



Visible light photocatalytic degradation of HDPE microplastics using vanadium-doped titania

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ABSTRACT

Efficient strategies are necessary to effectively remove microplastics (MPs), which are widely present in the environment. Among various techniques, photocatalysis using visible light has emerged as a promising approach to tackle the growing concerns surrounding microplastic waste. This research explored the potential of vanadium-doped titanium oxide as a photocatalyst for degrading high-density polyethylene (HDPE) microplastics under visible light irradiation. Vanadium-doped titanium oxide photocatalyst was synthesized using the sol-gel method, and then characterized through X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-visible spectroscopy. The XRD analysis confirmed the formation of the anatase phase, while the SEM imaging provided valuable information on the catalyst's morphology and elemental composition. The successful incorporation of vanadium ions into the structure was demonstrated by UV-visible spectroscopy that revealed a redshift in the absorption edge. The vanadium-doped titanium oxide photocatalyst was employed in the degradation of HDPE under visible light. The experimental results exhibited a significant reduction in the mass of the plastic after 350 hours of illumination. V-TiO₂ achieved a maximum reduction of 5.7%, while TiO₂ nanoparticles showed only the 2% decrease. This study demonstrates the potential of V-TiO₂ as an efficient visible-light-driven photocatalyst for HDPE degradation, contributing to the mitigation of microplastics pollution in a sustainable manner.

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1. Introduction

Polyolefins represent one of the most widespread types of plastics in use today mainly as packaging material due to their low cost and versatility. However, they are resistant to microbial decomposition, and huge amount of plastic waste gives rise to serious environmental concerns. Microplastics - particles measuring less than 5 mm in the largest dimension (Edo et al., 2019) - pose an emerging environmental pollution threat. There are two main categories of microplastics: primary and secondary. The former encompass items such as microbeads in personal care products, plastic pellets used in industrial manufacturing, and plastic fibers found in synthetic textiles. The latter form when larger plastic objects break down due to weathering caused, for instance, by wave action, wind abrasion, exposure to ultraviolet radiation from sunlight (Laskar & Kumar, 2019). Globally, different polymer types dominate the scale of plastics production, and consequently contribute to microplastics pollution in the environment. Among others, these polymers include polypropylene (PP), linear-low-density polyethylene (LLDPE) and low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyethylene terephthalate (PET), polyethylene (PE), and polystyrene (PS). HDPE were identified as one of the top toxic polymers based on probability factors, potential toxicity, as well as environmental impacts (Yuan et al., 2022).

Currently, there is no specific technique specifically designed for microplastics remediation from water or wastewater (Liu et al., 2021). Yet, researchers have embarked on designing various physical, chemical, and biological methods such as filtration, adsorption, coagulation, and biodegradation to tackle the issue. Filtration models have shown effectiveness in removing MPs, but they are phased by challenges like membrane fouling and require regular replacement of filter membranes. Adsorption and magnetic separation provide a straightforward approach to MP removal; however, the use of additive sorbents may lead to secondary pollution (Baskar et al., 2022; Sajid et al., 2022). Coagulation and oxidation treatments also encounter challenges related to chemical residues (Behera et al., 2021). Biodegradation and bioreactors often exhibit lower efficiency in degrading MPs (Zhu et al., 2023). In recent times, the photocatalytic technique has been proposed as a promising way of eliminating environmental pollution caused by non-biodegradable polymers.

Photocatalytic degradation involves the abstraction of electrons from the surface of semiconductor with a wide band gap by the effect of sunlight or UV light (Wu et al., 2020). The electrons are promoted from the valence band to the conduction band leaving holes on semiconductor surface. The holes oxidize molecules such as water to form hydroxide radicals, which subsequently initiate scission reactions on the polymer molecule resulting in the formation of novel non-oligomer structures

via cross-linking reactions, oxidation of organic compounds, and even production of gaseous products such as CO and CO₂, i.e. degrading a polymer material to low molecular weight and oxidized byproducts (Wu et al., 2020).

Titanium dioxide (Titania) is one of the most well-known and effective photocatalysts. Some studies on plastic degradation have shown that preliminary UV irradiation of a titania-polymeric composite material initiate its biodegradation (David et al., 2021) because of the formation of macromolecules resulting from chain splitting and creation of functional groups during photo-oxidative breakdown. The presence of shorter chains and unsaturated hydroxyl and carbonyl groups enable microorganisms to break down the degraded polymer to less toxic compounds in the environment (Chamas et al., 2020). Thus, the photocatalytic process is an effective and promising approach for the breakdown and elimination of plastic waste.

