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Carbon Emission Pathways of Biodegradable Thermoplastic-based Species in Natural and Simulated Aqueous Conditions

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Authors' contributions

This work was carried out in collaboration between both authors. Author OED did conceptualization, methodology, software, supervision, writing-reviewing and editing. Author AAB did data curation, writing-original draft preparation, visualization and investigation. Both authors read and approved the final manuscript.

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Original Research Article

ABSTRACT

This study assessed the carbon emission pathways of the biodegradation processes of bio-based thermoplastic moieties in two aqueous (surface and simulated marine water) environments and its implications on environmental quality. The physicochemical parameters of the aqueous media were determined using standard methods. The American Society for Testing and Materials' standard was used to assess amount of CO₂ evolved. Cellulose, bioplastic and polyethylene were inserted in two aquatic environments and arranged thrice in a randomized experimental arrangement of 2x4x3. Ultimate biodegradations of the test films were monitored using Scanning Electron Microscopy (SEM). The amount of $CO₂$ evolved was assayed using the titration method. Data obtained were

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subjected to descriptive and inferential statistical analyses using Statistical Packages for Social Sciences (SPSS) version 25.0. After biodegradation, the initial values of the physicochemical parameters were within recommended values of the WHO standards with slight (less than 2%) differences. Moreover, $CO₂$ captured from the two aqueous conditions were lower than the amount of $CO₂$ evolved in aqueous solution with cellulose which is a natural polymer in this order: 88.725 \times 10² mg from the soaked cellulose samples in marine > 85.215 \times 10² mg of CO₂ evolved from cellulose entrenched in surface water > 82.758×10^2 mg of CO₂ evolved from bioplastic soaked in marine water > 82.758×10^{2} mg of CO₂ evolved from bioplastic soaked in surface water > 65.046 \times 10² mg of CO₂ evolved from polyethylene soaked in marine water > 60.152 \times 10² mg of CO₂ evolved from polyethylene soaked in surface water. Moreover, the SEM results revealed high level of biodegradation and growth of biofilm on the biodegradable thermoplastics while the nylon 6 had little or no biofilm growth because of the recalcitrant nature. This study concluded that some biodegradable thermoplastics can biodegrade totally in aquatic environments without the release of greenhouse gases that could threaten the integrity of the aquatic environment as well as the release of toxic residues.

Keywords: Carbon emission; bioplastic packaging nylon; freshwater; marine water; bioremediation; plastic pollution.

1. INTRODUCTION

There has been a growing demand to use biodegradable bioplastics of natural origin as a suitable replacement for non-biodegradable traditional plastics because the proportion of non-biodegradable single-use plastics with shortterm benefits that are produced globally is up to 900 billion [1]. This amount constitutes a significant portion of the plastic waste structure in the environment in which the terrestrial and aquatic environments are affected as many single–use plastic wastes form the bulk of the litter found in them [2]. The use of natural biogenic polymers such as starch, and fiber in bioplastics provides a solution for waste disposal and reduction of carbon and energy footprints. Besides, natural polymers that are used to prepare bioplastics are renewable, biodegradable, cost effective, low density, sustainable, and environmentally-friendly [3]. These attributes confer the biodegradability potential of bioplastics. However, the biosafety of the bioplastic biodegradability process is germane to encouraging public acceptability and adoption of the bioplastic species in society across the globe. According to *[4]* the evolution of carbon dioxide gases during biodegradation confirms the ultimate biodegradation of bioplastic entities in any environment without toxic residues. Under specific conditions, water, carbon dioxide, and methane are the natural elements reported after the biodegradation of bioplastics as well as increased cell biomass [5]. Therefore, biodegradable bioplastics can be composted in industrial composting facilities or home composting systems leading to the

production of nutrient-rich compost. Thus, waste could be easily diverted from landfills through composting; thereby reducing environmental pollution [6]. Moreover, in assessing the biosafety of the biodegradation process, the amount of carbon dioxide released during bioplastic biodegradation is usually lower than the carbon footprints of conventional plastics derived from petrochemicals and some natural plastics [7]. Consequently, mitigating the impact of greenhouse gas emissions as well as contributing to the overall goal of reducing carbon emission pathways. The ecological benefits of this closed-loop cycle of organic matter ensures wastes minimization, reduced reliance on non-renewable resources while fostering sustainable practices that support the regeneration of natural systems [8] In addition, microbial diversities responsible for the breakdown of the bioplastic's species increase in cell biomass after assimilating part of the carbonbased nutrient released during the mineralization of the biodegradable bioplastics [9]. In another vein, physico-chemical properties of the medium such as aquatic environment are safe for use as microplastics and nanoplastics are not found in the environment as carbon-based residues [10].

