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# Synthesis, Characterization and Nutrient Release Study of Zinc (II)-Aspartic Acid Framework Fertilizer

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***Abstract:*** *The application of metal-organic frameworks (MOFs) in coating fertilizer nutrients is an innovative approach to forestalling problems observed from petroleum-based or polymer-based coating materials such as faster nutrient release and low hydrophobicity. Therefore, Zn-based MOF fertilizer has successfully been synthesized via co-crystallization from Zinc nitrate and aspartic acid with urea as the carrier encapsulants of Nitrogen, and phosphorus from potassium dihydrogen tetraoxophosphate(V) and ammonium tetraoxophosphate (V) respectively. The synthesized Zn-based MOF fertilizer was successfully characterized with FTIR-ATR, SEM-EDX, XRD, and TGA/DTG techniques. The FTIR-ATR affirms the successful incorporation of the precursors in the MOF fertilizer while the SEM coupled with EDX revealed polycrystalline morphology with the expected element in % weight. The XRD spectrum shows the Zn-based MOF fertilizer to be highly crystalline while the TGA/DTG curve indicates the material to stable up to 300 ℃. The nutrient release study indicates that the release of the nutrients at neutral pH environment is slow and sustainable while the mechanism of the release obeyed the Korsmeyer-peppas model.*

***Keywords:*** *Metal-Oragnic framework fertilizer, nutrient release profile, co-crystallization, microwave irradiation, korsmeyer-peppas model*

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## 1. 0 Introduction

The world's population has increased from 7.3 billion in 2015 to 8.2 billion in 2024, with Nigeria's population estimated at about 220 million. This growing population has intensified the demand for food production, placing significant pressure on farmers to improve crop yields (Adetunji *et al*., 2025). In 2024 for instance, the citizens in Nigeria protested scarcity of food with the tag 'end hunger in Nigeria' claiming that farmers lack the necessary farm inputs such as fertilizer to boost food production. Currently, most fertilizers available in Nigerian markets are fast nutrient release (FNR) fertilizers, which release nutrients rapidly, failing to meet the sustained nutrient requirements of crops and contributing to soil degradation (Matemilola & Elegbede, 2017; Ononogbo, *et al*., 2024).

Slow nutrient release (SNR) fertilizers, engineered through coating technologies, have been shown to address the limitations of FNR fertilizers by providing nutrients at a controlled and sustained rate (Katarzyna *et al*., 2020). The SNR fertilizers function by releasing both macronutrients and micronutrients to the crops based on the soil's pH and temperature, and thus providing the required nutrients to the crop at the controlled and sustained supply tailored to crop needs (Katarzyna et al., 2020). Petroleum-based and polymer-based carriers are commonly used in SNR fertilizer technology because they form robust barriers around fertilizer granules, helping to preserve the nutrients and release them precisely under the desired crop conditions (Hanafi *et al*., 2000; Morgan *et al*., 2025).

Despite the advancements in polymer and petroleum-based SNR fertilizers, challenges such as high production costs, environmental accumulation, and premature nutrient leaching limit their widespread adoption. Therefore, polyurethane and polyethylene waxes have been successfully developed as carriers for controlled nutrient release to crops; however, they have limitations due to residual accumulation, which cause environmental damage to the soil (Liu *et al*., 2025).-This has led to a call for the use of polymers in fabricating more effective and environmentally friendly carriers. Xiang et al., (2023) reported a novel biodegradable polymer-based fertilizer containing nitrogen and phosphorus, which effectively controlled and sustained the release of these nutrients. Similarly, Rafique et al., (2025) functionalized chitosan polymer with mica biochar through graft co-polymerization, producing slow-release fertilizers that achieved nutrient release rates of nitrogen, phosphorus, and potassium between 85% and 100%. Despite these advancements, polymer-based carriers face limitations such as premature nutrient leaching and high production costs, posing challenges to their widespread use. Therefore, metal-organic frameworks (MOFs), with their tunable properties, enhanced functionalities, and larger surface areas, have emerged as promising alternatives for nutrient delivery.

