Enhanced Photocatalytic Efficiency of Soft Chemically Synthesized MAI_2O_4 / Activated Carbon Based Composite in the Removal of Toxic Malachite Green Dye Under Visible Light

Manasai Arunkumar

Karunya Institute of Technology and Sciences

Arputharaj Samson Nesaraj (✉ drsamson@karunya.edu)

Karunya Institute of Technology and Sciences <https://orcid.org/0000-0003-0707-7804>

Clementz Edwardraj Freeda Christy

Karunya Institute of Technology and Sciences

Chinnappan Joseph Kennady

Karunya Institute of Technology and Sciences

Research Article

Keywords: Chemical synthesis, Activated Carbon - MAI_2O_4 photocatalyst, malachite green, Dye removal

Posted Date: September 7th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-697853/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Composites of spinel aluminate (MAl_2O_4) based materials having activated carbon (AC) as the base materials were synthesized using chemical precipitation method. The as synthesized photocatalyst was characterized using X-Ray Diffractometry (XRD), Fourier transform Infrared Spectrophotometry (FTIR), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDS) and UV- DRS studies. The XRD confirms the presence of amorphous phase along-with crystalline spinel phase. The bonds related to tetrahedral and octahedral sites of the spinel were confirmed by FTIR. EDS confirmed the presence of appropriate elements. The presence of pores in the sample was shown by SEM. The UV-Visible spectra of the spinel – AC composites exhibited λ_{max} in the range of 365–400 nm. The composites were very effective in the photo-degradation of MG dye from water. The photocatalytic degradation of MG follows pseudo first order reaction mechanism i.e., Langmuire and Hinshelwood kinetic model. Among the photocatalysts studied, $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}$ /AC exhibited excellent degradation efficiency in removing MG completely within 90 minutes under visible light irradiation.

Introduction

The extensive problem of water contamination is jeopardizing our health. Polluted water affects the health of many people every year across the globe. The water may undergo contamination may be due to the mixing of sewage or wastewater, industrial wastes, dumping of wastes, oil contamination, acid rain etc. Among all, the effluents from industries leave highly toxic inorganic pigments in pure water which becomes the main source of water contamination. So it was a great task for the scientists and researchers to purify the contaminated water [Esmaili et al. 2018]. They used different methods, namely coagulation [Gallego-Urrea et al. 2016], adsorption [Al-Anber et al. 2011], membrane filtration [Dickhout et al. 2017] and photocatalysis [Gnanam and Rajendran, 2018] to treat impure water. Photocatalysis is considered as one of the excellent techniques for the removal of organic impurities like dyes. Many benefits of this method over other techniques are: (1) full mineralization, (2) no waste-solids removal crisis, and (3) only gentle temperature and pressure situation are necessary [Konstantinou et al. 2004]. Metal oxides are extensively used as photocatalysts in removing organic effluents from wastewater because of its stability, high oxidizing ability, harmless phenomena, affordable price, and biocompatibility [Vacca et al. 2020]. Spinel aluminates (MAl_2O_4) attract more studies now-a-days because of their exceptional thermal stability, hydrophobicity and low surface acidity [Deraz and Fouda MMG 2013]. Aluminates were commonly utilized as a catalysts or supports in catalytic reactions [Mathur et al.] and also used as photo-luminescent materials [Sampath, Cordaro et al. 2005]. However, metal oxides like aluminates also have few serious disadvantages like high electron hole recombination rate of the light induced charge carriers [Coromelci-Pastravanu, et.al 2014], less adsorption capability, and larger band gap. Hence, the only light which can be used to produce electron-hole pairs is UV light source [Djellabi et al. 2019]. The main aim of this investigation is to develop a novel composite material based on carbon with aluminate which can delay the recombination rate with the enhancement in the active centers and having high surface area. It was reported that the insertion of metal oxides on the high surface area

materials may enhance the catalytic ability and exhibit efficient absorption characteristics [Mehdi 2017]. Now a days, carbon based materials created incredible significance due to their huge surface area, auspicious electronic conductance, less fabrication amount, and good thermal stability [Ye et al. 2012]. These kind of exceptional qualities make carbon based materials as the ideal materials for the improved photocatalytic efficiency in water treatment [Yu et al. 2014]. Generally, the most common carbon based materials employed in the preparation of composites are grapheme [Yu et al. 2015] carbon nanotubes (CNT) [Zhang et al. 2019], carbon quantum dots (CQD)[Li et al. 2018], fullerene[Song et al. 2017], activated carbon (AC)[Velo-Inmaculada et al. 2013] and graphitic carbon nitride (g-C₃N₄)[Zhang et al. 2019]. Incorporation of carbon based materials have appreciably enhanced the photocatalytic degradation behavior, which is mainly due to their textural properties [Puma et al. 2008]. Though in recent times, it has been exposed that the enhancement of the photocatalytic behavior examined with few carbon based materials surpass their textural involvement. The whole degradation of impurities in dye solution has been attained by simple oxidation process with light photons in the existence of activated carbon (AC) with no classic semiconductor materials [Velasco et al. 2010; Velasco et al. 2012]. Besides this property, activated carbon sustain the task of conserving their physicochemical uniqueness throughout the photocatalytic degradation method and their reusability has confirmed that these materials preserve their primary photocatalytic efficiency after many sequences [Mestre, Carvalho 2019; Velasco et al. 2014]. These properties strengthen the claim that activated carbon materials have significant photocatalytic efficiency under the light radiation. Some researchers developed activated carbon based composites and used them as photocatalysts. They reported the enhanced photocatalytic activity of these composites. Briche et. al have synthesized activated carbon based TiO₂ composite material using sol gel method and used it to degrade sulfamathazine, a pharmaceutical product under UV light radiation. The degradation efficiency of the composite is higher than that of the anatase TiO₂ nanoparticles [Briche et al. 2020]. Huang et al. have reported the photocatalytic efficiency of CdS – LAC (lotus derived activated carbon) nanocomposites using the degradation of rhodamine B under visible irradiation. The results revealed the higher photocatalytic efficiency of CdS-LAC composites under visible light [Huang et al. 2018]. Nethaji et al. have developed a novel BiOBr – activated carbon composites using hydrothermal method and used them in the photocatalytic degradation of malachite green dye under visible light irradiation [Nethaji et al. 2018]. In this research study, photocatalytic degradation of malachite green (MG) dye using metal aluminate – activated carbon (MAAC) based materials under visible light radiation was studied and reported.