In this study, the carbon emission footprints of the biodegradable thermoplastic blends were evaluated. Using the International Standard methods, three species of plastics which are biodegradable plastic blends of thermoplastic base, cellulose (positive control) and polyethylene (negative control) were subjected to two aqueous (surface water and simulated marine water) conditions with a view to assess the biosafety of the real biodegradable bioplastics in aqueous environment after mineralization.

2. MATERIALS AND METHODS

2.1 Preparations of Natural and Simulated Aqueous Conditions

The two aqueous environments used in this study are natural and simulated marine water. The natural aqueous condition was obtained from flowing stream in an unperturbed environment while the simulated aqueous conditions was prepared by adding each compound of 24.53 g/l of NaCl, 25.20 g/l of MgCl² ∙ 6H2O , 4.09 g/l of Na2SO4, 1.16 g/l of CaCl₂, 0.695 g/l of KCl, 0.201 g/l of NaHCO₃. 0.101 g/l of KBr, 0.027 g/l of H3BO3, 0.025 g/l of SrCl² ∙ 6H2O, 0.003 g/l of NaF dissolved in one liter of distilled water to feign marine water conditions. The mean monthly temperature ranged between 25°C and 30°C while the mean monthly relative humidity was below 65.

2.2 Sources of The Test Plastics

Three test materials used for the study are nylon 6 packaging bag, biodegradable thermoplastic blends and cellulose. The biodegradable thermoplastic blend was PBAT–PBS (30/70) (commercially named Bionolle 1020) obtained from the Council for Scientific and Industrial Research (CSIR), Pretoria, South Africa. The Nylon 6 was bought from a local store in Akure, Ondo State-Nigeria while cellulose was obtained from the Environmental Management and Toxicology (EMT) Laboratory, Department of Biological Sciences, Elizade University, Ilara-Mokin, Ondo State-Nigeria.

2.3 Determinations of the Physicochemical Properties of Water

The temperature readings of the natural and simulated aqueous conditions were taken with the aid of a digital thermometer on-site. The pH and total dissolved solids (TDS) and electrical conductivity (EC) of the water samples were measured with HANNA HI 9810 pH-TDS meter. The meter was standardized with a buffer solution (i.e., buffer 7 and 9). Total Suspended Solids (TSS) in natural and simulated aqueous conditions were measured using the filtering technique according to the established protocols of APHA [11]. The Dissolved Oxygen (DO) method was used using titration methods while

turbidity of the natural and simulated aqueous conditions were determined using Nephelometric method as described in [12]. The heavy metal contents of the natural and simulated aqueous conditions were determined using digestion and atomic spectrophotometry methods.

2.4 Experimental Design

Following the procedures of American Society of Testing and Materials [13], five hundred mls of natural aqueous solution (surface water) and simulated aqueous conditions (marine water) were added respectively to each 1000 mls of twenty-four respirometric glass jar of height 12 cm and width 4 cm. The test materials of bioplastic, nylon-6 films were cut into sizes of 2 cm by 2 cm. Five hundred grammes each of the bioplastic, nylon-6 films and the powdered cellulose as well as the blank were released into the surface and marine water samples. The experimental design was arranged in three replicates in a randomized design of 4x2x3. Thereafter, 40 ml of 1 N KOH (Potassium hydroxide) were poured into a sterilized 50 ml glass beaker and placed in all the respirometric glass jars to capture the evolved CO2. The respirometric jars were incubated at 58ºC for four months. Readings were taking every other day.

2.5 Analytical Characterization

2.5.1 Scanning Electron Microscopy (SEM)

The morphology of the polymers was characterized using a Scanning Electron Microscope (SEM). The samples sent out for the imaging were cleaned using distilled water, air dried and put into paper envelopes before the analysis. The standard procedures for sample preparation and analysis were followed to ensure the maximum results.