Titania-based photocatalysts have found applications in water purification due to their ability to decompose gaseous and aqueous contaminants (Mahlambi et al., 2015). However, because the light absorption edge of pure titania is lower than 380 nm, the majority of applications have been restricted to UV light irradiation. Therefore, the primary portion of the solar spectrum (mostly 400-600 nm) should be fully utilized in the production of modified titania with high activity under visible light (>380 nm). The most promising way to activate titania in the visible light region is by altering its chemical structure to broaden its absorption spectrum. One way of achieving this is by the addition of a dopant into the titania matrix. Metals as dopants are known to promote surface properties of the photocatalyst by preventing surface agglomeration and reducing the space charge region, thus enhancing the electron hole pair separation of titania as photocatalyst (Karthikeyan et al., 2020). This research aimed to enhance the light absorption ability of titania towards the visible region by doping it with vanadium oxide and then applying it in the photocatalytic degradation of HDPE as a technique to alleviate microplastics pollution in the nature.

2. Methods

Titanium (IV) isopropoxide, nitric acid, ethanol, and ammonium metavanadate were acquired from Sigma-Aldrich and used without further purification. Solutions were prepared based on distilled water. All glassware were washed with diluted nitric acid, sodium hydroxide, soap, and distilled water, and dried in oven at 100°C. High density polyethylene pellets were supplied by the Plast Packaging industries (Nairobi, Kenya). Commercially available HDPE pellets were utilized as the target material for photocatalytic degradation. Titanium (IV) isopropoxide was used as the source of TiO₂ for catalyst synthesis. Ammonium metavanadate was used to incorporate vanadium ions into the TiO₂ lattice. High-purity solvents (ethanol and distilled water) were used for catalyst synthesis and preparation of the HDPE pellet suspension.

2.1. Syntheses of pure and vanadium doped titanium oxide

Nanocrystalline titania was synthesized using the sol-gel process (Seck et al., 2013). A mixture of titanium isopropoxide (99.99%, 5 mL) and ethanol (15 mL) was subjected to continuous stirring in the 250 mL beaker to obtain a homogenous solution labeled as “Solution A”. The solvent mixture of ethanol (10 mL), nitric acid (0.5 mL) with molarity of 1.3 M, and distilled water (10 mL) was prepared in a separate beaker and labeled as “Solution B”. Solution B was added drop wise to Solution A while gently stirring to form a sol. The resulting sol was continuously stirred for 2 hours, and then aged for 24 hours. The sol was then dried in the oven for 4 hours at 100°C, and then crushed and calcined at 450°C for 4 hours. A similar procedure was followed to prepare vanadium-doped titania by replacing distilled water in Solution B with a vanadium solution produced by dissolving ammonium metavanadate (1 g) in distilled water (10 mL).

2.2. Characterization

Scanning electron microscopy (SEM: ZEISS Microscopy) was applied to examine the microstructural properties of the synthesized catalyst, while energy-dispersive X-ray (EDX) spectroscopy was used to determine the amount of vanadium doped in titania. X-ray diffraction (XRD) (RUKAGU Corp., Tokyo, Japan) was utilized to determine the crystalline phase and structure of nanoparticles. UV-VIS with integrated sphere (JENWAY 7315) was used to determine the light absorption properties of the prepared photocatalysts, and the photocatalysts' energy band gap was calculated as per the Tauc relation while fitting data to the Tauc plots. Fourier Transform Infrared Spectroscopy (FTIR) (Bruker TENSOR 27) was applied to analyze the HDPE polymer functional groups. Microscope (ZEISS Stemi 508) was used to observe the surface modifications of the polymer pellets, and photometer (Palintest 7100) was used to analyze the chemical oxygen demand (COD) levels in the solution under photocatalytic treatment.

2.3. Photocatalytic activity

The photocatalytic activity of degrading HDPE pellets was carried out in a wooden customized laboratory-scale reaction chamber (dimensions: 30x30x60cm) (Ali et al., 2016) lined inside with aluminum foil to minimize light absorbance by wood surface. A fitted tungsten light bulb of 200W served as the source of visible light. The HDPE pellets (100 mg) were placed into separate beakers containing TiO₂ (100 mg) and V-TiO₂ (100 mg) of the photocatalysts and distilled water (50 mL) at pH=2. The samples were exposed to the light source at the distance of 15 cm. The temperature in the chamber was varied between 60°C and 80°C. The average illuminance of the light in the chamber was 7K lux.

The mass change of the MPs were monitored and recorded at specific time intervals of 50 hours for 350 hours. The percentage mass loss was calculated as per the following expression (Thomas & Sandhyarani, 2013):

$$\text{Mass loss (\%)} = \frac{(M_0 - M)}{M_0} \times 100 \quad (1)$$

where M_0 represents the initial mass (mg) of the plastic pellets before the experiment, and M corresponds to their final mass (mg) after the experiment. The mass changes of the microplastics were fitted into the first-order expression. The comparison of rate constants obtained from the first order expression was used to quantitatively estimate the photocatalytic degradation as per the formula

$$\ln\left(\frac{C}{C_0}\right) = -\kappa_{app} t \quad (2)$$

where C_0 is the initial concentration of the organic compound (mg/L) (in this case, the mass of suspended plastics per volume of water), C is the concentration (mass) of plastic in (mg/L) at any given time during the experiment, and $-\kappa_{app}$ is the rate constant of the reaction at a particular irradiation time t .