Experimental

Materials

The reagents used in this research were cobalt nitrate (98%, Merck, India), nickel nitrate (98%, Merck, India), aluminium nitrate (98%, Merck, India), manganese nitrate (98%, Merck, India), sodium hydroxide (97%, Merck, India), ethanol (99.9%,CS, China), malachite green (90%, Isochem, India) and activated carbon

(core carbons private Ltd., India). The chemicals were used as purchased without any refinement. All the solutions were prepared and the reactions were carried out using double distilled water.

Facile chemical fabrication of metal aluminate – activated carbon composites (MAAC)

We already reported that the photocatalysts, such as NiAl_2O_4 , $\text{Zn}_{0.80}\text{Mn}_{0.20}\text{Al}_2\text{O}_{4-\delta}$ and $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}$ prepared by wet chemical synthesis in degrading the malachite green (MG) dye under visible radiation have shown good photocatalytic activity among the different compositions of Co doped NiAl_2O_4 , Mn doped ZnAl_2O_4 and Ni doped CoAl_2O_4 based materials [Arunkumar, Nesaraj 2020; Arunkumar, Nesaraj 2021]. In this research work, we have synthesized a set of metal aluminate – activated carbon (MAAC) based composites, such as NiAl_2O_4 - AC, $\text{Zn}_{0.80}\text{Mn}_{0.20}\text{Al}_2\text{O}_{4-\delta}$ - AC and $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}$ - AC using in-situ co-precipitation method as per the details mentioned below. In the typical synthesis, stoichiometric concentration of corresponding metal nitrate solutions were mixed with appropriate concentration of the precipitant (NaOH) along-with 0.5 g of activated carbon (AC) in a magnetic stirrer for about 1 hour. The resultant corresponding metal hydroxide precipitates with AC were washed with water – ethanol mixture (9:1 v/v) and dried at 60° C for about 2 hours. Then, the dried product was calcined at 600° C for 2 hours to get corresponding metal aluminate – activated carbon (MAAC) based composite materials. The amount of precursors used for the synthesis of MAAC is presented in Table 1.

Table 1
Amount of precursor material (dissolved in 100ml of distilled water) for the synthesis of aluminate based nanomaterials and carbon based composites by chemical precipitation method.

Sample	Concentration of metal nitrates/ Wt (g)	Concentration of dopant / Wt (g)	Concentration of $\text{Al}(\text{NO}_3)_3$ / Wt (g)	Concentration of NaOH / Wt (g)	Activated Carbon / Wt (g)
$\text{NiAl}_2\text{O}_4/\text{AC}$	0.1 M / 2.91g of $\text{Ni}(\text{NO}_3)_2$	-	0.2M / 7.5	0.8M / 3.2	0.5
$\text{Zn}_{0.80}\text{Mn}_{0.20}\text{Al}_2\text{O}_{4-\delta}/\text{AC}$	0.080M / 2.38 g of $\text{Zn}(\text{NO}_3)_2$	0.020M / 0.5741 of $\text{Mn}(\text{NO}_3)_2$	0.2M / 7.5	0.8M / 3.2	0.5
$\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}/\text{AC}$	0.085M / 2.47 g of $\text{Co}(\text{NO}_3)_2$	0.015M / 0.436 of $\text{Ni}(\text{NO}_3)_2$	0.2M / 7.5	0.8M / 3.2	0.5

Physico-chemical Characterization Of Prepared Nanophotocatalyst Materials

The crystallographic properties of activated carbon based nanophotocatalyst materials were studied by X-ray diffraction (Shimadzu XRD6000) studies. The intensity data were collected at 25°C over a 2θ range

of 5–80° with a scan rate of 10° min⁻¹. The FTIR spectra of carbon based composites were measured by FTIR spectrometer (Shimadzu IR Prestige 21) with KBr pellet method in the range from 4000 – 400 cm⁻¹ (special resolution was 4 cm and number of scans was 10). The morphology and the elemental composition of activated carbon based nanophotocatalyst materials were studied by scanning electron microscope (SEM JEOL JSM-6610) equipped with an energy dispersive X-ray (EDAX) spectrophotometer and operated at 20 kV. Absorbance spectra of the activated carbon based nanophotocatalyst materials were obtained by UV–Visible spectrophotometer (Shimadzu 1800). The samples were loaded into a quartz experimental set-up and the spectrum was recorded in the range 200–600nm using absorbance method.

Photocatalytic Experiments

The photocatalytic characteristics of the prepared photocatalysts was studied by using a simple photoreactor equipped with the visible light emitting source of 250W tungsten halogen lamp as shown in the Fig. 2. For each experiment, 5 mg of the photocatalyst was suspended in 100 ml of 1 x 10⁻⁴ M malachite green (MG) dye aqueous solution. The solution was stirred for 60minutes in the dark to ensure establishment of an adsorption / desorption equilibrium among the MG, photocatalyst and water. Then the solution was irradiated to visible light in the photoreactor. The suspension (3 ml) was collected at regular time intervals (0, 30, 60, 90 and 120 minutes) to measure the MG degradation from UV/vis absorption spectra measured at a wavelength of 612 nm. The percentage of degradation of dye [Mohamed et al. 2013] was calculated with the following formula [Equation 1]:

$$\% \text{ of degradation of dye} = (C_0 - C_t / C_0) \times 100 \quad (1)$$

Where, 'C₀' is the initial absorbance of the dye solution and 'C_t' is the absorbance at time interval, respectively.