2.5.2 Calculations for biodegradation test

To determine the concentration of $CO₂$ evolved by titration method, calculations were made using the formular below as described by [14]:

 $CO_{2(g)} = (NKOH x ml KOH - ml HCl x 1N)$ HCl) x 44 / 2.

 $CO_{2(q)}$ is the amount of Carbon (iv) oxide evolved, NKOH is the normality of KOH used during titration, ml HCl is the amount of HCl used during titration to get the endpoint of titration process.

1N HCl is the normality of the HCl used.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Properties of Natural Aqueous Conditions before and After Biodegradation

As reported, Table 1 displayed the physicochemical properties of natural aqueous condition before and after the biodegradation processes. The pH of the natural aqueous sample was slightly (7.7) alkaline in nature and after the test in water (7.8) with cellulose sample. Natural aqueous condition embedded with bioplastic, was 7.7 before the experiment and 7.9 after the experiment. Whereas, pH of water with nylon 6 was 7.7 before and 7.6 after the test. These results showed a decrease in pH by 0.1 after the test. The pH of the control sample (blank) was 7.7 before the experiment and same 7.7 after the experiment. This may be because no test polymer was added. Other parameters such as electrical conductivity, temperature, dissolved oxygen, turbidity, total dissolved solids, and total suspended solids, obtained before and after the test had slight differences across all water samples with values within the recommended values of the World Health Organization (WHO). This revealed that the aqueous media was obtained from unperturbed surface water because human activities were minimal around the sampling area. The concentrations of metals found in water were within the permissible level recommended by WHO. However, the concentrations of lead found in the initial concentrations of the aqueous solution were higher than the recommended allowance for aqueous medium. However, the concentrations of iron in the water after each medium with the polymers varies slightly at almost 2% reduction in the concentrations. This may be attributed to the fact that iron is a strong reducing agent because iron releases electrons to the available oxygen in the aqueous media containing the polymers [14].

3.2 Physicochemical Qualities of Marine Water Samples Before and After Biodegradation

The physicochemical properties of simulated aqueous conditions (marine water) before and after the biodegradation of the test polymers are shown in Table 1. The value (8.2) of the pH before biodegradation was basic in nature. In

water embedded with cellulose sample, the pH increased (8.3) after the experiment. A similar increase in pH values from 8.2 to 8.3 was reported in the natural aqueous condition with bioplastic sample. However, water with nylon 6 had pH value of 8.2 before the experiment and 8.1 after the experiment while in water as a control sample (blank), no changes in the pH (8.2) was reported. Nevertheless, the increase in the pH by 0.1 after the test in water samples with cellulose and bioplastic ascertains the validity criteria of the test. The values of the other variables, such as electrical conductivity, temperature, dissolved oxygen, turbidity, total dissolved solids, and total suspended solids, reported before and after the test also had slight differences across the different water samples; although with values within the recommended permissible limits of the World Health Organization. Similarly, the metal concentrations for cadmium, Lead, Zinc and Iron reduced after soaking the test polymers with about 1%.

3.3 Carbon (iv) Oxide (CO2) Evolution of Bioplastic Packaging Nylon, Cellulose and Synthetic Nylon in Natural and Simulated Aqueous Conditions Across Thirty (30) Days

Fig 1 revealed the carbon (iv) oxides $(CO₂)$ evolved in both natural aqueous condition with test materials for the first month. In the surface water, the amount of $CO₂$ evolved from natural aqueous condition sunk with test materials ranging from -0.799×10^2 mg to -1.775×10^2 mg. The CO2 evolved from bioplastic sunk in freshwater was -0.799×10^2 mg while that of cellulose was -1.322×10^2 mg with the synthetic nylon 6 having CO₂ evolution at - 1.775x10² mg and control were -1.337×10^2 mg. At the initial stage (Day 3) of experiment, no $(-1.322 \times 10^2 \,\text{mg})$, -0.799×10^2 mg, and - 1.775 $\times 10^2$ mg) CO₂ evolution was reported in natural aqueous condition with cellulose, bioplastics and synthetic nylon 6 respectively. Similarly, throughout the days in the first month up till the end of the month (Day 30), there were no amount of $CO₂$ captured. However, mean values of CO₂ recorded at the end of the month for natural aqueous condition containing the test materials were presented as followed; cellulose (- 4.040 \times 10² mg), bioplastic (-0.858 \times 10² mg), synthetic nylon 6 $(-8.751 \times 10^2 \text{ mg})$ and control $(4.349\times10^2$ mg). This result was similar to the report of the study carried out by [15]. The lack of CO2 evolved may be due to the fact that the microbial communities responsible for the