2.4. Characterization of HDPE microplastic during photocatalytic oxidation

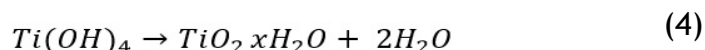
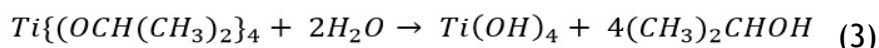
To investigate the properties of the surface of HDPE microplastics during photocatalytic oxidation, several assessments were conducted. First, FTIR was used to analyze the formation of functional groups. To gauge the extent of photo-oxidation, the carbonyl index was calculated. Additionally, the presence of oxidation by-products in the treated solution was determined by analysing its COD using the photometer. Lastly, surface modifications in the polymer pellets were observed via the microscope.

3. Results and discussion

3.1. Synthesis

The synthesis of titanium dioxide through the sol-gel (Seck et al., 2013) process involves two main steps. In the first step, titanium isopropoxide undergoes hydrolysis resulting in the formation of titanium hydroxide. The second step involves the condensation of the formed hydroxide leading to the formation of hydrated titanium oxide. Subsequently, the hydrated titanium oxide is subjected to calcination resulting in the formation of titania nanoparticles.

The reactions are represented in Equations 3 and 4, respectively:



During the precipitation of TiO_2 , two possible phases can be formed: anatase or rutile. Their formation is influenced by the pH and initial amount of water used. In an acidic environment, the anatase phase is favored (Wang et al., 2020). To prepare the TiO_2 and V- TiO_2 catalysts, the pH was adjusted to 2, and a water-to-titanium salt ratio of 2:1 was employed. These conditions were used to favor the formation of the anatase form.

3.2. Characterization

The results of powder X-ray diffraction studies of TiO_2 and V-doped TiO_2 samples, which provide information about their respective crystal structures, are presented in Fig. 1. below.

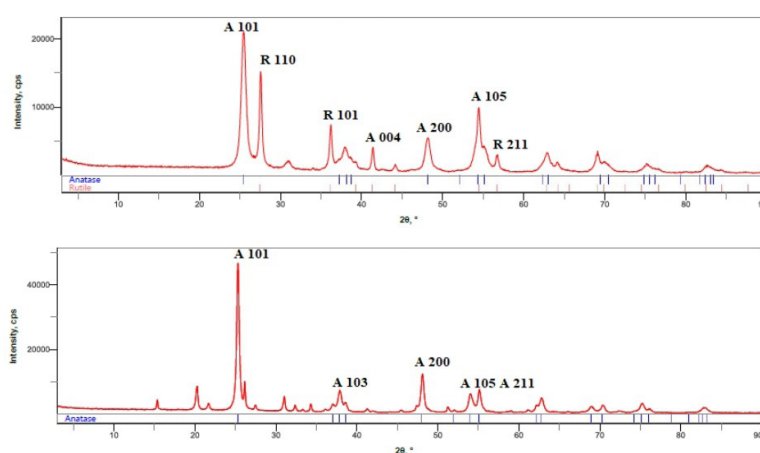


Figure 1. XRD patterns of a) TiO_2 and b) V-doped TiO_2 samples.

The crystalline forms of the unmodified titania showed a combination of the rutile and anatase phases (Fig. 1a.). However, when modified with vanadium only the anatase crystal form was obtained (Fig. 1b.). Both of them showed the tetragonal structural form, but the unit cell parameters of the V- TiO_2 increased due to the effect of vanadium ions in the structure of the titanium oxide. As the result, there was an overall growth in the lattice volume from 134.271 Å to 136.025 Å. The effect of modification was observed by the phase transformation from the rutile-anatase ratio of 1:2 in unmodified form to complete anatase form in the V-titania. The findings were in line with the study that observed the complete anatase form after doping

titanium oxide with vanadium (Bettinelli et al., 2007). The conversion of titanium oxide from the rutile to anatase phase is influenced by several factors, including calcination duration, temperature, synthesis method, and the type of metal dopant employed. The incorporation of V⁴⁺ cations into vacant Ti⁴⁺ positions in TiO₂ (rutile) was found to enhance the rutile to anatase phase transformation. This substitution was feasible due to the similar ionic radius of Ti⁴⁺ and V⁴⁺ measuring approx. 0.061 nm and 0.058 nm, respectively. Furthermore, the equal valency of these cations ensures electroneutrality within the TiO₂ anatase lattice. Consequently, the V⁴⁺ cations introduced into the rutile lattice served as nucleation sites for initiating the rutile-to-anatase phase transformation (De Yoreo, 2020).

