Tuning the structural, optical, and photocatalytic properties of V 2 O 5 /PMMA nanocomposite films for methylene blue photodegradation

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Abstract

In this work, the Poly (methyl methacrylate) (PMMA) films have been developed for the photodegradation of methylene blue (MB) by incorporating vanadium pentaoxide ($V_2O_5$) catalysts. The obtained films were characterized by SEM, XRD, UV-Vis, FTIR and Raman spectroscopy. The XRD patterns revealed the amorphous domains of the PMMA polymer, with an increase in these domains with increasing the $V_2O_5$ content. Moreover, the XRD showed shifts of $2\theta$ from 16.55° to 17.8°, which can be attributed to the structural irregularity of the PMMA backbone chain caused by the nanofiller doping with no impurity peaks. The observed SEM images showed that $V_2O_5$ has a hierarchical nanobelt interconnected structure with thicknesses of 30–150 nm and 50–300 nm in length. According to UV-Vis spectroscopy measurements, the absorbance shifts towards a longer wavelength (270–330 nm) and exhibits intensity increase as $V_2O_5$ nanoparticles amount increase. The band gap of PMMA was decreased after the incorporation of $V_2O_5$ NPs. The optical conductivity $\sigma_{op}$ exhibits an increase in the photon energy window (3.8 eV-4.2 eV) by values ($2\times10^{11} - 7\times10^{11}$) as the $V_2O_5$ nanoparticles ratio content increases. Interestingly, the 3.3 wt% $V_2O_5$/PMMA photocatalyst film exhibited the highest photocatalytic degradation of MB (97%) after 45 minutes of UV illumination.

1 Introduction

Pollution of water by toxic pollutants such as industrial dyes or pesticides has become a major driver of environmental degradation across the globe. The release of widespread industrial contaminants and wastewater containing synthetic organic dyes into land and aquatic ecosystems has resulted in severe contamination in many regions worldwide. During textile manufacturing processes, it is estimated that 1–20% of total annual dye production is lost and discharged as effluent. These coloring agents can have disastrous impacts on environmental and human health. Many common dyes are not biodegradable, meaning they persist in ecosystems. Additionally, hazardous metabolites can form when organic dyes undergo reactions like oxidation, hydrolysis, photolysis, or biotransformation in wastewater mediums. The accumulation of stable original dye compounds and dangerous daughter products makes wastewater dye pollution an urgent issue needing innovative treatment solutions. Implementing effective technologies to remove dyes from industrial discharge could help mitigate freshwater contamination and improve the health of ecosystems and communities dependent on access to clean water resources (Menazea et al. 2020) (Fayek and Khalafallah 2023) (Houas et al. 2001). The limited availability of freshwater globally makes wastewater reuse and recycling increasingly critical. Though over 70% of the Earth's surface is covered in water, less than 1% consists of readily accessible freshwater sources suitable for human use (UN Water, 2022). Meanwhile, global freshwater utilization has been growing at over twice the rate of population increase, with total water demand projected to rise by 20–30% above current levels by 2050 (WWAP, 2021). This surging freshwater demand, paired with widespread pollution from sewage, industrial, and agricultural sources, is creating severe water stress in many parts of the world (UNESCO, 2022). Effective wastewater treatment and reuse strategies are essential to supplement freshwater availability while reducing detrimental discharges. (Takeuchi and Tanaka 2020) Water, U.N. "UN World Water Development Report 2020." United Nation: New York, NY, USA (2020).

Methylene blue (MB), a cationic thiazine dye, is commonly used for coloring textiles and substrates like cotton, wood, and silk. However, this useful dye can have detrimental health and environmental impacts due to its high-water solubility. When released into aquatic systems through textile effluent discharges, methylene blue can persist and accumulate due to its stable aromatic molecular structure. This dye is toxic to many organisms, mutagenic in human cell studies, and potentially carcinogenic with chronic exposures. Specifically, methylene blue is thought to lead to neurological disorders in humans by inducing oxidative stress in the central nervous system. Additionally, textile mill
Effluents containing methylene blue have highly colored discharge, high salinity, and elevated biological and chemical oxygen demand. This makes effective wastewater treatment essential prior to release into the environment. Overall, removing methylene blue from industrial effluents is critical for protecting environmental and public health by reducing contamination of freshwater resources and preventing human exposure to this hazardous dye compound and its degradation byproducts. Implementing improved treatment solutions can help mitigate the adverse impacts of this widely used textile dye (Tsade Kara et al. 2021)(Bayomie et al. 2020)(Alswat et al. 2016). So, many researchers are working to discover effective techniques for eliminating these pollutants. Coagulation, chemical oxidation, adsorption, and photodegradation are some of the strategies utilized to treat wastewater (Han et al. 2009)(Qu et al. 2013).

Photodegradation of pollutants has become the most promising approach in water treatment due to its effectiveness and relatively low cost (Zedan et al. 2022a). Besides, it is considered a non-conventional sustainable method that utilizes renewable solar energy for environmental and economic concerns (Zedan et al. 2022b)(Kumar et al. 2018). Of particular interest, semiconductor-based-photocatalysis has gained considerable interdisciplinary attention as an eco-friendly and economical technology in various environmental applications. It can offer an exceptional performance toward a variety of water pollutants degradation (Zedan et al. 2022b)(Li et al. 2017)(Luo et al. 2019).

The difficulty of separating the catalyst for reuse is a key disadvantage in the case of employing it in the powdered form for the wastewater treatment processes. As a result, using membrane/film technology to solve this problem is a viable option. This technology is thought to be the most effective way to alleviate water scarcity by supplying high-quality fresh water to a large number of people. This system has numerous benefits over traditional water treatment techniques, including cheap operating costs, reliability, high separation efficiency, simplicity, and environmental friendliness. As a result, waste treatment, the dyestuff industry, and food manufacturing have all used this technology (Kadhim et al. 2020). In this aspect, the advancement of this technology relies heavily on the discovery of innovative materials. Over the last two decades, new research has concentrated on developing synthetic membranes/films with enhanced characteristics for various water treatment applications. Furthermore, problems to improve membrane long-term stability, durability, and cost efficiency have been identified. Various ideas using organic (polymers) or inorganic materials were developed for this purpose (García et al. 2021)(Kim and Van Der Bruggen 2010)(Nguyen et al. 2012).