Analysis	Cellulose		Bioplastics		Nylon-6		Blank		WHO/
	Before	After	Before	After	Before	After	Before	After	USEPA limits
Electrical conductivity $(\mu S/cm)$	306.00	307.00	306.00	308.00	306.00	306.00	306.00	305.00	NA
Temperature (°C)	20.30	20.40	20.30	20.50	20.30	20.20	20.30	20.30	NA
pH	7.7	7.8	7.7	7.9	7.7	7.6	7.7	7.7	$6.5 - 8.5$
Dissolved Oxygen (DO) Turbidity (m)	2.67 7.80	2.68 7.90	2.67 7.80	2.69 8.00	2.67 7.80	2.65 7.80	2.67 7.80	2.66 7.70	NA NA
Solid Dissolved Total (mg/L)	153.00	154.00	153.00	155.00	153.00	152.00	153.00	152.00	1000
Total Suspended Solid (mg/L)				0.8				0.9	NA
Cadmium (Cd) (ppm)	0.008	0.007	0.008	0.007	0.008	0.008	0.008	0.008	0.01
Lead (Pb) (ppm)	0.032	0.028	0.032	0.031	0.032	0.031	0.032	0.032	0.00001
$Zinc(Zn)$ (ppm)	0.272	0.262	0.272	0.270	0.272	0.270	0.272	0.271	3.0
Iron (Fe) (ppm)	0.2185	0.2181	0.2185	0.2178	0.2185	0.2180	0.2185	0.2182	0.3

Table 1. Physicochemical properties of the natural aqueous condition before and after

Table 2. Physicochemical properties of simulated aqueous condition before and after Biodegradation Processes of the Polymers

Key: NAC-BL = Natural Aqueous Condition-Blank, NAC -CE = Natural Aqueous Condition-Cellulose, NAC -BP = Natural Aqueous Condition-Bioplastics, NAC -NY = Natural Aqueous Condition-Nylon 6

SAC-BL = Simulated Aqueous Condition-Blank, SAC-CE = Simulated Aqueous Condition-Cellulose, SAC-BP = Simulated Aqueous Condition-Bioplastics, SAC -NY = Simulated Aqueous Condition-Nylon 6

Fig. 2. Carbon (iv) Oxide (CO2) evolution in natural and simulated aqueous conditions across sixty (60) Days

Key: NAC-BL = Natural Aqueous Condition-Blank, NAC -CE = Natural Aqueous Condition-Cellulose, NAC -BP = Natural Aqueous Condition-Bioplastics, NAC -NY = Natural Aqueous Condition-Nylon 6

SAC-BL = Simulated Aqueous Condition-Blank, SAC-CE = Simulated Aqueous Condition-Cellulose, SAC-BP = Simulated Aqueous Condition-Bioplastics, SAC -NY = Simulated Aqueous Condition-Nylon 6

Fig. 3. Carbon (iv) Oxide (CO2) Evolution in natural and simulated aqueous conditions across ninety (90) Days

Key: NAC-BL = Natural Aqueous Condition-Blank, NAC -CE = Natural Aqueous Condition-Cellulose, NAC -BP = Natural Aqueous Condition-Bioplastics, NAC -NY = Natural Aqueous Condition-Nylon 6

SAC-BL = Simulated Aqueous Condition-Blank, SAC-CE = Simulated Aqueous Condition-Cellulose, SAC-BP = Simulated Aqueous Condition-Bioplastics, SAC -NY = Simulated Aqueous Condition-Nylon 6

Simulated Aqueous Condition-Nylon 6

degradation processes are in their lag phase. According to [16] at this phase the microbes are acclimatizing to the environmental conditions of the medium as well as attempting to colonize the polymers respectively as potential carbon sources.

