposition of Ag enhances the photo catalytic activity of Co_3O_4 by preventing the recombination of electron and hole generated under irradiation [48-50]. The dependence of catalytic activity of Co_3O_4 on Ag content was also studied. Ag-Co_3O_4 with 3% Ag was found as optimum catalyst in present study.

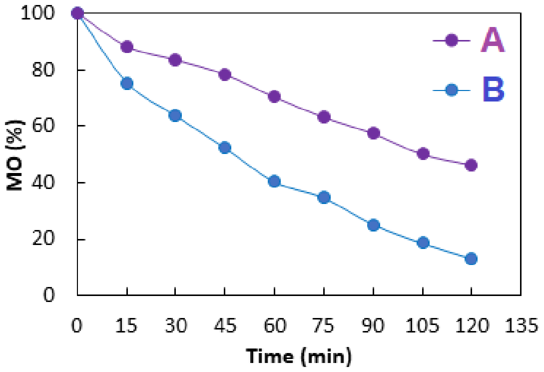

Figure 7: Comparison of photo catalytic activity of Co_3O_4 (a) and Ag-Co_3O_4 (b) in terms of concentration of methyl orange.

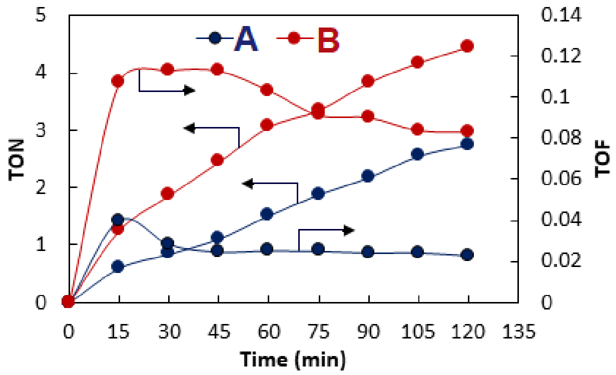

Figure 8: Comparison of photo catalytic activity of Co_3O_4 (a) and Ag-Co_3O_4 (b) in terms of TON and TOF.

The photocatalytic activity of prepared Ag-Co_3O_4 for photo degradation of methyl orange was compared with catalytic activities of various catalysts reported in literature. The comparison of present system with other catalysts is given in Table 1.

We have reported earlier [35,56] that decomposition of dye molecule occurs at azo bond (–N=N–) as it is comparatively more spread out within the molecule. Ultimately methyl orange dye was completely mineralized to water and carbon dioxide; however, existence of benzene sulfonate, naphthoquinone, and carboxylic acids were observed with HPLC, which were then mineralized to water and carbon dioxide.

3.3 Effect of temperature

The temperature dependence of photo degradation of methyl orange over Ag-Co_3O_4 was studied by performing degradation experiments at 30, 40 and 50°C with 50 mL of 100 mg/L dye solution over 0.1 g Ag-Co_3O_4 separately. The obtained data is given in Figure 9. Although the effect of temperature on photo catalytic activity of Ag-Co_3O_4 is not much significant as photo reaction are generally less temperature dependent. Increase in temperature helps the reaction to compete more efficiently with electron-hole recombination as a result of increased collision frequency of molecules; leading to an enhancement of the degradation activity. The experimental data given in Figure 9 was analyzed according to kinetic equation 3 and results are given in Figure 10. The best straight lines obtained indicate that reaction follow the pseudo first order kinetics. The rate constants determined are listed

Table 1: Comparison of catalytic activities of various catalysts for degradation of methyl orange (MO) in aqueous medium.

Catalyst	MO	Time (minutes)	Degradation (%)	References
$Ni(OH)_2$ (0.1 g)	50 mL (200 mg/L)	180	60	[35]
Tl_2O_3 (0.1 g)	100 mL (10 mg/L)	40	74	[51]
$CuO/ZnO/Al_2O_3$ (0.05 g)	50 mL (10 mg/L)	60	89	[52]
$CoFe_2O_4$-G (0.025 g)	100 mL (20 mg/L)	240	70	[53]
$CoFe_2O_4$-PANI (0.02 g)	100 mL (20 mg/L)	60	85	[54]
Cu_2O/ZnAl-CLDH (0.05g)	50 mL (20 mg/L)	420	90	[55]
ZnO (0.2)	50 mL (100 mg/L)	60	43	[56]
Pt/Al_2O_3 (0.05 g)	50 mL (100 mg/L)	120	60	[57]
Co_3O_4 (0.1 g)	50 mL (100 mg/L)	120	53	This work
Ag-Co_3O_4 (0.1 g)	50 mL (100 mg/L)	120	100	This work

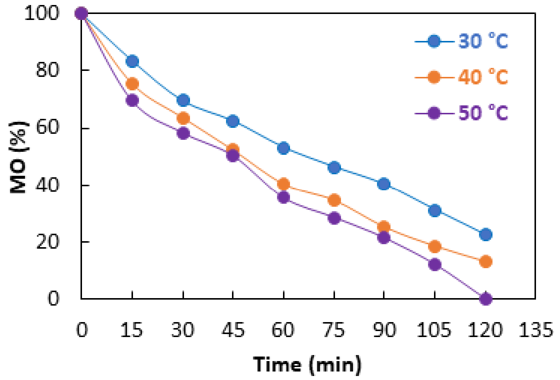

Figure 9: Time profile data of Ag-Co_3O_4 catalyzed photo degradation of methyl orange.