Poly(methyl methacrylate) (PMMA) has unique mechanical and chemical-physical properties (Ajibade and Mbese 2014). The polymer's selection depends on its magnetic, mechanical, optical, and thermal characteristics. Other properties, such as chemical stability and functionalities, hydrophilic/hydrophobic, and biocompatibility properties, were considered during the composite formation (Jeon and Baek 2010). It has -COOCH₃ group, 1.6 Debye dipole moment, and 3.4 dielectrics (Morsi and Abdelghany 2017)(Sheng et al. 2017). It can be utilized in many technological and productive areas (Kondawar et al. 2011). Some disadvantages have reduced global use to PMMA, such as the insufficiency of UV-light filters and thermal sensitivity. Still, incorporating some semiconductors may overcome some drawbacks (Ummartyotin et al. 2012). Developing effective, low-cost water treatment techniques is essential to human health (Hussien et al. 2020a). Heterogeneous photocatalysis is popular using semiconductor catalysts such as ZnS, ZnO, Fe₂O₃, TiO₂, PbS, and CdS. Polymeric nanocomposites have a combination of characteristics of nanomaterials with polymer properties, such as high durability, flexible nature, chemical resistance, low density, mechanical stability, ease of availability, and low cost (Hafizah et al. 2013). PMMA is a widely suitable material with thermoplastic features for water contact (Motaung et al. 2012). Photocatalytic oxidation technology is a practical, low-cost strategy for the degradation of the contaminants in wastewater; it takes less time than traditional
Vanadium is one of the amplest transition metals in the earth's crust. It has several valences from $2^+$ to $5^+$, developing different oxides such as $\text{VO}$, $\text{VO}_2$, $\text{V}_2\text{O}_5$, and $\text{V}_2\text{O}_6$ (Nihoul et al. 1999). Among these oxides, $\text{V}_2\text{O}_5$, known as vanadium pentoxide, is the most stable one through possessing the highest oxidation state ($5^+$) and has a layered structure (Wang et al. 2021). To date, numerous researchers have developed $\text{V}_2\text{O}_5$ based compounds for diverse applications. Jayaraj et al. (Armaković et al. 2023) showed that $\text{V}_2\text{O}_5$ has antibacterial activity against Staphylococcus aureus and Escherichia coli bacteria (Rong et al. 2016), Sreedhar et al. (Sreedhar et al. 2020) reported the photoelectrochemical water splitting and NO$_2$ sensing properties of $\text{V}_2\text{O}_5/\text{ZnO}$ and $\text{V}_2\text{O}_5/\text{Co–ZnO}$ films. Sribala et al. (Sribala et al. 2021) have modified polyimide with $\text{V}_2\text{O}_5$ to reduce nitro phenol, Cr (VI), and rhodamine 6G dye. Dong et al. (Dong et al. 2012) sensitized N-doped TiO$_2$ with various amounts of $\text{V}_2\text{O}_5$ for the photodegradation of toluene. $\text{V}_2\text{O}_5$ was used for photocatalytic degradation of organic dyes such as Rhodamine 6G (Rh-6G), methylene blue (MB), and methyl orange (MO) (Armaković et al. 2023). Wang et al. (Wang et al. 2011) prepared TiO$_2/\text{V}_2\text{O}_5$ for photodecomposition Rhodamine B (RhB) dye because $\text{V}_2\text{O}_5$ is an n-type semiconductor with narrow bandgap ($2.3$ – $2.8 \text{ eV}$), non-toxic, unique surface characteristics, photostability, good chemical stability, excellent optical and light absorption properties (Armaković et al. 2023)(Dong et al. 2012)(Wang et al. 2011). However, such substantial efforts, developing $\text{V}_2\text{O}_5$-based films to remove organic contaminants through simple adsorption or photodegradation, are seldom presented. A series of composite films with various amounts of sol-gel prepared $\text{V}_2\text{O}_5$ (0, 0.03, 0.16, 0.32, 1.7, and 3.3 wt%) and a polymer-making material were synthesized. Designing polymeric composite films based on $\text{V}_2\text{O}_5$ allows a more effortless recycling procedure. The introduction of $\text{V}_2\text{O}_5$ changed the surface morphology of pure polymer film from dense to a honeycomb-like structure with enhanced thermostability (Ali and Ismail 2022). The reason for that could be the layer structure of $\text{V}_2\text{O}_5$, excellent filling action of $\text{V}_2\text{O}_5$, good compatibility, and homogenous distribution of $\text{V}_2\text{O}_5$ into the polymer matrix. The composite films acquire a dual functionality: (1) Enhanced dye adsorption properties, which are deliberated through removing MB dye as a model of wastewater contaminant, and (2) A visible light active material for photocatalytic processes, as revealed from optical properties studies. These characteristics prove their potential applications in wastewater treatment. The influence of different photocatalytic parameters on decolorization efficiency was deeply studied. Various optical models and kinetics were used to investigate the degradation mechanism.

To the best of our knowledge, the photocatalytic degradation of water pollutants over x wt% $\text{V}_2\text{O}_5$/PMMA which synthesized using casting method has not been reported. In this work, a comprehensive study of the photocatalytic activity of different weight percentages of $\text{V}_2\text{O}_5$ doped onto PMMA was studied. $\text{V}_2\text{O}_5$ prepared via the combustion method, and calcined at 550°C. A series of x wt% $\text{V}_2\text{O}_5$/PMMA photocatalysts were fabricated using casting method. The prepared $\text{V}_2\text{O}_5$/PMMA films were fully characterized using several standards analytical and characterization techniques, including X-ray diffraction (XRD), electron scanning microscopy (SEM), FTIR, and UV-VIS spectrophotometer. The photocatalytic performance of a photocatalyst toward the removal of water pollutants is crucial for its practical application in large-scale environmental remediation. In this regard, the UV-C light-assisted photodegradation ability of the prepared materials was investigated toward water pollutants, MB. A mechanism for the photodegradation of water pollutants over the $\text{V}_2\text{O}_5$/PMMA has been proposed. The photostability and recyclability of the $\text{V}_2\text{O}_5$/PMMA films have been also studied.

2 Methodologies
2.1 Sample preparation

2.1.1 Materials

Poly (methyl methacrylate), PMMA, with an average molecular weight 400,000 g/mole purchased from Sigma-Aldrich. PMMA was used without any further purification. Ammonium metavanadate (NH₄VO₃, 99%) was obtained from Sigma-Aldrich.

2.1.2 Preparation of vanadium oxidenanoparticles

V₂O₅ was prepared via the combustion method. 5gm. of (NH₄VO₃) was added to 10gm. of glycine in the presence of 30 ml of double distilled water after well mixing; the solution was kept at 110° C till constant weight. Finally, the temperature was elevated to 550° C for two h.

2.1.3 Vanadium oxide NP/PMMA film preparation

Polymeric nanocomposite films (PNC) of PMMA dispersed with V₂O₅ NP (0, 0.03, 0.16, 0.32, 1.7, and 3.3 wt%) have been synthesized using the casting process for a solution concerning the PMMA's weight amount used. Initially, 1.46 gm. of PMMA was dissolved in 25 ml chloroform for each sample. For each sample, an appropriate quantity of V₂O₅ NP has been first highly dispersed through 3 ml of chloroform and then added to PMMA solution, and the homogeneous solution was achieved after 15 minutes sonication and 6 h of magnetic stirring. Finally, the solution has been decanted into a thoroughly cleaned Petri-dish, and then let till drying without further heating, at room temperature, to produce PNC freestanding films. Other films with different V₂O₅ NP content have been prepared simultaneously using the same steps. Finally, the x wt % V₂O₅ / PMMA was dried at 40⁰C for 2 days before being cut into 2 * 2 cm² for further research.

The resulting films of V₂O₅ NP /PMMA of different V₂O₅ NP content are abbreviated as (V₀,V₁,V₂, V₃,V₄ and V₅), for (0, 0.03, 0.16, 0.32, 1.7, and 3.3 wt%) respectively.

2.2 Analytical methods

The XRD patterns of the V₂O₅ NP, PMMA and V₂O₅ NP /PMMA films were obtained using a PANalytical’s X’Pert PRO diffractometer. The samples were scanned directly at 2θ angles between 0⁰ and 70° with a Cu Kα source at a wavelength of 1.5418 Å. SEM images were acquired for the pure PMMA, V₂O₅ NP and V₂O₅ NP /PMMA films to study the distribution and dispersion of V₂O₅ inside the PMMA. FTIR spectroscopy was performed for the polymeric films at RT (JASCO, FT/IR-6200) in the wavenumber range of 4000–400 cm⁻¹.