Similarly, in simulated aqueous samples, CO² evolution was not captured across all samples at the beginning of the experiment (Day 3). The $CO₂$ concentration was in this trend, $-1.447 \times 10²$ mg (control), -1.344×10^2 mg (water with cellulose), -0.917×10^2 mg (simulated aqueous samples with bioplastic), and -2.241×10^2 mg (simulated aqueous condition with synthetic nylon 6). All through the month up to the end of the month (Day 30), $CO₂$ evolution was not reported in all simulated aqueous condition inserted with cellulose, bioplastic, synthetic nylon 6 and control in this trend respectively; - 4.447×10²mg, -1.796×10²mg, -10.715×10²mg, and -5.473×10^2 mg. This may be due to the fact that the microbes responsible for the biodegradation processes are yet at the lag phase of their growth attempting to acclimatize to the conditions as well as trying to form biofilms around the polymeric samples [17].

3.4 Carbon (iv) Oxide (CO2) Evolution of Bioplastic Packaging Nylon, Cellulose and Synthetic Nylon in Natural and Simulated Aqueous Conditions Across Sixty (60) Days

The concentrations of carbon (iv) oxide $(CO₂)$ evolved in both freshwater and marine water with test materials were revealed in Fig 2. As shown, CO² evolved was not captured in the fresh water sample at the beginning of the month (Day 33) across all samples. However, there was a gradual improvement in the amount of CO² evolved from control with mean value of 0.504×10²mg at Day 51. Similarly, for the other samples, the amount of $CO₂$ evolved were 1.002×10^2 mg for water embedded with cellulose at Day 45 , 0.602×10^2 mg for freshwater embedded with bioplastic at Day 36, and 0.197×10^2 mg for water embedded with synthetic nylon 6 at Day 60, which was the last day of the second month. Moreover, at the last day of the month, the final amount of $CO₂$ evolved from the freshwater embedded with the test polymeric materials improved in this trend: 11.098×10^2 mg (freshwater with cellulose), 9.907×10^2 mg (freshwater with bioplastic) and 5.429×10^2 mg (freshwater with synthetic nylon 6) respectively.

At this stage, the polymers contain significant biofilms on it which increase the rates of biodegradation and the amount of $CO₂$ evolved [17].

Conversely to the evolution of $CO₂$ recorded at the second month in surface water, there was no CO² captured at the beginning of the second month (Day 33) in marine water samples; across all the samples with values ranged from - 1.077×10^2 mg (marine water embedded with bioplastics) to -10.377 \times 10² mg (marine water embedded with synthetic nylon 6). According to [18] this may be attributed to the fact that fewer microbes that are referred to as stenohalides are usually found as normal flora of marine environment. These stenohalides are the ones responsible for the biodegradation of the polymers. Although, the CO₂ evolution had an increase on Day 54 in the control sample (blank) $(0.156 \times 10^2 \text{ mg})$, also in water with cellulose $(0.947 \times 10^2 \text{ mg})$ at Day 45 and in water with bioplastic (0.664×10²mg) at Day 39. However, in water embedded with a nylon-6 sample, there was no $CO₂$ evolution captured throughout the month of March. This may be due to the recalcitrant nature of the synthetic nylon 6 polymer [19]. Moreover, at Day 60, water sample as control, water sample embedded with cellulose and bioplastic were 2.797×10^2 mg, 12.914×10^2 mg, 11.415×10^2 mg, respectively.

In comparing the amount of $CO₂$ evolved in freshwater and marine water, the highest $(12.914 \times 10^2 \text{ mg})$ CO₂ evolved was in marine water samples with cellulose and 11.415×10^2 mg for marine water with bioplastic sample; followed by that of freshwater samples, which were 11.098×10^2 mg for water with cellulose and 9.907×10² mg for water embedded in bioplastic sample in the second month. According to [20] naturally occurring mineral components in marine water are higher than that of surface water and this available mineral wealth may increase the biodegradation process of the polymers by microbial communities. Thereby, increasing the amount of $CO₂$ evolved.