Results And Discussions

X-Ray Diffraction studies

Figure 2 shows the XRD pattern obtained on metal aluminate-activated carbon based photocatalyst materials. Figure 2A represents the XRD pattern of activated carbon which reveals broad diffraction peaks. The lack of sharp peaks indicates the presence of amorphous structure [Wang, Lu 1997]. The broad diffraction peaks at 2θ = 24.1° and 43.8° were attributed to the (002) and (001) planes of the activated carbon. The peaks were in good accordance with the standard JCPDS data (82-1691) of activated carbon [Sulistianti, 2017].

The XRD spectrum of the NiAl₂O₄/AC nanocomposite are shown in Fig. 2B. The diffraction peaks appeared at 2θ = 19.4°, 24.1°, 37.3°, 43.6°, 43.8°, 63.1° and 65.9° which correspond to the (111), (002),

(311), (400), (001), (511) and (440) planes of NiAl_2O_4 and activated carbon. The results were in good agreement with the standard JCPDS data (10-0339)[33] for NiAl_2O_4 and (82-1691) for activated carbon.

The XRD spectrum of the $\text{Zn}_{0.80}\text{Mn}_{0.20}\text{Al}_2\text{O}_{4-\delta}$ /AC nanocomposite is shown in Fig. 2C. The diffraction peaks at $2\theta = 24.1^\circ, 31.5^\circ, 36.6^\circ, 43.8^\circ, 44.9^\circ, 56.2^\circ, 59.3^\circ$ and 65.2° corresponds to the (002), (220), (311), (001), (400), (422), (511) and (440) planes of Mn doped ZnAl_2O_4 and activated carbon. The results were in good agreement with the standard JCPDS data of ZnAl_2O_4 (82-1043) [Anchieta et al. 2015] and activated carbon (82-1691). The XRD spectrum of the $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_4$ /AC nanocomposite is displayed in Fig. 2D. The diffraction peaks found at $2\theta = 24.1^\circ, 31.5^\circ, 37.1^\circ, 43.8^\circ, 44.9^\circ, 55.8^\circ, 59.4^\circ$ and 65.4° attributed to the (002), (220), (311), (001), (400), (422), (511) and (440) planes of Ni doped CoAl_2O_4 and activated carbon. The results were in good agreement with the standard JCPDS data for CoAl_2O_4 (82-2249) [Kumari et al. 2018] and activated carbon (82-1691).

Ftir Studies

Figure 3A shows the FTIR spectrum of metal aluminate-activated carbon based photocatalyst materials. The peak found at $3350\text{--}3450\text{ cm}^{-1}$ reveals the existence of C-OH bond in the sample. The peak appeared at around 1635 cm^{-1} may be due to the C = O group in carboxylic or carbonyl functions and the large peak found at 1425 cm^{-1} can be due to carboxylic carbon [Pereira et al. 2003]. The broad peak found near 1050 cm^{-1} can be assigned to the saturated aliphatic carbon. In the FTIR spectrum of NiAl_2O_4 /AC (Fig. 3B), the presence of some new peaks indicate the existence of metal oxide groups. The peaks found at 734 cm^{-1} and 540 cm^{-1} are very significant that can be associated to the bonds of the tetrahedral and octahedral sites of the spinel [Ahangaran et al. 2013]. In Fig. 3C ($\text{Zn}_{0.80}\text{Mn}_{0.20}\text{Al}_2\text{O}_{4-\delta}$ /AC), the peaks appeared between $400\text{--}500\text{ cm}^{-1}$ may be due to the metal-oxygen (Zn-O) vibrational frequency as reported [Bouzid et al. 2009]. In Fig. 3D ($\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_4$ /AC), the bands found at $670, 560,$ and 495 cm^{-1} are ascribed to the vibration forms of M - O, Al - O, and M - O-Al in the spinel structure [Ouahdi et al. 2008; Salleh et al. 2005]. The peak found at 1618 cm^{-1} can be assigned to the H-O-H bending vibration and the band appeared at 1013 cm^{-1} may be due to the M-O-M stretching vibration [Li et al. 2020].

Sem Studies

Figure 4 shows the SEM micrographs of the metal aluminate-activated carbon based photocatalyst materials. Fig. 4 A shows the absorbent characteristics of activated carbon. These pores afforded a decent opportunity for aluminate based nanoparticles to be confined into them. Figure 4B exhibits the surface morphology of NiAl_2O_4 assisted on the activated carbon. This micrograph revealed that NiAl_2O_4 nanoparticles were accumulated into uneven pores and also irregularly dispersed on the surface of

activated carbon. Similarly the morphological images of $\text{Zn}_{0.80}\text{Mn}_{0.20}\text{Al}_2\text{O}_{4-\delta}$ and $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_4$ nanoparticles supported on activated carbon are displayed on Fig. 4C and Fig. 4D respectively.

Edax Analysis

Figures 5A, B, C and D represent the EDAX spectra obtained on activated carbon (AC), $\text{NiAl}_2\text{O}_4/\text{AC}$, $\text{Zn}_{0.80}\text{Mn}_{0.20}\text{Al}_2\text{O}_{4-\delta}/\text{AC}$ and $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_4/\text{AC}$ based nanophotocatalysts respectively. Existence of appropriate elements in appropriate levels in the samples has been confirmed based on EDAX data. The data clearly inferred that the presence of appropriate metal aluminates on the surface of activated carbon.