The X-ray diffraction (XRD) analysis revealed presence of distinct peaks at specific 2θ values corresponding to (101), (004), (200), (105), and (211) crystallographic planes. These peaks were observed at 2θ values of 25, 37, 48, 54, and 55 degrees, respectively. The existence of the peaks indicated that the dominant phase of the formed titania was anatase. Although the particle sizes of the modified samples were found to be within the nano-range, it was observed that the modification led to an increase in particle sizes. This increase in size was confirmed by analyzing the crystalline dimensions using the Debye Scherrer's Equation (5). The unmodified TiO₂ particles exhibited sizes ranging 9.2 to 30.0 nm, while the V-TiO₂ particles displayed sizes in the 13.2-66.0 nm range.

(5)

where **D** is the particle size, **K** is the Scherrer constant, **λ** is the wavelength of the X-ray beam used (1.54, 184 Å) $D = \frac{K \lambda}{\beta \cos \theta}$ **l** width at half maximum (FWHM) of the peak, and **θ** is the Bragg angle.

Fig. 2. shows the SEM micrographs illustrating the morphology of the prepared particles. Both TiO₂ and V-TiO₂ powders appeared as spherical particles; the micrograph of V-TiO₂ revealed a consistent and uniform spherical particle morphology with some surface charge; while the TiO₂ micrograph showed some well dispersed irregular particles. The presence of vanadium ions within the structure of titanium oxide enhanced nanoparticle dispersion. The elemental composition of the synthesized nanoparticles was analyzed using EDX spectroscopy that indicated a modification of approx. 20% vanadium within the structural composition of titanium oxide.

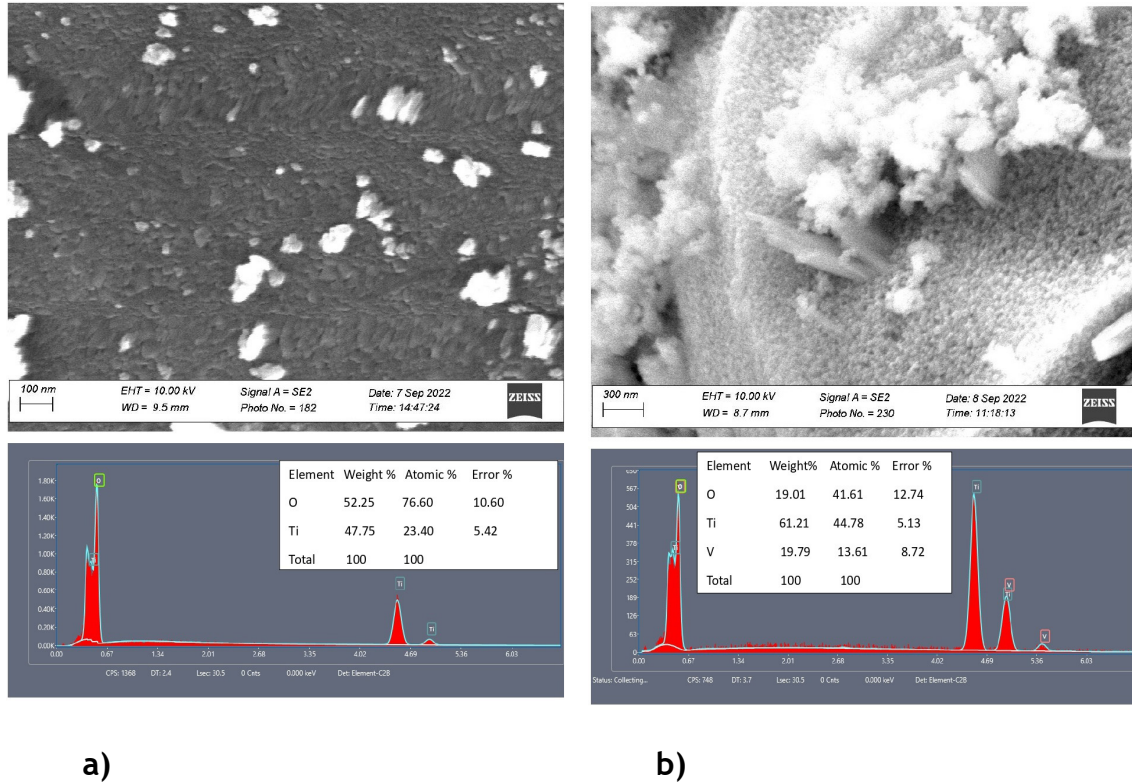


Figure 2. SEM images of a) TiO_2 and b) V-doped TiO_2 samples.