Optical characterization by using a Shimadzu UV- 3600 ultraviolet–visible–near infrared (UV-VIS-NIR) spectrophotometer in the wavelength range of 200–1200 nm at an accuracy of 0.2 nm. The thickness of the films was evaluated using a digital micrometer at an accuracy of 0.001mm.

2.3 Photodegradation setup

The photocatalytic activities of the as prepared (wt% V₂O₅ NP /PMMA) films were evaluated by decomposing (MB) in aqueous solution under UV-C irradiation (the most vigorous emission at 254 nm) using a self-made photodegradation setup. The samples were immersed in an organic dye solution (50 mL, 10 mg/L) in a typical experiment. The exposed zone (2 cm²) for dye photodegradation was in the face of the UV lamp (distance 7 cm), and the intensity of UV irradiation was around 8 Mw/cm². Before irradiation, the aqueous solution was magnetically
stirred in the dark for 30 min to reach the adsorption-desorption equilibrium of organic dyes with the catalyst. The residual dye content was calculated as A/A0, where A and A0 are the absorbance values corresponding to the tested and the original control solution, respectively.

3 Result and discussion

3.1 Analytical studies

3.1. 1 Powder characterization

The structural properties of the powders prepared using the sol–gel method were assessed by XRD, one of the most effective methods for quickly completing the material structure, crystalline nature of NP and films. The d spacing is determined from the peak position using Bragg’s law

\[ n\lambda = 2d\sin\theta \]

Where \( \lambda \) is the wavelength (1.5406 Å) of X-rays and \( n = 1 \)

As shown in Fig. 1.a. The XRD pattern obtained for the powder calcinated at 550°C indicated that the powder comprised the crystalline nature of the prepared (\( V_2O_5 - V_6O_{13} \)) NP. A mixture of vanadium pentoxide \( V_2O_5 \) and vanadium oxide \( V_6O_{13} \) by a percentage of 68.2% and 31.8%, respectively, are obtained due to different diffraction angles \( \theta \).

15.384 °, 20.310 °, 21.740 °, 25.578 °, 31.055 °, 32.398 °, 33.343 °, 34.320 °, and 41.295 °, which are assigned to (200), (010), (110), (210), (400), (011), (111), (301), and (020) reflection planes. All peaks are consistent with JCPDS no. 01-072-0433]. This result indicates that as-prepared \( V_2O_5 \) Reveals an orthorhombic structure with (001) predominant orientation and good crystallinity.

JCPDS no. 01-075-5982 shows an excellent matching with the obtained diffraction angle values, 8.875, 15.122, 16.038, 17.803, 18.965 21.118, 25.350, 26.161 and 30.132, which are assigned to (001), (200), (-201), (002), (201), (-202), (110), (101) and (-401) reflection planes. This result indicates that \( V_6O_{13} \) reveals a Monoclinic structure with (101) predominant orientation and good crystallinity.

The crystallite size (D) for predominant orientation was estimated using Scherer’s formula:

\[ D = 0.9\lambda / (\beta \cos (\theta)) \]

where \( \lambda \) is the X-ray wavelength (0.154 nm), \( \beta \) is the peak width at half-maximum FWHM (in radians), and \( \theta \) is the angle of the corresponding peak. The calculation for \( V_2O_5 \) NP yielded a D value of 84.33 nm for predominant orientation (001) where FWHM = 0.0017 in radian and \( \theta = 20.311 ° \), also the mean crystallite size estimated using Scherer's formula (D_{avg} = 73.17 nm). The specific surface area (A) of \( V_2O_5 \) NP is related to D by the formula: A = 6/\( \rho D \) (Mohammed et al. 2018), where \( \rho \) is the density of \( V_2O_5 \) NP (3.36 gcm^{-3}), and A = 21.18 m²/g according to this equation.
The prepared $V_2O_5$ NP powder's morphology was examined by SEM as shown in Fig. 1.b. It is seen that $V_2O_5$ has a hierarchical nanobelt interconnected structure with 50–300 nm in length. The histogram Fig. 1b(insert) shows the range of the nanobelt with 100 to 150 nm dominant length. Y. Rong et al. (Rong et al. 2016) prepared $V_2O_5$ with comparable morphology. It is known that $V_2O_5$ has a layered structure of VO$_5$ square pyramids that share edges and corners and are attracted by Van der Waals interactions (Ali and Ismail 2022).

Also, Du et al. (Du et al. 2019) reported that this architecture can enhance the interaction with organic materials and also avoid the aggregation of $V_2O_5$. These data confirm the XRD results of $V_2O_5$ NP.

### 3.1.2 Structural and properties of the polymeric nanocomposite films

**XRD and SEM analysis**

To explore the influence of vanadium oxide NP on the amorphous PMMA polymer chain, the diffraction patterns for the amorphous PMMA are displayed in Fig. 2.

PMMA has diffraction peaks of 16.55° and 30.2°, this is the polymer's crystalline phase. Mervat I Muhammed et al., estimated the diffraction peaks of PMMA at comparable values (Muhammed et al. 2022). The 1st-peak shape represents that extended polymer chains have been packed, while the 2nd-peak showed that the major chains had been ordered with gradually decreasing in their intensity (Rathika et al. 2018). The strength and width of the first peak changed when Nano filler is added to the polymeric host. The addition of nano-filler to the polymeric host alters the width and intensity of the initial peaks. The increase has influenced the crystallinity of the polymer in width or decrease in intensity due to polymer nano-filler (Hussien et al. 2020b). It could imply that some interactions between the polymer chains and the nano filler are possible. After doping PMMA with (0, 0.03, 0.17, 0.32, .1.67, and 3.3 wt%) $V_2O_5$, the observed broad peak shifts from 16.55° to 17.8° this shift can be attributed to the structural irregularity of the PMMA backbone chain caused by the Nano filler doping.

No obvious diffraction peaks of $V_2O_5$ NP are detected in the XRD patterns after mixing with polymer, which could be ascribed to the excellent compatibility between vanadium oxide and the polymer matrix as will be revealed from surface SEM images.

The morphological change owing to the incorporation of $V_2O_5$ NP into the polymer, it studied by examining the surface structure of the (V$_0$, V$_2$ and V$_5$) by scanning electron microscope (SEM).

Figure. 3a. displayed that pure PMMA film has a clear, smooth and transparent surface. Figure 3b. shows that the film morphology is dramatically changed when $V_2O_5$ NP mixed with the polymer matrix. From Fig. 3b and c, we can speculate that $V_2O_5$ NP is homogeneously distributed and interspersed among the polymer chains as matched with the SEM images. This morphology may be attributed to the interpenetrating architecture of $V_2O_5$, which enhances the interaction with organic materials and avoids aggregation (Du et al. 2019).

The cross-section image, Fig. 3c, for V$_5$ proves the presence of abundant voids inside the film. The micrograph, Fig. 3d, shows the mean diameter of the voids is about 250 nm. These higher internal pores usually provide a more active surface area, enhancing radical production process in the photodegradation process.
3.1.3. FTIR spectroscopy data of V$_2$O$_5$/PMMA nanocomposite polymeric films

Our results represented information about internal interaction effects between different constituents within polymer composites and described the induced changes in the vibrational and rotational transition modes, different types of absorption bands and band positions. The FTIR absorption spectra for PMMA and nanocomposite films are shown in Fig. 4. It is clear from the figure that, the spectra of the nanocomposite film looks to a great extent similar to that of the PMMA sample except the absorption peaks slight shift that has been observed for certain peaks in the case of doped film.