Uv Spectroscopic Studies

The optical properties of the as-synthesized nanophotocatalysts were investigated using UV visible technique. The UV spectrum of the prepared nanophotocatalysts are displayed in Fig. 6. In Fig. 6A, represents the absorption spectrum of activated carbon. Then by improving the surface area of the dispersion, a larger absorption in the UV spectra is anticipated [Sharif et al. 2009]. The strong absorption band in carbon materials is correlated to electronic transitions among bonding and anti-bonding π orbital [Green et al. 1991]. Usually, the $\pi - \pi^*$ transitions emerge in between 180–260 nm in activated carbon materials, as reported [Jager et al. 1999]. Figure 6B explains the UV spectra of carbon based NiAl_2O_4 composite. $\text{NiAl}_2\text{O}_4/\text{AC}$ nanophotocatalyst shows a strong peak at around 360 to 390nm, with the maximum value at 380 nm approximately. Figure 6C displays the UV spectra of $\text{Zn}_{0.80}\text{Mn}_{0.20}\text{Al}_2\text{O}_{4-\delta}/\text{AC}$ nanocomposites achieved between the wavelength range of 200 to 800 nm. The excitation wavelength of $\text{Zn}_{0.80}\text{Mn}_{0.20}\text{Al}_2\text{O}_{4-\delta}/\text{AC}$ was in the range of 340 to 370nm, with the maximum absorption around 365nm. Figure 6D shows the UV visible absorption spectra of $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}/\text{AC}$ nanocomposites. All these samples show a uniform feature, a strong and triple absorption band (540-650nm) and also a peak around 400nm is located at the visible region of the spectrum [Llugar et al. 2001].

From the UV results, we can calculate the direct band gap from Tauc plot [Cimino et al. 1971]. The Tauc equation is indicated below in Equation no. 2.

$$\alpha h\nu = A(h\nu - E_g)^n - (2)$$

where, ' α ' = absorption coefficient,

' h ' = Planck's constant,

' ν ' = photon's frequency,

' A ' = constant,

'E_g' = Band gap energy,

'n' = ½ (for direct band gap).

An extrapolation of the linear region of a plot of $(\alpha h\nu)^2$ vs $h\nu$ gave the value of the optical band gap (E_g) as shown in the Fig. 7. The band gap values were found to be 3.15, 2.21, 1.51 and 1.07eV for NiAl₂O₄/AC, Zn_{0.80}Mn_{0.20}Al₂O_{4-δ}/AC, Co_{0.85}Ni_{0.15}Al₂O_{4-δ}/AC and activated carbon respectively which are in line with the recent reported data [Karpinska, Kotowska, 2019; Somraksa et al. 2019; El Jabbar et al. 2019].

Photocatalytic Studies

The photocatalytic efficiency of activated carbon based metal aluminate nanocrystalline photocatalyst materials was examined by the removal of malachite green dye under visible light irradiation for 120 minutes. The results are shown in Fig. 8. To determine the photocatalytic activity of the prepared nanophotocatalysts on the elimination of malachite green dye under visible light, a series of experiments were carried out. The adsorption of the MG solution was carried out for 60 minutes in the absence of light to attain the adsorption - desorption equilibrium of the photocatalysts before exposing to the visible light. Blank test was performed under visible light irradiation without addition of any photocatalyst in which the removal of MG dye is very less. From Fig. 8, it was revealed that the photocatalytic activity enhances with the addition of carbon amount. The activated carbon based composites shows greater efficiency in degrading the malachite green dye than the metal aluminate based nanoparticles alone [Arunkumar, Nesaraj 2020; Arunkumar, Nesaraj 2021]. The carbon based photocatalyst absorbs large photons, creating large electron-hole pairs in the carbon based photocatalyst surface, which enhances the hydroxyl ions liberation and correspondingly enhances the degradation process [Ahmed et al. 2011]. This is because of the fact that activated carbon has larger surface area and also increases the adsorption sites and active centers [Li et al. 2012]. The best photocatalytic activity was observed in Co_{0.85}Ni_{0.15}Al₂O_{4-δ} /AC (0.50g) photocatalyst, which degraded all the MG dye present in the solution within 90 minutes of visible light irradiation.

In Fig. 9, the first order rate constant of carbon based composites was presented. A plot drawn between $\ln C_t/C_0$ against time is shown in Fig. 9. The slope of the straight line gave the value of first order rate constant, k. The photocatalytic reaction obeys pseudo first order reaction mechanism explained by Langmuire and Hinshelwood kinetic model [Pan, Liu, 2012].

$$\ln C_t/C_0 = -kt \quad (3)$$

Where 'C₀' is the initial concentration, 'C_t' is the concentration after time t, and k is the first order rate constant. The rate constant values were found to be 0.0199 min⁻¹ (NiAl₂O₄/AC), 0.0196 min⁻¹ (Zn_{0.80}Mn_{0.20}Al₂O_{4-δ} /AC), 0.0278 Co_{0.85}Ni_{0.15}Al₂O_{4-δ} /AC) and 0.0085 min⁻¹ (AC).

The efficient photocatalyst ($\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}$ /AC) has been employed to investigate its reusability performance. Reusability of the photocatalyst is one of the significant requirement of any photocatalyzed reaction, but very few tests are reported so far on reusability investigations [Sridewi et al. 2011; Markovic et al. 2013]. The degradation time for every recycling process has been set to 2 hours. After 2 hours of photocatalytic degradation, the photocatalysts were removed from the photoreactor, filtered off, dried in an oven at 80 °C for 2 hours and calcined at 600 °C for 2 hours to eliminate any kind of impurities. The reusability characteristics of $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}$ /AC after 4 recycles are presented in Fig. 10. As the cycle enhances, the degradation efficiencies are going downward slowly from the first time (100%) to the fourth time (84%). This may be due to the reduction of active centers of the photocatalysts after recycling process. These results show that $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}$ /AC photocatalyst has outstanding photocatalytic properties as well as an admirable recycling characteristics under visible light. The reusability performance of $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}$ /AC on the degradation of malachite green under visible irradiation is reported in Fig. 10.