Fig. 3. shows the UV-Vis absorption spectra of TiO_2 and V- TiO_2 , respectively. In the spectra of pure TiO_2 , a peak was observed around 215 nm. However, V- TiO_2 exhibited a red-shift, with its peak reaching a maximum at 265 nm and extending up to 600 nm. This is associated with the vanadium dopant effect within the structure of titanium oxide. The band gaps were determined using Tauc relation and fitting the data into the Tauc plots, as illustrated in Fig. 4. Pure TiO_2 possessed the band gap energy of 3.45 eV, whereas V- TiO_2 had a lower band gap energy of 2.8 eV. This alteration in the band gap was attributed to the influence of the 3d orbital of vanadium, enabling V- TiO_2 catalysts to absorb energy within the visible light region of the electromagnetic spectrum (Wang & Xu, 2017).

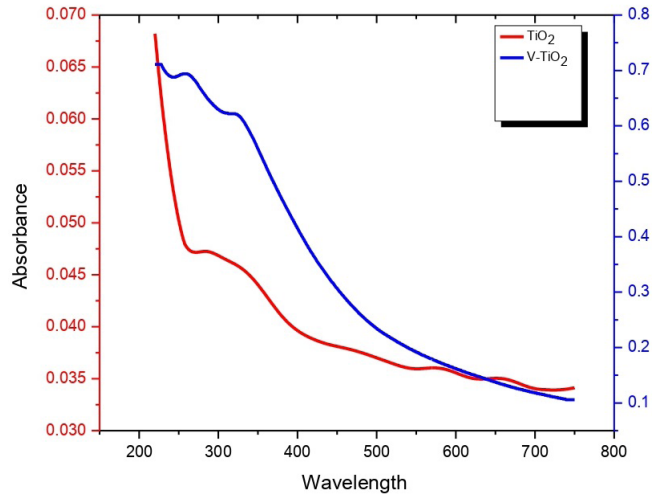


Figure 3. UV-Vis (integrated sphere) absorption of pure and V-doped TiO_2 samples.

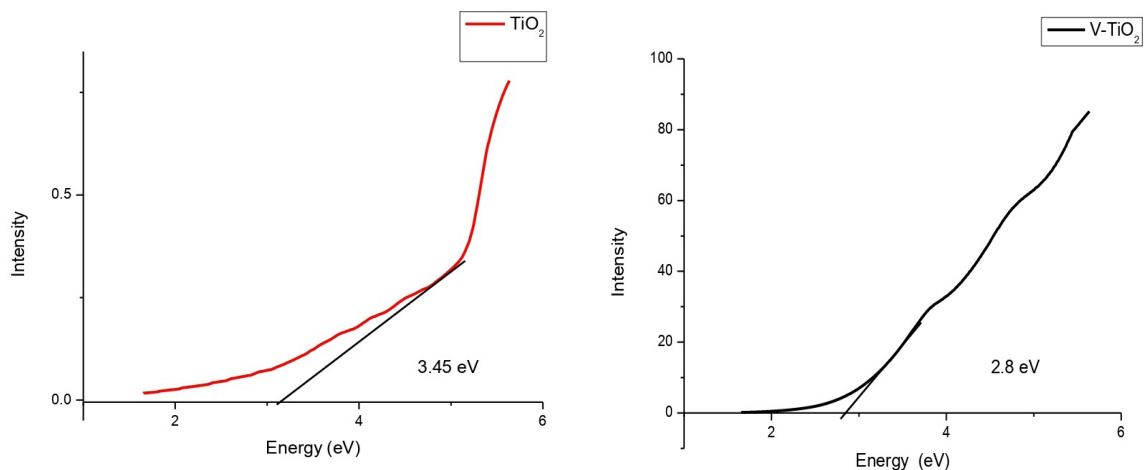


Figure 4. The band gap energies for the pure and V-doped TiO_2 samples.

3.4. Photocatalytic activity on microplastics

To assess the photocatalytic activity of V- TiO_2 , the degradation efficiency of HDPE pellets was quantitatively analyzed. The pellets measuring 1.9 mm in diameter and classified as microplastics were subjected to visible light irradiation for the duration of 350 hours in water at pH=2. The mass of the HDPE pellets was monitored at 50-hour intervals. The results revealed a significant reduction in plastic mass after 200 hours of illumination. Fig. 5. shows that the maximum reduction was 5.7% after 350 hours for V- TiO_2 , while TiO_2 nanoparticles exhibited only the 2% decrease.