These results proved that no modifications occurred in the sample's chemical structure due to the doping effect. The most common characteristic peaks that confirmed the existence of PMMA samples are centered at 1435 cm$^{-1}$, 1484 cm$^{-1}$, 2848 cm$^{-1}$, 2994 cm$^{-1}$, and 1730 cm$^{-1}$ assigned for O–CH$_3$ bending vibration, CH$_2$ bending vibration, aliphatic CH$_2$ stretching vibration, asymmetric (O–CH$_3$, C–H) stretching vibration, and the ester carbonyl group C=O stretching, respectively (Heiba et al. 2020). The absorption bands centered at 2949 cm$^{-1}$, 1270 cm$^{-1}$ and 852 cm$^{-1}$ are due to asymmetric stretching of C–CH$_3$ band, C–O stretching vibration and C–O–C stretching of PMMA (Badran et al. 2002). Earlier studies (Arif et al. 2016) showed a slight difference in the peak position centered at 840 cm$^{-1}$ and returned this to CH$_2$ rocking modes within PMMA. Other absorption bands appeared at 1190 cm$^{-1}$, 753 cm$^{-1}$, 960 cm$^{-1}$, and 1144 cm$^{-1}$ corresponding to C–O–C bending, CH$_2$ rocking mode of PMMA, C–CH$_3$ bending vibration and C–O asymmetric stretching (Mahasin and Wafaa 2013), some pronounced variations occur at these characteristic peaks in the form of modifications in the intensity of typical absorption bands. The characteristic absorption peak at 1388 cm$^{-1}$ can be assigned to C–CH$_3$ deformation within PMMA. This peak showed lower intensity for V$_5$. This can be attributed to the cleavage process that occurred to the C–H bond due to the addition of nanoparticles. As the results of this C–H bond cleavage, unstable hydrogen free radicals and carbon rich structures were produced within films and some of the hydrogen atoms may escape while the residual atoms may be captured by low electron density (Zhang et al.).

Pronounced variations in the shape and position of the carbonyl bond assigned to 1729 cm$^{-1}$ can be observed and discussed as: a slight decrease in the peaks intensity and shift in position can be noticed for V$_5$. The decrease in the absorption peak intensity related to the carbonyl (C=O) bond can be explained on the basis of the breakage that occurred to the bond within nanocomposite films. This continuous breakage can be considered the main source of the released oxygen atoms, which recombine with some hydrogen free radicals forming −OH bonds. An obvious absorption band centered at 3452 cm$^{-1}$ justifies the appearance of −OH bonds within PMMA and nanocomposite films. A little variation in the shape of the peak (slight increase in width) of nanocomposite films can be observed in the wavenumber range 1500–1650 cm$^{-1}$, which reflects the amorphous nature of the films with the doping. Such variations are attributed to the presence of carbon rich structures within it. The absorption band appeared in this region at 1630 cm$^{-1}$ was related to the C=CH stretching vibration (Tawansi et al. 2002). Others showed a nearly closed position for this band at 1637 cm$^{-1}$ (Zhang et al.).

3.1.4 Optical characterization

Electronic transitions occurring in polymer nanocomposite films can be achieved via ultraviolet-visible (UV–Vis) spectroscopy. The implications of V$_2$O$_5$ NP addition to PMMA matrix can especially be derived from optical
measurements. The UV–vis absorption spectra of pure PMMA and PMMA films doped with V$_2$O$_5$ NP are illustrated in Fig. 5a. It can be clearly seen that there is a sharp absorption increase below 280 nm which corresponds to the π-π* transition of PMMA carbonyl groups (Švorčík et al. 2008). Meanwhile, an absorbance band is displayed by the pure PMMA spectra at about 340 nm, which corresponds to the n-π* electronic transition (El-Zaheer and Osiris 2005) induced by the non-bonding electrons (Yaragalla et al. 2016). Furthermore, in the 200–350 wavelength range, there is a reduction in the absorption spectra of pure PMMA, while at higher wavelengths, they become stable, thus indicating the transparent nature of the freestanding PMMA film to the whole visible wavelength over 300 nm (Aziz et al. 2019a) (Abdel-Kader and Mohamed 2020). The onset of PMMA absorption shifted to a higher wavelength and began from 365 nm when vanadium oxides nanoparticles were added. The formation of micro strain in the (V$_0$, V$_1$, V$_2$, V$_3$, V$_4$, and V$_5$) (when V$_2$O$_5$ NP are added (Hemalatha et al. 2014) or occurrence of extra defects in the energy band gap (Aziz et al. 2019b) are potential reasons for such a shift. Figure 5a. clearly shows that addition of vanadium oxides nanoparticles to the polymer matrix enhances the intensity of pure PMMA absorbance band at 280 nm.

The types of electron transitions that can occur in materials can be derived from the examination of alterations in absorption spectra. Band-to-band or exciting transitions are associated with fundamental absorption, which takes the form of fast rise in absorption, called the absorption edge, and is indicative of the optical band gap energy.

Figure 5b. represents the transmittance of the studied samples in the wavelength region from 200 to 1600 nm for more illustration for (V$_0$, V$_1$, V$_2$, V$_3$, V$_4$ and V$_5$). The pure PMMA has ~ 88.6% transparency with a decrease in its values by increasing V$_2$O$_5$ NP contents, and the T(λ) values is around 25% for V$_5$. The transmittance of these films decreases as the amount of V$_2$O$_5$ NP added to the PMMA matrix increases. It is noteworthy that the reduced transmittance of the films, due to the surface's Smoothness, that resembles that of a mirror and causes high reflectivity, as well as the scattering of V$_2$O$_5$ NP, cause a loss of incident spectral range intensity or the formation of larger aggregates through the polymeric films (Al-Taa'Y et al. 2014). The expression of the absorption is based on an absorption coefficient (α) representing the relative rate at which the incident light intensity declines in a unit length of the medium (Hussien et al. 2020a) (Aziz et al. 2015).

Although V$_2$O$_5$ NP have a lower absorption spectrum in the visible region, the transmittance of the nanocomposite films for this spectral region declined with an increase in V$_2$O$_5$ NP concentration due to the smoothness of the surface, which appears to be a specular surface with high reflectivity and low transmittance for the visible range. Furthermore, the scattering of V$_2$O$_5$ NP could cause the incident intensity to lose in this spectral range (Ennis and Kaiser 2010). Figure 5c shows the reflectance spectra of (V$_0$, V$_1$, V$_2$, V$_3$, V$_4$ and V$_5$). PMMA film's reflection is less than the studied nanocomposites films. It is clear from the spectral behavior of R(λ) that the film reflectance is increased by increasing V$_2$O$_5$ NP loadings.