The photocatalysts with lower band gap exhibits better photocatalytic efficiency. Because electrons in the valence bands could easily excited to conduction bands, holes (h^+) were remain in the valence bands. Then the photoexcited electrons reacted with adsorbed O_2 and the holes reacted with H_2O at the surface of the photocatalysts to generate superoxide ($\bullet\text{O}_2^-$) radicals and hydroxyl ($\text{OH}\bullet$) radicals, respectively. The above reactive species ($\bullet\text{O}_2^-$, $\text{OH}\bullet$ and h^+) were the reason for the degradation of MG in solution [Somraksa et al. 2020]. From the results, it was understand that the photocatalysts with the highest carbon concentration, displays better photocatalytic activity than the other samples. The photocatalytic mechanism suggested for the degradation of MG dye present in water sample with carbon based composites in presence of visible light can be indicated as shown in Equations 3–7 [Wilhelm, Stephen, 2007; Mills et al. 1993].

Step 1. $\text{AAC composite} + h\nu \rightarrow \text{AAC composite} (e^- + h^+) - (3)$

Step 2. $e^- + \text{O}_2 \rightarrow \bullet\text{O}_2^- - (4)$

Step 3. $2e^- + \text{O}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 - (5)$

Step 4. $\text{H}_2\text{O}_2 + \bullet\text{O}_2^- \rightarrow \text{OH}^- + \text{OH}\bullet - (6)$

Step 5. $\text{OH}\bullet / h^+ / \bullet\text{O}_2^- + \text{MG} \rightarrow \text{Degraded product} - (7)$

Conclusion

Metal aluminate - activated carbon (MAAC) based composites have been synthesized by wet chemical method. Powder XRD studies reveals the presence of cubic structure. The FTIR studies assured the existence M-O bond, C-O bond, C = C (aromatic) stretching vibration in the MAAC samples. EDAX results revealed that the presence of appropriate elements in the samples. Solid UV analysis explains the

maximum absorbance value of the samples. The photocatalytic efficiency of the carbon based composites is reported to be good when compared with the reported data on metal aluminate photocatalysts. The best photocatalytic activity was observed in $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}$ /AC photocatalyst, which degraded all the MG dye present in the solution within 90 minutes of visible light irradiation. Also the reusability photocatalytic characteristics of $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}$ /AC is found to be excellent.

Declarations

Acknowledgements

ASN thanks Karunya Institute of Technology and Sciences (KITS) for promoting nanomaterials chemistry based research activity in the Department of Applied Chemistry. MAK and CFC thank KITS for providing necessary research facilities to carry out this research work.

-Ethical Approval – Not applicable

-Consent to Participate – Yes

-Consent to Publish – Yes

-Authors Contributions – Manasai Arunkumar – Resources, design of work, investigation Writing – review & editing; Arputharaj Samson Nesaraj – Conceptualization, Methodology, design of work, writing - original draft; Clementz Edwardraj Freeda Christy – the acquisition, analysis and Chinnappan Joseph Kennady – Interpretation of data.

-Funding – No funding received

-Competing Interests – The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

-Availability of data and materials – Yes. Available

References

1. Ahangaran F, Hassanzadeh A, Nouri S (2013) Surface modification of $\text{Fe}_3\text{O}_4@\text{SiO}_2$ microsphere by silane coupling agent. *Int Nano Lett* 3 (2013) 23. <https://doi.org/10.1186/2228-5326-3-23>
2. Ahmed S, Rasul M G, Martens W N, Brown R, Hashib M.A (2011) Advances in heterogeneous photocatalytic degradation of phenols and dyes in wastewater: A review. *Water Air Soil Pollut* 215: 3-29. <https://doi.org/10.1007/s11270-010-0456-3>
3. Anchietta C G, Tochetto L, Madalosso H B, Sulkovski R D, Serpa C, Mazutti M A, De Almeida A R F, Giindel A, Foletto E L (2015) Effect of thermal treatment on the synthesis of NiAl_2O_4 spinel oxide

using chitosan as precursor. *Cerâmica* 61:477–481. <http://dx.doi.org/10.1590/0366-69132015613601925>

4. Arunkumar M, Samson Nesaraj A (2020) Photocatalytic degradation of malachite green dye using NiAl_2O_4 and Co doped NiAl_2O_4 nanophotocatalysts prepared by simple one pot wet chemical synthetic route. *Iran J Catal* 10(3): 235-245
5. Arunkumar M, Samson Nesaraj A (2021) Facile chemical fabrication of Ni doped CoAl_2O_4 nano-spinel photocatalysts: Physico-chemical properties and photodegradation of toxic malachite green dye under visible light. *Int J Environ Anal Chem*. <https://doi.org/10.1080/03067319.2020.1867722>
6. Al-Anber ZA, Al-Anber MA, Matouq M, Al-Ayed O, Omari NM (2011) Defatted Jojoba for the removal of methylene blue from aqueous solution: Thermodynamic and kinetic studies. *Desalination* 276: 169 – 174. <https://doi.org/10.1016/j.desal.2011.03.043>
7. Bouzid K, Djelloul A, Bouzid N, Bougdira J (2009) Electrical resistivity and photoluminescence of zinc oxide films prepared by ultrasonic spray pyrolysis. *Phys Status Solidi a* 206 (1): 106-115. <https://doi.org/10.1002/pssa.200824403>
8. Briche S, Derqaoui M, Belaiche M, Mouchtari E M E, Wong-Wah-Chung P, Rafqah S (2020) Nanocomposite material from TiO_2 and activated carbon for the removal of pharmaceutical product sulfamethazine by combined adsorption/photocatalysis in aqueous media. *Environ Sci Pollut Res Int* 27(20): 25523-25534. <https://doi.org/10.1007/s11356-020-08939-2>
9. Cimino A, Lo Jacono M, Schiavello M (1971) Structural, magnetic, and optical properties of nickel oxide supported on .eta.- and .gamma.-aluminas. *J Phys Chem* 75(8):1044–1050. <https://doi.org/10.1021/j100678a005>
10. Coromelci-Pastravanu C, Ignat M, Popovici E, Harabagiu V (2014) TiO_2 -coated mesoporous carbon: Conventional vs. microwave-annealing process. *J Hazard Mater* 278: 382-390.
11. Deraz NM, Fouda MMG (2013) Fabrication and magnetic properties of cobalt-copper nano-composite. *Int J Electrochem Sci* 8: 2682–2690.
12. Dickhout JM, J. Moreno J, Biesheuvel PM, Boels L, Lammertink RGH, de Vos VM (2017) Produced water treatment by membranes: A review from a colloidal perspective. *J. Colloid Interface Sci* 487: 523-534. <https://doi.org/10.1016/j.jcis.2016.10.013>
13. Djellabi R, Yang B, Wang Y, Cui X, Zhao X (2019) Carbonaceous biomass-titania composites with Ti-O-C bonding bridge for efficient photocatalytic reduction of Cr(VI) under narrow visible light. *Chem Eng J* 366: 172-180. <https://doi.org/10.1016/j.cej.2019.02.035>
14. Esmaili H, Kotobi A, Sheibani S, Rashchi F (2018) Photocatalytic degradation of methylene blue by nanostructured Fe/FeS powder under visible light. *Int J Miner Metall Mater* 25(2): 244-252. <https://doi.org/10.1007/s12613-018-1567-x>
15. El Jabbar Y, El Hafdi M, Benchikhi M, El Ouati R, Er-Rakho L, Essadki A (2019) Photocatalytic degradation of navy blue textile dye by nanoscale cobalt aluminate prepared by polymeric precursor method. *Environ. Nanotechnol Monit Manag* **12: 100259**. <https://doi.org/10.1016/j.enmm.2019.100259>