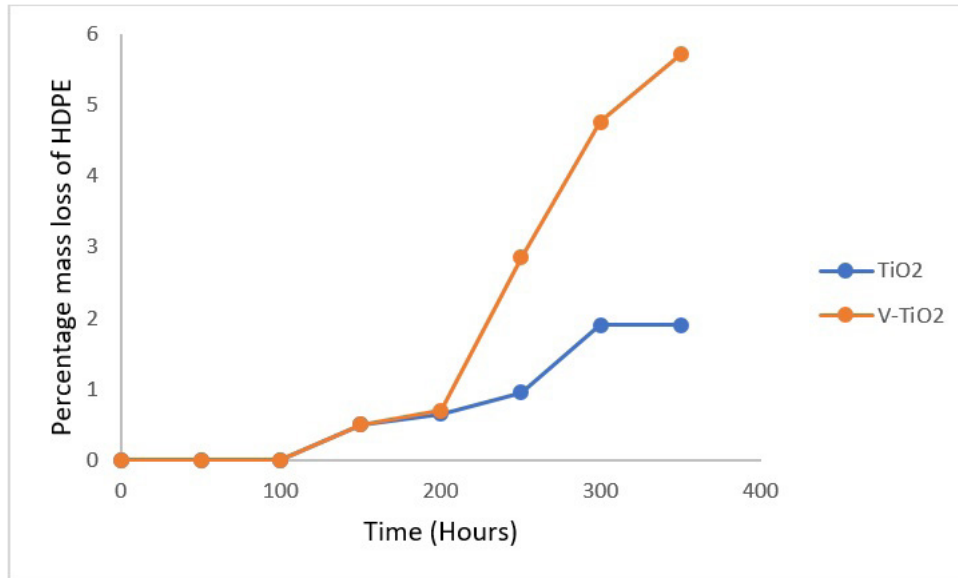


Figure 5. Percentage mass change of HDPE against time.

In a first-order reaction, the rate constant (k) plays a crucial role in determining the reaction rate. It measures the speed at which reactants are converted into products. When the mass change information was fitted into first-order kinetics (Fig. 6.), the rate constants obtained for TiO₂ and V-TiO₂ equaled 0.0019 and 0.0054, respectively, indicating that the reaction proceeded at a faster rate when V-TiO₂ was used as the photocatalyst compared to TiO₂. Furthermore, regression analysis was performed to examine the correlation between the catalysts and the photodegradation of HDPE pellets. The regression constants (R^2) for TiO₂ and V-TiO₂ were calculated as 0.5494 and 0.773, respectively. The higher R^2 value was associated with V-TiO₂, indicating a stronger correlation between the V-TiO₂ catalyst and photodegradation of HDPE pellets.

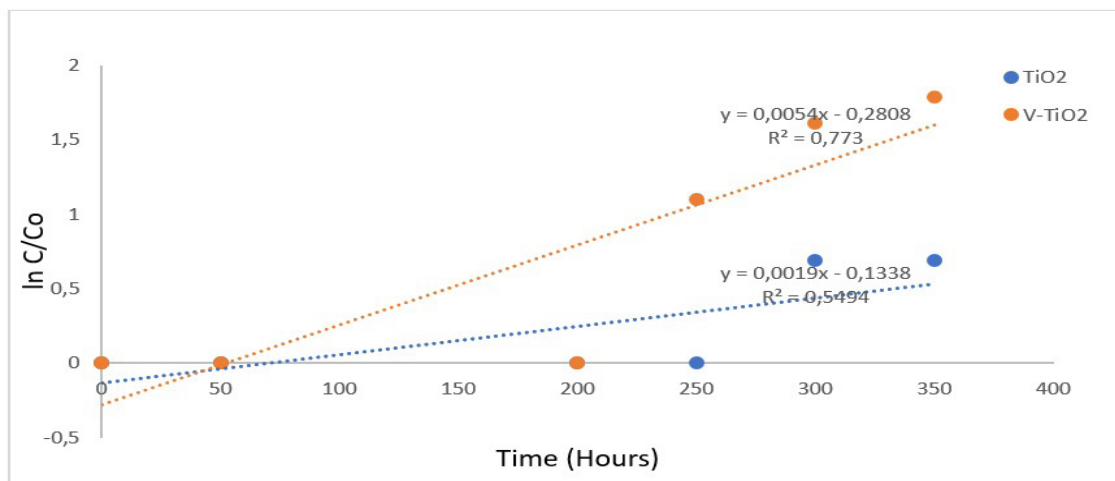


Figure 6. Mass change of HDPE fitted onto the pseudo-first-order kinetic model.