The absorption coefficient (α) can calculate the optical dispersion parameters. Beer-Lambert’s relation was applied to determine the α at the equivalent frequency ( ) from the absorbance spectra $A( )$ (Yakuphanoglu et al. 2006) (Mohammed 2018) by using the equation given below:

$$\alpha(\lambda) = \frac{2.303}{d} \log \frac{I}{I_0} = \frac{2.303}{d} A(\lambda) \quad (3)$$

where d is the sample thickness, A is the absorbance, and α is the absorption coefficient, I$_0$ denotes the incident light intensity, the transmitted light intensity is denoted by I.
The extinction index, $k$, is a significant parameter (Hussien et al. 2020b) characterizing photonic substances. In addition, $k$ measures the rate of reduction of transmitted light via scattering and absorption in an optical medium and calculates the probability of electronic transition.

$$k = \frac{\lambda \alpha}{4\pi}$$ (4)

In this case, $\alpha$ indicates the absorption coefficient, and $\lambda$ is the photon wavelength. Calculation of the $k$ values with Eq. 4 and reliance on $\lambda$ are given in Fig. 6a. In Fig. 6a, as the wavelength gets longer, the extinction coefficient rises, suggesting that the fraction of light lost due to scattering rises as well. The rise in the amount of $V_2O_5$ NP content attributable to the rise in the absorbent portion of incident light is increased, and therefore, the energy loss occurs (Muhammed et al. 2022).

For the studied nanocomposite polymeric films, the refractive index ($n$) was obtained using the corrected relation of refractive index and reflectance ($R$) (Gomaa et al. 2022b):

$$n = \frac{1 + \left(\frac{R}{4}\right)^{1/2}}{1 - \left(\frac{R}{4}\right)^{1/2}}$$ (5)

The refractive index ($n$) of pure and ($V_0$, $V_1$, $V_2$, $V_3$, $V_4$, and $V_5$) as a function of photon energy is shown in Fig. 6b. It can be noted that $n$, gradually increases to the highest value near the absorption edge. Furthermore, with growing filler content, $n$ rises dramatically due to the interactions between the $V_2O_5$ NP as a filler and PMMA chain segments leading to an increased density of the films and the resulting is the greater refractive index. The rising trend of $n$ refractive index with increased photon energy shows that the electrons in the studied material have important relationships with the photon incident.

Various plots have been applied for determining the optical energy gap in greater depth. An electron can be brought from a lower to a higher energy state by absorbing an ultraviolet photon with exactly the difference in energy between the band gap of the material's absorption and emission maximus.

Equation (6) was applied to calculate the optical gap (also known as the edge optical band) of these energy-absorbing polymer nanocomposite (PNC) films, which was measured near the fundamental edge as follows (Ali and Ismail 2022) (Mohammed et al. 2022)

$$\alpha \hbar = B(h - E_g)^m$$

6

Where $B$, $h\nu$, and $E_g$ are constants, photon energy, and optical energy gap, respectively and $m = 1/2$ or $2$ for indirect and directly allowed transitions, respectively. Both indirect and direct transitions have previously been confirmed close to the main band edge (Abdelghany et al. 2016). Tauc's method which involves plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ values concerning $h\nu$, incident photon energy values, can be used to find the transitions to determine the band edges. $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ against $h\nu$ plots of the $V_2O_5$ NP / PMMA films were shown in Fig. 7a and 7b. The values of the indirect optical band gap $E_g(\text{ind})$ and direct optical band gap $E_g(\text{d})$ of these PNC films have been calculated using the extrapolated linear portions of the band gaps. All these values have been reported in Table 1. The $E_g(\text{d})$ values are found to be greater than the $E_g(\text{ind})$ values for all the PNC materials studied. The linear portion dependence for pure PMMA is also observed in two regions representing the two absorption edges.
Table 1 shows that as the amount of V$_2$O$_5$ NP in these PNC films increases, the optical band gap values decrease due to interaction coordinated PMMA chains (functional groups and V$_2$O$_5$ NP), the creation of charge transfer complexes between HOMO and LUMO energy bands allows for lower energy transfers (Abdelghany et al. 2016)

The decrease in a nanocomposite material’s optical band gap with changes in constituent amounts is thought to raise the disorder for generating localized states in the material (Kiran Kumar et al. 2011)

The band gap $E_{g(o)}$ can be estimated by another method based on absorption spectra fitting (ASF) model (Ali 2019) according to the relation:

$$\omega^2 A = (\hbar \omega - E_{g(o)})^2$$

Where $\omega$ is the angular frequency which is equal to $2\pi = 2\pi c/\lambda$ and $\lambda$ is the wavelength of photons incident at velocity c. Figure 8a shows plot $(A^{1/2}/\lambda$ versus $1/\lambda)$ for these PNC. The values of $\lambda_g$ were found by extrapolating this line segments of the curves to get band gap $E_{g(o)}$ through the following relation

$$E_{g(o)} = \frac{hc}{\lambda_g}$$

7

Table 1 also includes the evaluated $E_{g(o)}$ values of the PNC. These $E_{g(o)}$ values are found to be between the $E_{g(d)}$ and $E_{g(ind)}$ values.

Also, Table 1 includes the evaluated $E_a$ of the PNC that was observed. These PNC films’ absorption edge energy $E_a$ values were calculated using $\alpha$ verses $h$ plots shown in Fig. 8b, which have also been used for other materials (Kiran Kumar et al. 2011)

It is apparent that V$_2$O$_5$ NP addition causes the pure PMMA absorption edge to shift in the direction of low photon energy.

Modifications in the sample band structure are reflected by the drop in the absorption edge value caused by V$_2$O$_5$ NP addition and may be the result of the development of new localized states within the band gap (Aziz 2017)

This may indicate that addition of V$_2$O$_5$ NP in the PMMA matrix leads to a reduction in band gap energy (Abdel-Kader and Mohamed 2020).
The Urbach's energy ($E_U$) can be estimated by the relationship.

\[ \alpha (h) = \alpha_0 \exp(h / E_U) \]

The width of the band tail of the localized states at the optical bandgap is measured by the Urbach's energy $E_U$, corresponding to the disorder in amorphous semiconductor materials (Farid and Hegab 2019).