3.5 Carbon (iv) Oxide (CO2) Evolution of Bioplastic Packaging Nylon, Cellulose and Synthetic Nylon in Natural and Simulated Aqueous Conditions Across Ninety (90) Days

Concentrations of carbon (iv) oxide (CO_2) evolved in fresh and marine water samples with

test materials in the third month were shown in Fig 3. The $CO₂$ evolved in fresh water at the beginning of the month (Day 63) was 7.321×10² mg for the control water sample, 13.670×10² mg for the water with cellulose sample; 11.460×10^2 mg for water embedded with bioplastic and 2.128×10² mg for water with synthetic nylon 6. There was a constant increase in the $CO₂$ evolved across the whole month in all the samples up till the end of the month on Day 90 with mean values of 29.840×10^2 mg, 41.210×10^2 mg, 36.553×10^2 mg, and 25.360×10^2 mg for the control, water embedded with cellulose, bioplastic, and synthetic nylon 6 samples, respectively.

Moreover, in marine water samples, CO₂ evolution also maintained a constant increase, the same as that of fresh water samples from the beginning of the month at Day 63, 4.343×10²mg for control, 15.692×10^2 mg for water samples with cellulose, 13.723×10^2 mg for water with bioplastic, which continuously increased in the CO² evolved throughout the month up to Day 90 (end of the month). In the control samples, water with cellulose, and bioplastic, the values were 24.996×10²mg, 43.601×10²mg, and 39.937×10² mg, respectively. The amount of $CO₂$ released from the experiment throughout the months revealed that amount of $CO₂$ released from bioplastic in both surface and marine water were lower than amount of $CO₂$ released from the two aqueous solutions containing cellulose. This is an indication that the biodegradation processes of bioplastic in water environment is safe [21]; as well as sustainable [22]. Physical examination of the water revealed that residues of cellulose and bioplastics were not present in the aqueous solution. Therefore, at the end of 120 days, there were no residues observed in the medium. This result corroborated with the report carried out by [23] and [24].

Nylon 6 sample had a value of -1.855×10²mg at Day 63, up until Day 69, there was an improvement $(1.784 \times 10^2 \text{ mg})$ of CO₂ evolved, similarly, up to the end of the month (Day 90) the amount of $CO₂$ evolved were 19.871 \times 10² mg.

Moreover, cellulose and bioplastic in marine water had the highest $(43.601 \times 10^2 \text{ mg}$ and 39.937×10² mg respectively) amount of CO² evolution than that of fresh water, with the mean values of 41.210×10² mg for water sunk with cellulose and 36.553×10^{2} mg for water sunk with bioplastic films. Similarly, this result corroborated with the result obtained from [25]. Although in

fresh water, the control and water embedded with synthetic nylon 6 have the highest $(29.84 \times 10^2 \text{ mg and } 25.36 \times 10^2 \text{ mg, respectively})$ concentrations of $CO₂$ than that of marine water, which had $CO₂$ concentration of 24.996 \times 10² mg for the control and 19.871×10^2 mg for the water sunk with synthetic nylon 6 sample.

3.6 Carbon (iv) Oxide (CO2) Evolution of Bioplastic Packaging Nylon, Cellulose and Synthetic Nylon in Natural and Simulated Aqueous Conditions Across One-hundred and Twenty (120) Days

Fig 4 showed the carbon (iv) oxide evolution in the fresh and marine water samples with test materials in the fourth month of the experiment. In fresh water samples, the $CO₂$ evolution was in this order, 32.929×10^2 mg for control, 44.725×10² mg for water sunk with cellulose, 40.394×10² mg for water embedded with bioplastic and 28.591×10^2 mg in water embedded with synthetic nylon 6 at the beginning of the month (Day 93). There was a constant increase in the concentration of CO₂ evolved across all the samples up to Day 120. These results were similar to the reports presented by [26] on plastic biodegradation processes. The amount of CO₂ evolved reported were in this trend; 65.046×10^2 mg, 85.215×10^2 mg, 83.660×10^2 mg, and 63.514×10^2 mg for control, water embedded with cellulose, bioplastic, and synthetic nylon 6, respectively.