3.5. Surface changes on HDPE pellets

The microscope photographs shown in Fig. 7. demonstrate the surface modifications that occurred on the HDPE pellets, including color changes, morphology, and brittleness. The changes served as indicators of the photocatalytic degradation process. Normally, HDPE pellets have a whitish and translucent appearance, reflecting their natural color. Yet, after undergoing photodegradation the surface of the HDPE pellets exhibited a yellowish or brownish hue. This color change is attributed to the formation of carbonyl groups as well as presence of conjugated double bonds (Gewert et al., 2015). Additionally, the degradation process caused the HDPE surface to deform from its original circular shape resulting in an irregular form. The surface roughness grew, and cracks and depressions became evident as the degradation progressed. Furthermore, the photodegraded HDPE became opaquer with a more pronounced yellow or brown coloration. The pellets likewise displayed higher brittleness manifesting structural changes induced by the degradation process.

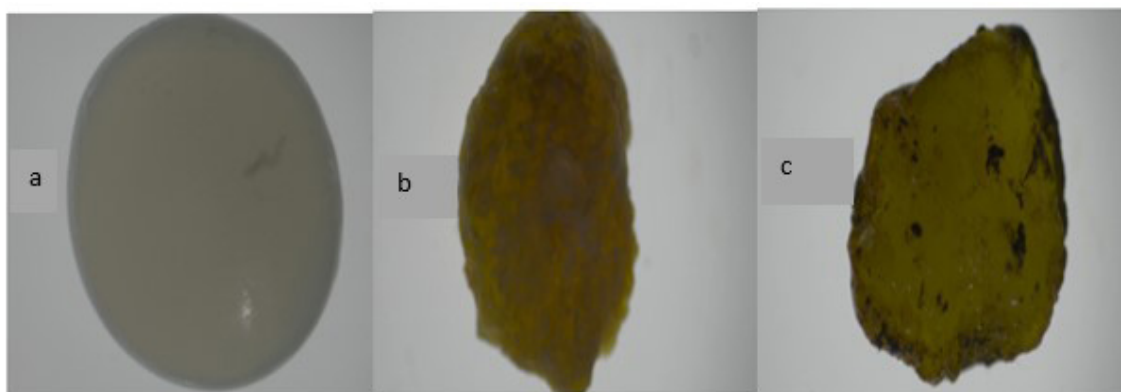


Figure 7. Microscope photographs illustrating the alterations on the surface of HDPE pellets (a) pure pellet, b) TiO_2 treated, c) V-TiO_2 treated)

To investigate the chemical changes induced by photodegradation in HDPE, the specific functional groups were analyzed using FTIR spectroscopy. The obtained spectra shown in Fig. 8. exhibited characteristic peaks in the range of $1705\text{-}1750\text{ cm}^{-1}$ after treatment with TiO_2 and V-TiO_2 catalysts. The peaks were indicative of carbonyl groups that formed as the result of polymer oxidation. Moreover, an additional broad band peak around 3200 cm^{-1} was observed specifically with the V-TiO_2 catalyst suggesting the presence of O-H groups. The peaks evidenced the formation of compounds such as ketones and carboxylic acids during the oxidation process, thereby confirming the occurrence of oxidation in HDPE pellets under visible light. Additionally, the presence of the V-TiO_2 catalyst implied an accelerated rate of oxidation resulting in the formation of carboxylic acids.

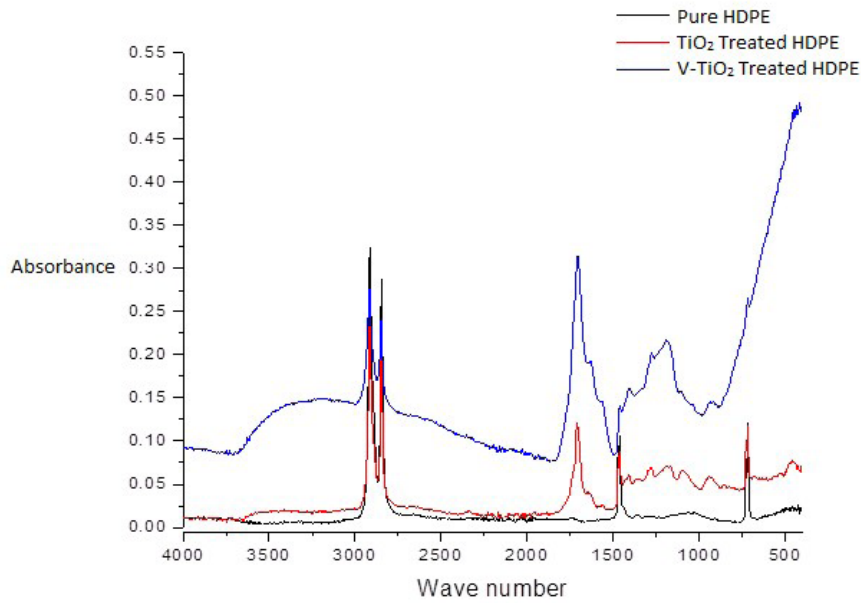


Figure 8. FTIR spectra for the photodegraded HDPE pellets.