16. Gallego-Urrea JA, Hammes J, Cornelis G, Hassellöv M (2016) Coagulation and sedimentation of gold nanoparticles and illite in model natural waters: Influence of initial particle concentration. *NanoImpact* 3-4: 67-74. <https://doi.org/10.1016/j.impact.2016.10.004>
17. Gnanam S, Rajendran V (2018) Facile sol-gel preparation of Cd-doped cerium oxide (CeO₂) nanoparticles and their photocatalytic activities. *J Alloys Compd* 735: 1854-1862. <https://doi.org/10.1016/j.jallcom.2017.11.330>
18. Green D C, McKenzie D R, Lukins P B (1991) The microstructure of Carbon thin films. *Mater Science Forum* 52-53:103-124. <https://doi.org/10.4028/www.scientific.net/MSF.52-53.103>
19. Jager C, Henning T H, Schlögl R, Spillecke O (1999) Spectral properties of carbon black. *J Non Cryst Solids* 258 (1-3):161-179. [https://doi.org/10.1016/S0022-3093\(99\)00436-6](https://doi.org/10.1016/S0022-3093(99)00436-6)
20. Huang H, Wang Y, Jiao W, Cai F, Shen M, Zhou S, Cao H, Lü J, **Cao R (2018)**, Lotus-leaf-derived activated-carbon-supported nano-cds as energy-efficient photocatalysts under visible irradiation. *ACS Sustainable Chem Eng* 6(6): 7871 – 7879. <https://doi.org/10.1021/acssuschemeng.8b01021>
21. Karpinska J, Kotowska U (2019) Removal of organic pollution in water environment. *Water* 11(10):2017. <https://doi.org/10.3390/w11102017>
22. Konstantinou IK, Albanis TA (2004) TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations: A review. *Appl Catal B* 49(1): 1-14. <https://doi.org/10.1016/j.apcatb.2003.11.010>
23. Kumari P, Dwivedi Y, Bahadur A (2018) Analysis of bright red-orange emitting Mn²⁺: ZnAl₂O₄ spinel nanophosphor. *Optik* 154:126-132. <https://doi.org/10.1016/j.ijleo.2017.10.023>
24. Li Y, Feng X, Lu Z, Yin H, Liu F, Xiang Q (2018) Enhanced photocatalytic H₂-production activity of C-dots modified g-C₃N₄/TiO₂ nanosheets composites. *J Colloid Interface Sci* 513: 866–876. <https://doi.org/10.1016/j.jcis.2017.12.002>
25. Li X, Bai J, Li J, Li C, Zhong X, Deng S (2020) The effect of n-π* electronic transitions on the N₂ photofixation ability of carbon self-doped honeycomb-like g-C₃N₄ prepared *via* microwave treatment, *RSC Adv* 10:7019-7025. <https://doi.org/10.1039/D0RA00101E>
26. Li L, Li X, Lee J Y, Keener T C, Liu Z, Yao X (2012) The effect of surface properties in activated carbon on mercury adsorption. *Ind Eng Chem Res* 51(26):9136–9144. <https://doi.org/10.1021/ie2028156>
27. Llusar M, Fores A, Badenes J A (2001) Colour analysis of some cobalt-based blue pigments. *J Eur Ceram Soc* 21(8):1121–1130. [https://doi.org/10.1016/S0955-2219\(00\)00295-8](https://doi.org/10.1016/S0955-2219(00)00295-8)
28. Markovic D, Jokic B, Saponjic Z, Potkonjak B, Jovancic P, Radetic M (2013) Photocatalytic degradation of dye C.I. direct blue 78 using TiO₂ nanoparticles immobilized on recycled wool-based nonwoven material. *CLEAN—Soil, Air, Water* 41 (10):1002–1009. <https://doi.org/10.1002/clen.201200413>
29. Mills A, Davies R H, Worsley D (1993) Water purification by semiconductor photocatalysis. *Chem Soc Rev* 22:417-425. <https://doi.org/10.1039/CS9932200417>