The variation of ln($\alpha$) with the photon energy is shown in Fig. 9, and the value of $E_U$ is constant, may be calculated using Eq. (9). The reciprocal slope of the straight lines yields $E_U$ for the films under consideration. Table 1 shows the $E_U$ and values that were achieved. The variation was small at low frequencies, but it grew as the frequency climbed. This could be attributed to the inter band transition (El-Mongy et al. 2020), which occurs at high photon energies.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$E_{g1(\text{ind})}$ (eV)</th>
<th>$E_{g2(\text{ind})}$ (eV)</th>
<th>$E_{g1(\text{d})}$ (eV)</th>
<th>$E_{g2(\text{d})}$ (eV)</th>
<th>$E_{g(O)1}$ (eV)</th>
<th>$E_{g(O)2}$ (eV)</th>
<th>$E_{a1}$ (eV)</th>
<th>$E_{a2}$ (eV)</th>
<th>$E_U$ (eV)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>$V_0$</td>
<td>4.1</td>
<td>3.42</td>
<td>4.7</td>
<td>3.75</td>
<td>4.31</td>
<td>3.64</td>
<td>4.74</td>
<td>3.81</td>
<td>0.19</td>
<td>This work</td>
</tr>
<tr>
<td>$V_1$</td>
<td>4.01</td>
<td>3.39</td>
<td>4.49</td>
<td>3.75</td>
<td>4.30</td>
<td>3.62</td>
<td>4.72</td>
<td>3.66</td>
<td>0.2</td>
<td>This work</td>
</tr>
<tr>
<td>$V_2$</td>
<td>3.94</td>
<td>3.34</td>
<td>4.46</td>
<td>3.75</td>
<td>4.29</td>
<td>3.59</td>
<td>4.45</td>
<td>3.58</td>
<td>0.22</td>
<td>This work</td>
</tr>
<tr>
<td>$V_3$</td>
<td>3.89</td>
<td>3.34</td>
<td>4.45</td>
<td>3.74</td>
<td>4.26</td>
<td>3.57</td>
<td>4.34</td>
<td>3.58</td>
<td>0.22</td>
<td>This work</td>
</tr>
<tr>
<td>$V_4$</td>
<td>3.79</td>
<td>3.08</td>
<td>4.42</td>
<td>3.66</td>
<td>4.23</td>
<td>3.5</td>
<td>4.24</td>
<td>3.37</td>
<td>0.4</td>
<td>This work</td>
</tr>
<tr>
<td>$V_5$</td>
<td>3.68</td>
<td>2.99</td>
<td>4.37</td>
<td>3.61</td>
<td>4.19</td>
<td>3.45</td>
<td>4.02</td>
<td>3.27</td>
<td>0.44</td>
<td>This work</td>
</tr>
<tr>
<td>Pure PMMA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(Abdel-Kader and Mohamed 2020)</td>
</tr>
<tr>
<td>Pure PMMA</td>
<td>4.64</td>
<td>-</td>
<td>4.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(Hussien et al. 2020b)</td>
</tr>
<tr>
<td>(PMMA-PVDF)/ZnO (0–20 wt%)</td>
<td>-</td>
<td>-</td>
<td>5.85–5.22</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.56–0.84</td>
<td></td>
<td>(Lee et al. 2016)</td>
</tr>
<tr>
<td>ZnO/PMMA (0-2.5 wt%)</td>
<td>4.83–3.7</td>
<td>-</td>
<td>4.98–4.47</td>
<td>-</td>
<td>4.88–3.49</td>
<td>-</td>
<td>4.88–4.05</td>
<td>-</td>
<td></td>
<td>(Mohammed et al. 2022)</td>
</tr>
<tr>
<td>$V_2O_5$/PEO-PVDF (0-30wt%)</td>
<td>-</td>
<td>-</td>
<td>5.04–2.88</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(Ali and Ismail 2022)</td>
</tr>
</tbody>
</table>
To elucidate the detailed optical behavior of the films, the dielectric constant is estimated. It is closely related to the electronic band structure. The complex dielectric function can be written as \( \varepsilon = \varepsilon' + \varepsilon'' \), where \( \varepsilon' \) and \( \varepsilon'' \) are the real and imaginary parts of the dielectric function. The real and imaginary parts of the dielectric function are related to the refractive index \( (n) \) and the extinction coefficient \( (k) \) via the following relations respectively (Dhas et al. 2017) (Barış et al. 2014).

\[
\varepsilon' = n^2 - k^2
\]

And

\[
\varepsilon'' = 2nk
\]

The values of \( \varepsilon' \) and \( \varepsilon'' \) are plotted as a function of the incident photon energy as shown in Fig. 10a and b, respectively. Both \( \varepsilon' \) and \( \varepsilon'' \) exhibit a gradual increase as the concentration of \( V_2O_5 \) NPs in the films increased. This may be attributed to the rise in the absorption of the incident photon by \( V_2O_5 \) NP/ PMMA films. Estimating both constants is essential because they are closely related to microelectronic applications and energy absorption by the electric field due to dipole motion (Dhas et al. 2017). Moreover, in the limit, \( n >> k \) the behavior of \( \varepsilon' \) is similar to that of \( n \); whereas the behavior of \( \varepsilon'' \) is similar to the behavior of extinction coefficient \( k \). Having estimated \( \varepsilon' \) and \( \varepsilon'' \), they could be employed to determine the loss factor (dissipation) as,

\[
\tan\delta = \frac{\varepsilon''}{\varepsilon'}
\]

It could provide information about the effective photonic zone (Boulahlib et al. 2021). Figure 10c shows the variation of \( \tan\delta \) as a function of the incident photon energy of PMMA films incorporated by various concentrations. In the energy window (2 eV– 3.6 eV), \( \tan\delta \) of pure PMMA thin film remains constant. It then exhibits a drastic increase in the energy range (3.6 eV– 5 eV). It then slightly decreases in the energy window (5 eV–6 eV). This is substantial evidence that \( V_2O_5 \) NP/ PMMA films are photoactive at the photon energies close to the band gap energy. Moreover, the higher values of \( \tan\delta \) in the visible may be understood in terms of the strong electronic transitions into the inner bands. The \( \tan\delta \) exhibits a continuous gradual increase as the concentration of \( V_2O_5 \) NP is increased.

When the energetic electrons are incident on the bulk of the material, part of their energy inside is lost. This energy loss is known as the volume energy loss function \( (VELF) \). However, low-energy electrons lose an amount of their energy on the surface of solid materials. This energy loss is known as the surface energy loss function \( (SELF) \). The \( VELF \) and \( SELF \) could be estimated by the following two equations (Barış et al. 2014) (Migdadi et al. 2022) (Ali et al. 2013).

\[
VELF = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \tag{13}
\]

\[
SELF = \frac{\varepsilon''}{(\varepsilon' + 1)^2 + \varepsilon''^2} \tag{14}
\]
Figure 11a,b present the dependency of the Volume Energy Loss Function (VELF) and the Surface Energy Loss Function (SELF) on the photon energy. The response of VELF and SELF is delineated within three discrete spectral domains, classified by the incident photon energy. In the initial spectral region, characterized by photon energies below 4 eV, an augmentation in the concentration of V$_2$O$_5$ NPs correlates with an increase in the values of both VELF and SELF. This indicates an enhanced probability of energy loss through interactions with valence electrons as the nanoparticle concentration rises. The second region is defined for photon energies exceeding 4 eV. In this domain, VELF and SELF not only continue to escalate but also attain their maximal values. This elevation suggests a greater degree of energy dissipation via electronic interactions at these higher energy levels. Beyond the threshold of 4.75 eV, there is a marginal reduction in the values of both VELF and SELF, which points to an increased energy dissipation by electrons in the higher energy zone. This implies a saturation point whereby the energy transfer efficiency to electrons decreases as the incident photon energy surpasses a certain level.

The analogous trajectories of VELF and SELF imply that the mechanisms governing the energy loss of electrons traversing the bulk material (as described by VELF) and those transiting across the material’s surface (as described by SELF) are comparable. These findings suggest that the surface and bulk properties of the material have a similar influence on electron energy dissipation within the examined energy range.

The integration of V$_2$O$_5$ (NPs) into the Poly(methyl methacrylate) (PMMA) matrix is posited to introduce novel energy states as a result of perturbations in the local energy configurations of the PMMA. This incorporation can facilitate the migration of charge carriers, enhancing the transition rates between the conduction and valence bands within the composite material. As a consequence of the altered energy landscape, the optical behavior of the resultant nanocomposite films warrants investigation, particularly through the lenses of optical and electrical conductivities. These properties provide insight into the interplay between the electronic structure and the photon-induced excitations in the material.