3.6. Carbonyl index

To quantify the extent of photo-oxidation in HDPE pellets, the carbonyl index was measured. The index value was determined by comparing the absorbance of the carbonyl group at approx. 1710 cm^{-1} to the reference peak at 1380 cm^{-1} representing an internal thickness band used as shown in Equation 6 (Llorente-García et al., 2020) below. Table I presents the HDPE carbonyl index values showing an increase following irradiation in the presence of a catalyst. The results demonstrated a higher value in the presence of V-TiO₂ compared to TiO₂ alone. The addition of vanadium dopant to titanium dioxide contributed to the enhancement of HDPE oxidation elevating the carbonyl index from 1.97 to the maximum of 2.809.

$$\text{Carbonyl index (C.I)} = \frac{\text{Absorbance (1710)}}{\text{Reference (1380)}} \quad (6)$$

Table I. Carbonyl index values.

Entry	Polymer type	Carbonyl index
1	Pure HDPE	0.07
2	TiO ₂ treated HDPE	1.97
3	V-TiO ₂ treated HDPE	2.809

3.7. Chemical oxygen demand (COD) of the treated water

COD is a measurement indicating the quantity of organic compounds present in a water sample, which can be oxidized by strong chemical oxidizing agents. It provides an estimation of the amount of oxygen needed to chemically oxidize the organic substances in water. In this research, the COD values of the solutions were analyzed (see Table II). It was observed that both treatments resulted in the introduction of COD into the water during the degradation process. That occurred as the polymer molecules underwent fragmentation due to chain scission (Lin et al., 2020). However, the amount of COD present in the solution was higher when vanadium-modified titanium oxide was employed, which can be attributed to the accelerated oxidation rate of the reaction that led to the formation of smaller fragments. As the result, the vanadium-modified catalyst produced a greater quantity of smaller organic fragments resulting in a higher COD value in the resulting solution.

Table II. COD values.

Solution	COD (mg/L)
Distilled water	0
Solution with TiO ₂	72
Solution with V-TiO ₂	230

Some previous works on the photocatalysis of HDPE microplastics and their respective % mass loss are shown in Table III.

Table III. Comparison of HDPE results.

Entry	Nature of HDPE	Size (µm)	Catalyst used	% mass loss	Reference
1	Microbeads	814	N-TiO ₂	0.22	(Llorente-García et al., 2020)
		382		4.65	
2	Microbeads	725	N-TiO ₂	1.85	(Ariza-Tarazona et al., 2019)
3	Pellets	1900	V-TiO ₂	5.7	This study

3.8. Degradation mechanism

The degradation of HDPE polymer is caused by the formation of reactive species O₂•⁻ and free OH•. These species are produced through a series of reaction pathways involving the photogeneration of electrons (e⁻) and positively charged holes (h⁺) in

the photocatalyst. When light energy is absorbed by the V-TiO₂ catalyst, electron-hole pairs are generated; and water and oxygen molecules nearby are adsorbed onto the photocatalyst's active sites resulting in the formation of O₂•⁻ and OH• species.

The OH• breaks the C-H bonds of the polymer backbone, and/or O₂•⁻ abstracts a hydrogen atom from the polymeric chain of HDPE forming polyethylene alkyl radicals and peroxy radicals (ROO•). These species enhance the propagation process leading to the formation of hydroperoxide species. Peroxy radicals (ROO•) further react with HDPE or other radicals generating hydroperoxides (ROOH). These generated radicals (alkyl radicals, peroxy radicals) undergo further reactions with HDPE chains leading to more chain scission and formation of smaller fragments. Termination occurs when the smaller fragments resulting from chain scission undergo further oxidation and rearrangement reactions leading to the formation of ketones and carboxylic acids as end products.

4. Conclusion

This study investigated the application of vanadium-modified titanium oxide as a photocatalyst for the degradation of high-density polyethylene under visible light and acidic conditions (pH=2). The research results demonstrate the efficacy of vanadium modified titanium oxide in promoting HDPE degradation as well as formation of ketones and carboxylic acids as degradation products. The utilization of visible light as an energy source for the photocatalytic degradation of HDPE is particularly promising as it expands the range of available light sources and enhances the potential for practical applications. The incorporation of vanadium into titanium oxide facilitated the absorption of visible light and increased the separation of electron-hole pairs leading to improved photocatalytic performance. The acidic environment facilitated the generation of reactive species - hydrogen ions (H⁺) and hydroxyl radicals (•OH) - that promoted the degradation reactions. The COD measurements indicated the presence of organic compounds in the water, with the V-TiO₂ treatment generating a higher COD due to the formation of more numerous and smaller organic fragments through accelerated oxidation. The study findings shed light on the potential of vanadium-modified titanium oxide as an efficient photocatalyst for HDPE degradation under visible light and acidic conditions as a sustainable method for eradicating microplastics in water.

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