30. Mohamed R M, Baeissa E S, Mkhallid I A and Al-Rayyani M A (2013) Optimization of preparation conditions of ZnO–SiO₂ xerogel by sol–gel technique for photodegradation of methylene blue dye. *Appl Nanosci.* 3: 57-63. <https://doi.org/10.1007/s13204-012-0074-z>
31. Mathur S, Veith M, Haas M, Shen H, Lecerf N, Huch V, Hufner S, Haberkorn R, Beck HP, Jilavi M (2004) Single-source sol-gel synthesis of nanocrystalline ZnAl₂O₄: Structural and optical properties. *J Am Ceram Soc* 84(9): 1921-1928. <https://doi.org/10.1111/j.1151-2916.2001.tb00938.x>
32. Mehdi T (2017) Selective adsorption and photocatalytic degradation of dyes using polyoxometalate hybrid supported on magnetic activated carbon nanoparticles under sunlight, visible, and UV irradiation. *Int J Photoenergy* Article ID: 8575096. <https://doi.org/10.1155/2017/8575096>
33. Mestre A S, Carvalho A P (2019), Photocatalytic degradation of pharmaceuticals carbamazepine, diclofenac, and sulfamethoxazole by semiconductor and carbon materials: a review. *Molecules* 24(20): 3702. <https://doi.org/10.3390/molecules24203702>
34. Nethaji S, Tamilarasan G, Neehar P, Sivasamy A (2018) Visible light photocatalytic activities of BiOBr-activated carbon (derived from waste polyurethane) composites by hydrothermal process. *J Environ Chem Eng* 6(3):3735–3744. <https://doi.org/10.1016/j.jece.2017.02.037>
35. Ouahdi N, Guillemet S, Durand B, El Ouati R, Rakho L E, Moussa R, Samdi A (2008) Synthesis of CoAl₂O₄ by double decomposition reaction between LiAlO₂ and molten KCoCl₃. *J Eur Ceram Soc* 28 (10): 1987–1994. <https://doi.org/10.1016/j.jeurceramsoc.2007.12.035>
36. Pan S, Liu X (2012) CdS–Graphene nanocomposite: synthesis, adsorption kinetics and high photocatalytic performance under visible light irradiation. *New J. Chem.* 36(9): 1781 – 1787. <https://doi.org/10.1039/C2NJ40301C>
37. Pereira M F R, Soares S F, Orfao J J M, Figueiredo J L (2003) Adsorption of dyes on activated carbons: influence of surface chemical groups. *Carbon* 41:811–821. [https://doi.org/10.1016/S0008-6223\(02\)00406-2](https://doi.org/10.1016/S0008-6223(02)00406-2)
38. Puma G L, Bono A, Krishnaiah D, Collin J G (2008) Preparation of titanium dioxide photocatalyst loaded onto activated carbon support using chemical vapor deposition: a review paper. *J Hazard Mater* 157(2-3): 209–219. <https://doi.org/10.1016/j.jhazmat.2008.01.040>
39. Salleh N F M, Jalil A A, Triwahyono S, Efendi J, Mukti R R, Hameed B H (2015) New Insight into electrochemical-induced synthesis of NiAl₂O₄/Al₂O₃: Synergistic effect of surface hydroxyl groups and magnetism for enhanced adsorptivity of Pd(II). *Appl Surf Sci* 349 (2015) 485–495. <https://doi.org/10.1016/j.apsusc.2015.05.048>
40. Sampath SK, Cordaro JF (2005) Optical properties of zinc aluminate, zinc gallate, and zinc aluminogallate spinels *J Am Ceram Soc* 81(3): 649-654.
41. Sharif S H, Golestani-Fard F, Khatibi E, Sarpoolaky H (2009) Dispersion and stability of carbon black nanoparticles, studied by ultraviolet–visible spectroscopy. *J Taiwan Inst Chem Eng* 40(5):524–527. <https://doi.org/10.1016/j.jtice.2009.03.006>

42. Song L, Guo C, Li T, Zhang S (2017) C₆₀/graphene/g-C₃N₄ composite photocatalyst and mutually-reinforcing synergy to improve hydrogen production in splitting water under visible light radiation. *Ceram Int* 43(10): 7901–7907. <https://doi.org/10.1016/j.ceramint.2017.03.115>
43. Somraksa W, Suwanboon S, Amornpitoksuk P (2019) Enhanced visible-light driven photocatalytic property of g-C₃N₄/ZnAl₂O₄ nanocomposites. *J Phys Conf Ser* 1380: 012021. <https://doi.org/10.1088/1742-6596/1380/1/012021>
44. Somraksa W, Suwanboon S, Amornpitoksuk P, Randorn C (2020) Physical and photocatalytic properties of CeO₂/ZnO/ZnAl₂O₄ ternary nanocomposite prepared by co-precipitation method. *Mater Res* 23(1):e20190627. <https://doi.org/10.1590/1980-5373-MR-2019-0627>
45. Sridewi N, Tan L T, Sudesh K (2011) Solar photocatalytic decolorization and detoxification of industrial batik dye wastewater using P(3HB)-TiO₂ nanocomposite films. *CLEAN—Soil, Air, Water* 39 (3): 265–273. <https://doi.org/10.1002/clen.201000344>
46. Sulistianti I, Krisnandi Y K, Moenandar I (2017) Study of CO₂ adsorption capacity of mesoporous carbon and activated carbon modified by triethylenetetramine (TETA). *IOP Conf Ser: Mater Sci Eng* 188: 012041. <https://doi.org/10.1088/1757-899X/188/1/012041>
47. Vacca A, Mais L, Mascia M, Usai EM, Palmas S (2020) Design of experiment for the optimization of pesticide removal from wastewater by photo-electrochemical oxidation with TiO₂ nanotubes. *Catalysts* 10:512. <https://doi.org/10.3390/catal10050512>
48. Velasco L F, Parra J B, Ania C O (2010) Role of activated carbon features on the photocatalytic degradation of phenol. *Appl Surf Sci*, 256: 5254–5258. <https://doi.org/10.1016/j.apsusc.2009.12.113>
49. Velasco L F, Fonseca I M, Parra J B, Lima J C, Ania C O (2012) Photochemical behaviour of activated carbons under UV irradiation. *Carbon* 50(1):249–258. <https://doi.org/10.1016/j.carbon.2011.08.042>
50. Velasco L F, Carmona R J, Matos J and Ania C O (2014) Performance of activated carbons in consecutive phenol photooxidation cycles. *Carbon* 73 (2014) 206–215. <https://doi.org/10.1016/j.carbon.2014.02.056>
51. Velo-Inmaculada G, López-Jesús J, Sanchez-Polo M, Rivera-Utrilla J (2013) Activated carbon as photocatalyst of reactions in aqueous phase. *Appl Catal B* 142-143: 694-704. <https://doi.org/10.1016/j.apcatb.2013.06.003>
52. Wang S B, Lu G Q (1997) Effects of oxide promoters on metal dispersion and metal-support interactions in ni catalysts supported on activated carbon. *Ind Eng Chem Res.* 36(12):5103-5109. <https://doi.org/10.1021/ie9703604>
53. Wilhelm P, Stephen D (2007) Photodegradation of rhodamine B in aqueous solution via SiO₂@TiO₂ nano-spheres. *J Photochem Photobiol A* 185 (1):19-25. <https://doi.org/10.1016/j.jphotochem.2006.05.003>
54. Ye A, Fan W, Zhang Q, Deng W, Wang Y (2012) CdS–graphene and CdS–CNT nanocomposites as visible-light photocatalysts for hydrogen evolution and organic dye degradation. *Catal Sci*