To quantify these effects, the optical and electrical conductivities of the PMMA films, embedded with varying concentrations of V$_2$O$_5$ nanoparticles, have been estimated. The assessment of these conductivities aims to elucidate the impact of nanoparticle concentration on the charge transport and optical interactions within the films, thereby contributing to a comprehensive understanding of their optoelectronic characteristics (Fouad et al. 2018) (El Radaf et al. 2020). The optical and electrical conductivities can be expressed as (Gomaa et al. 2022a)

$$\sigma_{op} = \frac{\alpha n c}{4 \pi}$$

$$\sigma_e = \frac{n \sigma_{op}}{k}$$

where $\sigma_{op}$ is the optical conductivity, $\sigma_e$ is the electrical conductivity, $c$ is the speed of light in a vacuum, $\alpha$ is the absorption coefficient, and $n$ is the refractive index. The $\sigma_{op}$ and $\sigma_e$ parameters are strongly related to the optical band gap energy, the absorption coefficient, refractive index, and dielectric function (Khalaf et al. 2021). Figure 12a and b display the variation of optical conductivity $\sigma_{op}$ and the electrical conductivity $\sigma_e$ of PMMA films incorporated by various concentrations of V$_2$O$_5$ NPs as a function of photon energy. Both increase as different amounts of V$_2$O$_5$ NPs are added to the PMMA matrix. As a result, a noticeable decrease of the optical band gap energy is obtained.
Furthermore, $\sigma_{op}$ and $\sigma_e$ increase as the photon energy of incident light increases. $\sigma_{op}$ exhibits an abrupt increase in the photon energy window (3.8 eV-4.8 eV). This behavior could be attributed to the enhanced electronic excitations and thus the increase of the absorption coefficient(Fouad et al. 2018)(El Radaf et al. 2020).

### 3.2 Photodegradation kinetics and spectrum studies for $V_2O_5$/PMMA nanocomposite polymeric films

$V_2O_5$ has a 2.6 eV bandgap; Vanadium is considered as one of the ampest transition metals in the earth’s crust. Vanadium pentaoxide has the highest oxidation state (5 +) and has a layered structure(Wang et al. 2021), so it is the most stable one of the vanadium oxides family. PMMA is the most common thermoplastic, affordable, and transparent polymeric material. The degradation of methylene blue MB dye has been applied under certain experimental conditions.

#### 3.2.1 Suggested photocatalytic mechanism.

When a photon with an energy equal to or higher than the energy band gap of $V_2O_5$/PMMA is absorbed, electron-hole pairs ($e_c^-, h_v^+$) are formed. Superoxide ($O_2^{*-}$) and hydroxyl radicals (OH*) are created during the photochemical reaction of holes and electrons with oxygen. The PMMA, as excellent carrier transport, played a role in reducing photogenerated $e^-/h^+$ pair recombination rates and prolonged the photogenerated center life(Mohammed et al. 2022). Eventually, OH* radicals and $O_2^{*-}$ active species mineralize dye molecules into CO$_2$ and water.

A suggested tool for MB photodegradation was proposed under UV-C illumination in the presence of $V_2O_5$/ PMMA nanocomposite membranes based on the above findings and discussions. MB photodegradation herein was affected by $V_2O_5$ nanoparticles and PMMA as a matrix. The photogenerated electrons have been transmitted from conduction to the valence band after absorbing sufficient photons(Xu et al. 2020). Delocalization charge significantly decreases the electron-hole recombination rate and thus promotes the oxidation-reduction process. The $O_2$ traps CB electrons for $O_2^{*-}$ and H$_2$O$_2$ creation. These intermediates respond to form the OH, a strong oxidizing agent that can degrade organic pollutants(Zedan et al. 2022b)(Natarajan et al. 2017). Prospective reactions to photocatalytic degradation of MB are as follows:

\[
V_2O_5/PMMA + h\nu \rightarrow V_2O_5/PMMA(h^+ + e^-) \\
\]

\[
e_{CB}^- + O_2 \rightarrow O_2^{*-} \\
\]

\[
h_{VB}^+ + OH^- \rightarrow OH \\
\]

\[
O_2^{*-} + 2h^+ + 2e^- \rightarrow O_2 + H_2O_2 \\
\]

\[
O_2^{*-} + H_2O \rightarrow H_2O_2 + OH \\
\]

\[
H_2O_2 \rightarrow 2OH \\
\]

\[
OH^* + dye \rightarrow CO_2 + H_2O \\
\]

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The obtained $V_2O_5$/PMMA nanocomposite films had long durability, stability, and reusability as elucidated through the characterization and applications. It helps raise the photostability of $V_2O_5$ nanoparticles against environmental conditions. PMMA was used as a matrix film due to its optical transparency. It provides a higher nanoparticle semiconductor surface area. Recently, the eco-friendly and low cost-effective technologies based on polymeric nanocomposites were considered the primary objective and point of interest for most researchers (Zhong et al. 2020). Moreover, heterojunction photocatalysts can accelerate the photo-excited electron-hole separation in the photocatalytic application (Xu et al. 2020).

### 3.2.2 Photodegradation spectrum studies for $V_2O_5$/PMMA nanocomposite polymeric films

The photodegradation of MB in the presence of UV light irradiation was utilized to assess the photocatalytic activity of the materials under investigation. The photocatalytic degradation of MB over the prepared $V_2O_5$/PMMA was evaluated under UV-C irradiation. The as-prepared polymeric nanocomposite films showed acceptable adsorption ability, and thus the time for the adsorption-desorption equilibrium was set at 30 min in darkness for all experiments. The UV–vis absorption spectra of MB solutions over PMMA and x wt% $V_2O_5$/PMMA under UV light irradiation are presented in Fig. 13. There is no obvious hypsochromic shift in the UV–vis absorption peaks of MB during the photodegradation process as shown in Fig. 13. The experimental results depicted that, with increasing $V_2O_5$ concentration in PMMA, the MB solution degraded more quickly. This effect was more apparent when the radiation time was increased; decreasing the absorption peak intensity of the MB solution, indicating that $V_2O_5$ photocatalyst was effectively applied in MB photodegradation at a certain concentration.

### 3.2.3 Kinetic studies of photocatalytic activity for $V_2O_5$/PMMA nanocomposite polymeric films

Figure 14a displayed the plots of $C/C_0$ vs time of MB solution over the prepared $V_2O_5$/PMMA nanocomposite polymeric films under UV–visible light irradiation. Figure 14b displayed the plots of the pseudo-first-order kinetics as the equation was applied (Hussien et al. 2020a);

$$\ln(\frac{C}{C_0}) = -kt$$

Where $k$ is the constant rate (min$^{-1}$), initial MB concentration is $C_0$ (mg/L), and at time $t$ (min) the concentration of MB is $C$.

The reaction rate has reached the maximum while using 3.3 wt% $V_2O_5$/PMMA photocatalyst, indicating $V_2O_5$ is an effective photocatalyst. This performance is significantly increased after increasing $V_2O_5$ concentration in the PMMA film. Compared to the previous reports, powder photocatalysts need more steps (Šutka et al. 2016) (Mondal et al. 2019). The collective of morphological and optical effects is primarily responsible for the increased rate constant of the reaction using $V_2O_5$/PMMA sheets. The addition of $V_2O_5$ increased the crystallite size that raised the surface area of the $V_2O_5$ nanoparticles by increasing their growth rate. Adding $V_2O_5$ nanobelts changed PMMA electronic structure, resulting in a good decrease in the bandgap value. The presence of $V_2O_5$ also increases the rate of adsorbed $O_2$ molecules and OH ions on the surface of the film. The majority of the photo-excited electrons and holes have been formed and reacted to form activated radicals. The obtained radicals are powerful oxidizers that can
break up MB’s chemical bonds and produce the colorless solution, leading to degraded molecules (Qu et al. 2013). The degradation rate was then calculated using the absorbance data, as shown in Fig. 14c, which depicts the change in % degradation as a function of irradiation time. The following relationship was used to determine % degradation (Hussien et al. 2020a)