Similarly, in marine water samples, the CO₂ evolved at the beginning of the fourth month (Day 93^{rd}) was in this order; 28.040×10^2 mg for control, 47.214×10^2 mg for water sunk with cellulose, 43.50×10² mg for water with bioplastic, and 23.135×10^2 mg for water embedded with synthetic nylon 6. However, the amount of $CO₂$ evolved increased throughout the months across all samples in this trend: 62.185×10² mg for control > 82.725×10^2 mg for water embedded with cellulose > 82.758×10^2 mg for water with bioplastic $> 60.152 \times 10^2$ mg for water embedded with synthetic nylon 6 by the end of the fourth month (Day 120).

In comparison, the concentration of $CO₂$ evolved in fresh and marine water samples with cellulose samples respectively had the highest $(88.725\times10^2 \text{ mg})$ concentration of $CO₂$ released, followed by bioplastic in marine water samples $(82.758\times10^2$ mg) while that of fresh water samples with cellulose $(85.215 \times 10^2 \text{ mg})$ and bioplastic (83.660×102 mg) were reported as

presented [27]. In contrast, the concentration of CO² evolved in fresh water samples had the highest (63.514 \times 10² mg for control > 65.046 \times 10² for synthetic nylon 6) than that of marine water samples, the concentration of CO₂ evolved were 60.152×10² mg for synthetic nylon 6 and 62.185×10² mg for control.The reduction in the amount of CO² evolved could be attributed to the recalcitrant nature of the nylon 6 [28]. This is because polymer characteristics such as tactility, crystallinity, molecular weight, type of functional groups and substituents such as plasticizers or additives presents in the chemical structure of the polymer are germane factors influencing the biodegradation of polymers [29].

3.7 Scanning Electron Microscope (SEM) of the Test Materials

SEM imageries showing the changes in surface morphologies of the films due to microbial activity on the plastic films (bioplastics and nylon 6) used in the degradation test were shown in Plates 1, 2, 3 and 4. The SEM imaging was done on the samples before and after the degradation test (four months).

Plates 1 and 2 also showed the differences in the morphologies of bioplastic material (PBS 1020) samples before microbial attack and after microbial activity when the bioplastic was soaked in the natural and simulated marine aqueous solutions.

Plate 1. SEM Image of bioplastic (PBS 1020) before test and 4 months after in fresh water

Plate 2. SEM Image of bioplastic (PBS 1020) before test and 4 months after in marine water

Plate 3. SEM Image of synthetic nylon 6 before test and 4 months after in fresh water

Plate 4. SEM Image of synthetic nylon 6 before test and 4 months after in marine water

However, Plates 3 and 4 showed the degree of biodegradation of nylon 6 in the natural and the simulated aquatic environments respectively. In the two aquatic environments, little microbial attack was observed on the film. This may be because of the non-biodegradable nature of the nylon 6 [30] and [31]. The plates showed the level of degradation of bioplastics with the production of biofilms after the degradation test in the different sampled environments [32]. Nylon 6 showed fewer biofilms before or after the degradation test due to its slow rate of degradation across the four months.

4. CONCLUSION

The backlog of plastic wastes in aquatic ecosystems is one of the unconquered global
environmental problems because global environmental problems because global production of plastics and their consumption increased indiscreetly daily. Importantly, biodegradable plastics has been adjourned the best solution to the challenge. Yet, there is need to take into account and ascertain the biosafety of the biodegradation process by assessing the

magnitude of carbon footprint released and the physicochemical status of the aquatic environment after the experiment. This is necessary because each biodegradable plastic has specific biodegradation conditions and may not biodegrade ultimately as claimed by some manufacturers. Otherwise, one may assume that they are impeccably safe for aquatic ecosystems due to their biodegradable characters and ability to evolve carbon (iv) oxide $(CO₂)$ as sign of ultimate biodegradation. However, this study concluded that the bioplastic studied biodegrade ultimately and that the amount of carbon (iv) oxide that were released were lower than the amount of CO₂ evolved by natural biodegradable plastic such as cellulose. Thus, they are safe in aquatic ecosystem. Besides, the physiochemical parameters of the two aqueous solutions assessed after the biodegradation processes were within the recommended allowance permitted by Standard Organization across the globe. Therefore, the study recommends that the biodegradable thermoplastic species can be used to replace the non-biodegradable conventional ones.

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COMPETING INTERESTS

The authors declare no conflict of interest. The study did not involve any work with live animals or human subjects.

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