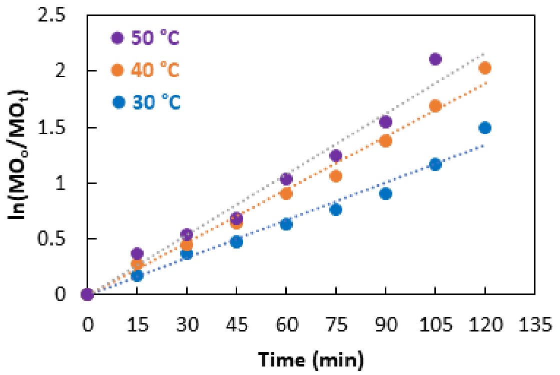

Figure 10: Analyses of experimental data of Ag-Co_3O_4 catalyzed photo degradation of methyl orange according to pseudo first order kinetics equation (Eq. 3).

in Table 2. The energy of activation was determined by applying Arrhenius equation to rate constants at various temperatures and was found to be 16 kJ/mol.

3.4 Effect of initial concentration

Similarly, the concentration dependence of photo degradation of methyl orange over Ag-Co_3O_4 was studied by performing degradation experiments with 50 mL of 100, 200 and 300 mg/L dye solution over 0.1 g Ag-Co_3O_4 at 40°C separately. The obtained data is given in Figure 11. This data was analyzed according to kinetic equation 3 and results are given in Figure 12. The rate constants determined are listed in Table 3. It can be observed that increase in concentration caused a decrease in reaction rate. At high concentration, the dye molecules block the active site of catalyst resulting in prevention of access of photons to the catalyst surface. Furthermore, the solution becomes intensely colored at high concentration which

Table 2: Rate constants of Ag-Co_3O_4 catalyzed photo degradation of methyl orange.

T (°C)	k (per mint)	R^2
30	0.0122	0.977
40	0.0158	0.987
50	0.0181	0.972

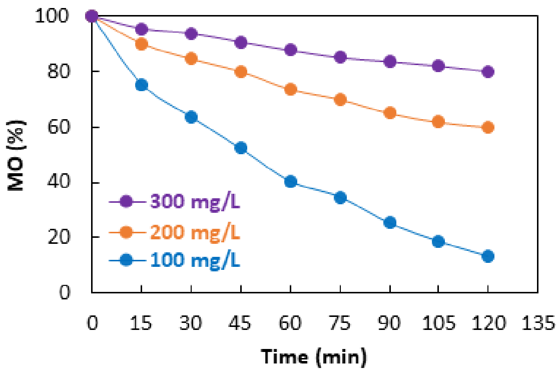

Figure 11: Time profile data of Ag-Co_3O_4 catalyzed photo degradation of methyl orange at 40°C with various initial concentration of methyl orange.

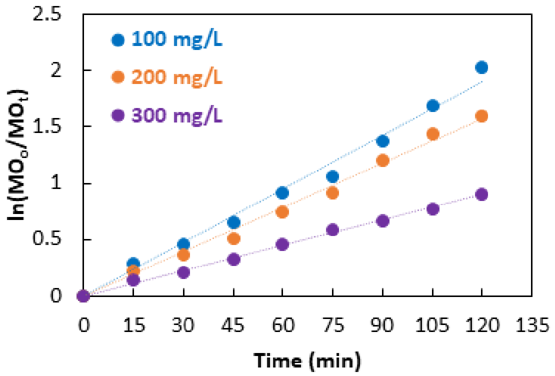

Figure 12: Analyses of experimental data of Ag-Co_3O_4 catalyzed photo degradation of methyl orange with various initial concentration of methyl orange according to pseudo first order kinetics equation (Eq. 3).

Table 3: Rate constants of Ag-Co_3O_4 catalyzed photo degradation of methyl orange with various initial concentration of methyl orange.

MO (mg/L)	k (per mint)	R^2
100	0.0158	0.987
200	0.0131	0.992
300	0.0075	0.998

cause inhibition to penetration of photons. Furthermore, as other experimental conditions are kept constant, therefore the number of OH radicals are also constant. Hence the number of OH radical per molecule of dye decreases as the concentration is increased. That's why degradation decreased with increase in concentration of dye in present study [50,58-60].

4 Conclusions

Co_3O_4 and Ag-Co_3O_4 were successfully fabricated by environmentally friendly and low cost green method using *Helianthus annuus* (Sun flower) leaves extract from cobalt nitrate and silver nitrate and characterized by advanced techniques. The photo catalytic activities of prepared particles were evaluated by degrading methyl orange dye under irradiation of visible light. In response, 53 and 87% degradation of methyl orange achieved within 120 minutes of irradiation over Co_3O_4 and Ag-Co_3O_4 as catalysts respectively. The Eley-Rideal mechanism was operative in reaction following the pseudo first order kinetics model. The method is simple, cost effective and environmental benign which could be extended for the synthesis of other metal-metal oxides.

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