% degradation = \( \left(1 - \frac{C}{C_0}\right) \times 100\% \) (19)

It depicts the photocatalytic degradation of (MB) on \( V_2O_5/PMMA \) with various \( V_2O_5 \) contents using a UV-C lamp as a function of irradiation time. The percentage of MB degraded by \( V_2O_5/PMMA \) varies depending on the \( V_2O_5 \) content. It also showed how the \( V_2O_5 \) concentration affects the photodegradation reaction after 1 h of exposure. The degradation rate increases with increasing \( V_2O_5 \) content, with 3.3 wt% \( V_2O_5/PMMA \) achieving the optimum degradation. Upon UV light irradiation for 60 min, the degradation of MB over the pure PMMA degraded only 31% of MB. The x wt% \( V_2O_5/PMMA \) films showed an increase in the photodegradation efficiency with the increase in the loading amount of the \( V_2O_5 \) NPs Fig. 15c. The 0.03%, 0.16%, 0.32%, 1.7% and 3.3% \( V_2O_5/PMMA \) exhibited enhanced degradation of 76%, 67%, 85%, 88% and 99% of MB within 60 min of irradiation, respectively.

### 3.2.4 The reusability and Photostability of \( V_2O_5/PMMA \) nanocomposite polymeric films

The reusability of any photocatalyst and its photostability are influential factors for practical applications in large-scale and economic considerations. The reusability experiments were performed by repeating the same photodegradation experiment steps as described previously. Figure 15 showed remarkable stability and reusability of 3.3% \( V_2O_5/PMMA \) nanocomposite polymeric films for several successive experimental runs of MB photodegradation under UV-C light irradiation. 3.3% \( V_2O_5/PMMA \) nanocomposite polymeric films exhibited great stability and reusability over MB photodegradation after six consecutive runs under UV-C light irradiation. After the fourth run, the photocatalytic efficiency of the tested films was slightly decreased due to the decrease in the transparency of the used catalyst film.

### 4. Conclusion

Polymer photocatalysis presents an innovative approach to address water treatment challenges through the development of efficient photocatalysts. This work presents the synthesis of light-sensitive photocatalysts, incorporating \( V_2O_5 \) nanoparticles into a poly (methyl methacrylate) (PMMA) matrix. These nanocomposite films, with an average thickness of 0.2 mm, were prepared using a sol-gel method and solution casting.

The optical properties of these nanocomposite films were characterized using X-ray diffraction (XRD), UV-Vis absorbance, and FTIR spectroscopy. Additionally, the morphological properties of selected samples were examined using scanning electron microscopy (SEM). The photocatalytic performance of these materials for degrading the organic pollutant methylene blue (MB) under UV-C illumination was evaluated.

The findings demonstrated that the presence of \( V_2O_5 \) nanoparticles significantly enhanced the photocatalytic efficiency of PMMA for MB degradation, with an optimal loading ratio. Importantly, the \( V_2O_5/PMMA \) film retained its photocatalytic activity during recycling processes, indicating its potential as a recyclable photocatalyst for pollutant degradation.
This work introduces a novel strategy for developing advanced polymeric photocatalyst films, incorporating inorganic semiconductors, such as V$_2$O$_5$ nanostructures, into the PMMA matrix. Notably, the highest photocatalytic degradation of MB was achieved with a 3.3 wt% V$_2$O$_5$/PMMA photocatalyst under UV-C irradiation.

In conclusion, polymeric nanocomposite films demonstrate great promise for environmentally and economically beneficial applications in the field of water treatment, addressing the critical issue of pollutant degradation.

Declarations

**Author Contributions:** Redha A. Alkhadry: Methodology, Investigation, Data collection, Formal analysis, Data curation, Writing – original draft. Ibrahim S. Yahia: Conceptualization, Resources, Writing – review & editing, Supervision. Mostafa Zedan: Investigation, Data collection, Formal analysis, Data curation, Writing – review & editing, Supervision. Souad A. Elfeky: Resources, Writing – review & editing, Supervision. M. I. Mohammed: Data collection, Formal analysis, Data curation, Writing – review & editing, Supervision. Diaa A. Rayan: Data collection, Formal analysis, Data curation. Walid Tawfic: Resources, Writing – review & editing, Supervision. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

**Conflicts of Interest:** The authors declare no conflicts.

**References**


**Figures**

![XRD pattern and SEM image](image)

**Figure 1**

(a) XRD pattern and (b) SEM image and nanobelt length histogram (inset) of the prepared V$_2$O$_5$ NP powder.
Figure 2

XRD pattern for pure PMMA and the as-prepared x wt% V$_2$O$_5$ NP/PMMA films.
Figure 3

(a-c) SEM micrographs for (a) pure PMMA, (b) V$_2$ and (c) V$_5$ films. (d) the voids diameter histogram of V$_5$ film.
Figure 4

FTIR spectra of pure PMMA and V₅ samples.

Figure 5

The spectra of (a) absorbance, (b) transmittance and (c) reflectance of (V₀, V₁, V₂, V₃, V₄ and V₅)
Figure 6

(a) The extinction coefficient $k$ versus $\lambda$ and (b) the refractive index versus $\lambda$ for $(V_0, V_1, V_2, V_3, V_4$ and $V_5)$.

Figure 7

The plots of (a) $(\alpha h \nu)^2$ and (b) $(\alpha h \nu)^{1/2}$ versus the photon energy $(h \nu)$ for (PMMA, $V_1, V_2, V_3, V_4$ and $V_5$).
Figure 8

The plots of (a) $A^2/\lambda$ versus the $1/\lambda$ and (b) $\alpha$ versus the photon energy ($h\nu$) for (PMMA, $V_1$, $V_2$, $V_3$, $V_4$ and $V_5$) respectively.

Figure 9

The plot of $\ln \alpha$ versus the photon energy ($h\nu$) for (PMMA, $V_1$, $V_2$, $V_3$, $V_4$ and $V_5$).
Figure 10

The plots of (a) $\varepsilon'$, (b) $\varepsilon''$ and (c) $\tan\delta$ versus the photon energy ($h\nu$) for (PMMA, V1, V2, V3, V4 and V5).

Figure 11

The plots of (a) SELF and (b) VELF versus the photon energy ($h\nu$) for (PMMA, V1, V2, V3, V4 and V5).
Figure 12

The plots of (a) $\sigma_{op}$ and (b) $\sigma_{el}$ versus the photon energy ($h\nu$) for (PMMA, V1, V2, V3, V4 and V5).
Figure 13

(a-f) UV–Vis spectra of MB photodegradation over pure PMMA and different wt. % of V$_2$O$_5$/PMMA nanocomposites (a: PMMA, b: V$_1$, c: V$_2$, d: V$_3$, e: V$_4$ and f: V$_5$), respectively
Figure 14

(a-c) The plots of (a) $C/C_0$, (b) kinetic and (c) degradation percentage of MB photodegradation over different wt% of $V_2O_5/PMMA$ nanocomposite films compared to pure PMMA under UV-C light irradiation.

![Bar graph showing degradation percentage over different cycles.]

Figure 15

The reusability of 3.3 wt% of $V_2O_5/PMMA$ ($V_5$) nanocomposites for photocatalytic degradation of MB after six successive cycles under UV-c light irradiation.