Technol 2(5): 969–978. <https://doi.org/10.1039/C2CY20027A>

55. Yu H, Zhao Y, Zhou C, Shang L, Peng Y, Cao Y, Wu L Z, Tung C H, Zhang T (2014) Carbon quantum dots/TiO₂ composites for efficient photocatalytic hydrogen evolution. *J Mater Chem A*, 2 (10): 3344–3351. <https://doi.org/10.1039/C3TA14108Jv>
56. Yu W, Xu D and Peng T (2015) Enhanced photocatalytic activity of g-C₃N₄ for selective CO₂ reduction to CH₃OH via facile coupling of ZnO: a direct Z-scheme mechanism. *J Mater Chem A*, 3 (39): 19936–19947. <https://doi.org/10.1039/C5TA05503B>
57. Zhang Y, Liu Y, Gao W, Chen P, Cui H, Fan Y (2019) MoS₂ nanosheets assembled on three-way nitrogen-doped carbon tubes for photocatalytic water splitting. *Front Chem* 7: 325. <https://doi.org/10.3389/fchem.2019.00325>
58. Zhang S, Gu P, Ma R, Luo C, Wen T, Zhao G, Cheng W, Wang X (2019) Recent developments in fabrication and structure regulation of visible-light-driven g-C₃N₄-based photocatalysts towards water purification: a critical review. *Catal. Today* 335:65–77. <https://doi.org/10.1016/j.cattod.2018.09.013>

Figures

Figure 1

Photocatalytic set up used in this study

Figure 2

XRD pattern obtained on (A) Activated Carbon, (B) $\text{NiAl}_2\text{O}_4 / \text{AC}$ (0.50g), (C) $\text{Zn}_{0.80}\text{Mn}_{0.20}\text{Al}_2\text{O}_{4-\delta} / \text{AC}$ (0.50g), (D) $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta} / \text{AC}$ (0.50g) photocatalyst materials

Figure 3

FTIR spectrum obtained on (A) Activated Carbon, (B) NiAl₂O₄ /AC, (C) Zn_{0.80}Mn_{0.20}Al₂O_{4-δ} /AC, (D) Co_{0.85}Ni_{0.15}Al₂O_{4-δ} /AC photocatalyst materials

(A)

(B)

(C)

(D)

Figure 4

SEM photographs obtained on (A) Activated Carbon, (B) NiAl_2O_4 / AC, (C) $\text{Zn}_{0.80}\text{Mn}_{0.20}\text{Al}_2\text{O}_{4-\delta}$ / AC, (D) $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}$ / AC photocatalyst materials

(A)

(B)

(C)

(D)

Figure 5

EDAX spectra obtained on (A) Activated Carbon, (B) NiAl_2O_4 / AC, (C) $\text{Zn}_{0.80}\text{Mn}_{0.20}\text{Al}_2\text{O}_{4-\delta}$ / AC, (D) $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}$ / AC photocatalyst materials

(A)

(B)

(C)

(D)

Figure 6

UV visible spectrum obtained on (A) Activated Carbon, (B) NiAl_2O_4 / AC, (C) $\text{Zn}_{0.80}\text{Mn}_{0.20}\text{Al}_2\text{O}_{4-\delta}$ / AC, (D) $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_{4-\delta}$ / AC photocatalyst materials

Figure 7

Band gap plot obtained on (A) activated carbon (B) NiAl₂O₄/AC, (C) Zn_{0.80}Mn_{0.20}Al₂O_{4-δ} /AC and (D) Co_{0.85}Ni_{0.15}Al₂O_{4-δ} /AC photocatalyst materials

Figure 8

Degradation spectrum of MG dye in presence of (A) activated carbon only, (B) NiAl₂O₄/AC, (C) Zn_{0.80}Mn_{0.20}Al₂O_{4-δ} /AC, (D) Co_{0.85}Ni_{0.15}Al₂O_{4-δ} /AC and (MG) Malachite Green Dye alone (without any photo catalyst)

Figure 9

First-order kinetic plot of MG dye using (A) Activated Carbon only, (B) NiAl₂O₄/AC, (C) Zn_{0.80}Mn_{0.20}Al₂O_{4-δ} /AC, (D) Co_{0.85}Ni_{0.15}Al₂O_{4-δ} /AC photocatalyst materials

Figure 10

Reusability performance of $\text{Co}_{0.85}\text{Ni}_{0.15}\text{Al}_2\text{O}_4$ / AC on the degradation of malachite green under visible irradiation