Metal-organic frameworks (MOFs) are crystalline porous materials composed of metal ions or clusters coordinated to organic linkers. Their tunable structures, high surface areas, and porosity make them excellent candidates for controlled nutrient delivery in agriculture (Kamalesh *et al*., 2026; Md Zahidul *et al*., 2025). Various synthesis techniques have been extensively reported in the literature, including thermal methods using a hotplate magnetic stirrer or Teflon autoclave, mechanochemical synthesis via ball milling, sonochemical processes employing ultrasonication, and microwave-assisted synthesis (Ahmed & Gavin, 2025; Syed, 2025). Among these, microwave-assisted synthesis is considered the most environmentally friendly, as it enables refined nucleation and produces highly engineered surfaces within a shorter time frame.

Zinc-based MOFs are widely recognized as++ exceptional materials due to their environmentally friendly synthesis conditions compared to other metal-based MOFs. Literature reports demonstrate that Zn-based MOFs exhibit significant nutrient loading capacity along with sustained nutrient release behaviour (Hanfang *et al*., 2024). Thus, attention on MOF fertilizer chemistry had drifted towards Iron-based MOF because of its micronutrient contributions to the crops, however, zinc-based MOF fertilizers offer greater benefits, as zinc plays a crucial role in enzyme activation, regulate auxin from cell division and root growth within plants.

However, limited research has focused on the application of Zn-based MOFs as fertilizers under simulated soil conditions, despite their potential to provide environmentally friendly, slow-release nutrients.

The objective of this study is to synthesize, characterize, and evaluate the nutrient release behavior of a Zn-based MOF fertilizer under varying pH conditions in a simulated soil environment. This study is significant because it presents a sustainable and environmentally friendly alternative to conventional fertilizers, potentially enhancing crop productivity while reducing soil degradation.

## 2.0 Materials and Methods

### *2.1 Materials*

The chemicals zinc (II) nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), aspartic acid ($C_4H_7NO_4$), urea ($CO(NH_2)_2$), potassium dihydrogen phosphate ($KH_2PO_4$), ammonium phosphate ($(NH_4)_3PO_4$), phosphate buffer, ascorbic acid, and Murphy reagent were procured from Sigma-Aldrich Chemical Limited and British Drug House Chemical Limited. All reagents were of analytical grade and used as received without additional purification.

### *2.2 Synthesis of Zn-based MOF fertilizer*

The Zn-based MOF fertilizer was synthesized via a co-crystallization microwave-assisted method as reported elsewhere (Hanfang et al., 2024 & Kaana and Denen, 2024). Briefly, $Zn(NO_3)_2 \cdot 6H_2O$, urea, ammonium phosphate, potassium dihydrogen phosphate, and aspartic acid were weighed in a molar ratio of 1:3:3:3:1 and dissolved in 100 mL of distilled water (DW) in a flat-bottom flask. The solution was stirred at 100 rpm for 60 minutes, followed by microwave irradiation at 250W and 100 °C for 10 minutes. The resulting precipitate was allowed to cool, then filtered and washed multiple times with DW before being dried in an oven at 50 °C and stored in a desiccator for further analysis.

### *2.3 Characterization of Zn-based MOF fertilizer*

Functionalities check of Zn-based MOF fertilizer was carried out using Fourier Transform Infrared Attenuated Total Reflectance (FTIR-ATR), was used to scan the fertilizer in the range 400 – 4000 cm$^{-1}$ on a PerkinElmer FT-IR Spectrometer Spectrum 2 while the morphology and elemental analysis of the fertilizer was run on SEM-Phenom ProX. The phase identification was determined with an X-ray diffractometer (Rigaku MiniFlex 600) over the 2θ range of 3 ° to 70 ° by using CuKα radiation at 15 kV and 15 mA while the BET surface area, $N_2$ adsorption-desorption isotherms at 77 K, and the pore volume of the fertilizer were determined on a Quantachrome model Autosorb IQ-x. The thermal stability was determined by TGA machine-TGA 4000 (Perkin Elmer, Netherlands). Ultraviolet and Visible Spectroscopy and Atomic absorption Spectrophotometer (AAS) were used in the determination of nitrogen (N), phosphorus (P), and Zinc (Zn) nutrient release respectively.

### *2.4 Nutrient Release Profile of Zn-based MOF fertilizer*

Zn-based MOF fertilizer nutrient release was carried out in line with Suganathan and Suganthy, (2025), with slight modification. Two different release approaches were used to determine the nutrients released. Firstly, 0.385 g of Zn-based MOF fertilizer was dissolved in 100 ml of DW in a reagent bottle and incubated in triplicate at room temperature for 21 days, such that 5 ml aliquot of each bottle content were collected every week for the determination of nitrogen using the sodium salicylate method via UV spectrophotometric technique at 420 nm, phosphorus via methylene blue method at 660 nm on spectrophotometer while the trace elements such as zinc was determined via Atomic

Absorption Spectrometry (AAS). It is worthy to note that 5 ml distilled water was used to replace the 5 ml aliquot removed at each time interval. The second method is based on PBS buffer medium conditioned pH 5.5 and 7.5, to mimic the soil physiology, such that 0.385 g of Zn-based MOF fertilizer in a beaker at each pH was carried out at triplicate, and cultured for 21 days. 5ml aliquot of beaker is taken every week for the determination of Zn, N, and P as being carried out in step one. The release kinetic of the fertilizers was determined using Korsmeyer-Peppas models as shown in equations 4.

$$\log\left(\frac{Mt}{M\infty}\right) = \log K + nlog\ t \quad (4)$$

where, Mt/M∞ represents the fractional nutrient release at time t, K is the kinetic constant, and n is a diffusional exponent characterizing the release mechanism.

## 3. 0 Results and Discussion

### *3.1 Functional Group Checks*

The synthesis of a Zn-based metal-organic framework (MOF) fertilizer via co-crystallization of hydrated zinc nitrate, aspartic acid, urea, ammonium dihydrogen phosphate, and potassium dihydrogen phosphate was initially characterized using Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy to confirm the incorporation of these precursors. **Fig. 1** presents the FTIR-ATR spectrum of the Zn-based MOF fertilizer, which reveals distinct bands indicative of the hydroxyl and carbonyl components of carboxylic acid groups of aspartic acid at 3213.43 $cm^{-1}$ and 1625 $cm^{-1}$ respectively, and to the carbonyl groups of urea at 1445.88 $cm^{-1}$ (Ruimin et al., 2025 & Muradiye et al., 2025). Coordination of ammonium dihydrogen phosphate to the zinc center via the P-O bond is evidenced by the band at 886.9 $cm^{-1}$, while the band at 1041.8 $cm^{-1}$ corresponds to zinc coordination with potassium dihydrogen phosphate through the P-OH moiety (Sushma et al., 2024). The formation of the MOF fertilizer was further corroborated by the emergence of new bands at 510.20 $cm^{-1}$ and 533.57 $cm^{-1}$, attributed to Zn-O and Zn-N stretching vibrations, respectively (Vincent et al., 2024).

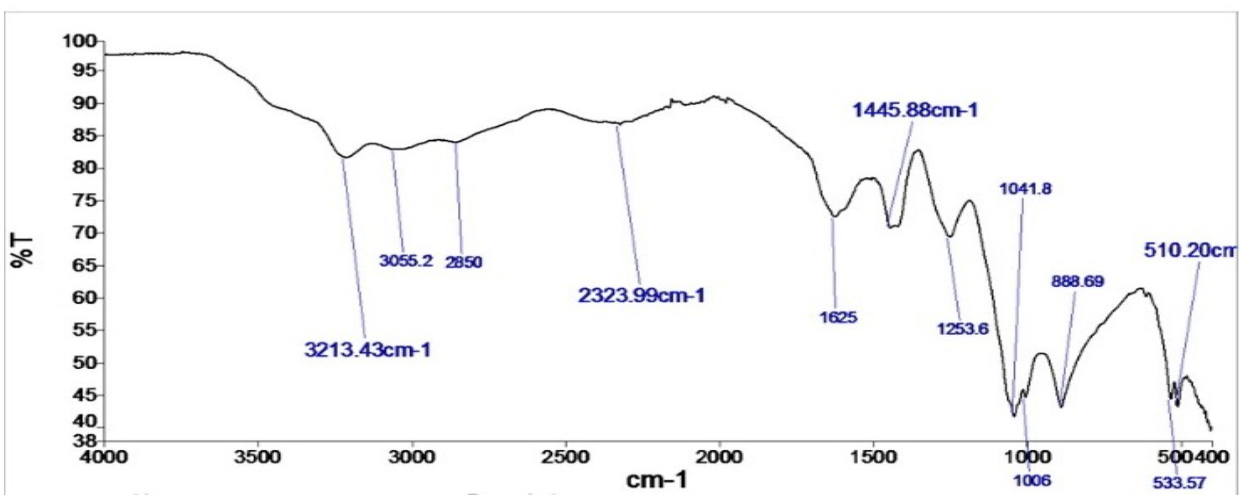


**Fig. 1: FTIR-ATR spectrum of Zn-based MOF fertilizer**

### *3.2 Morphology and Elemental Analysis*

The surface morphology of the Zn-based MOF fertilizer was characterized using scanning electron microscopy (SEM), as presented in Fig. 2. At a scale of 100 µm **(Fig. 2),** the material exhibits aggregate of crystalline particles with varying sizes, characteristic of polycrystalline MOF composites and lacking distinct voids, unlike in many typical MOF morphologies (Gaurav et al., 2024 & Mercedes et al., 2023). The energy-dispersive X-ray (EDX) spectrum (**Fig. 3**) further validates its composition, revealing elemental peaks for zinc, carbon, oxygen, nitrogen, and phosphorus, respectively being the constituents of the starting materials (Norbert et al., 2012).

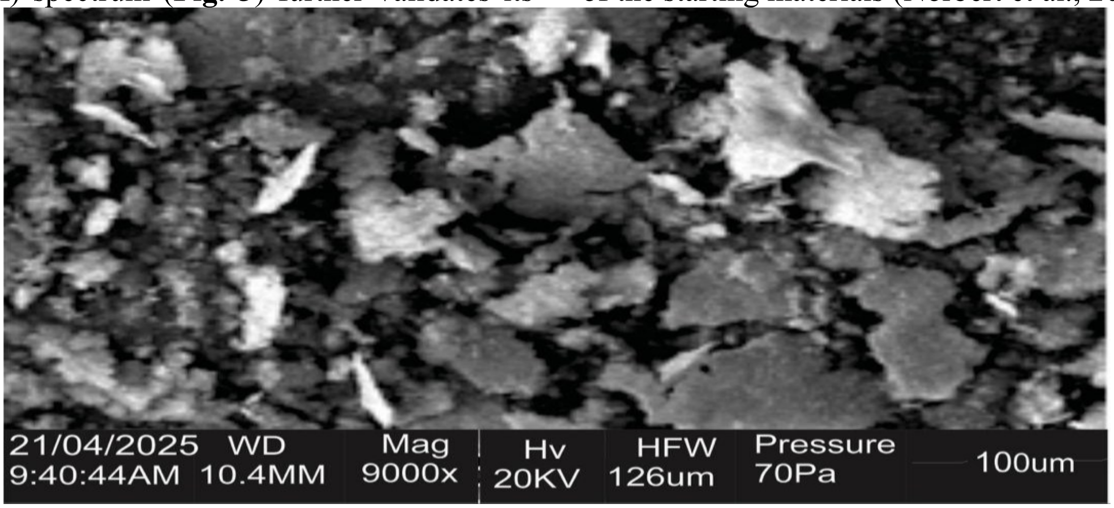


**Fig.2: SEM image of Zn-based MOF fertilizer**

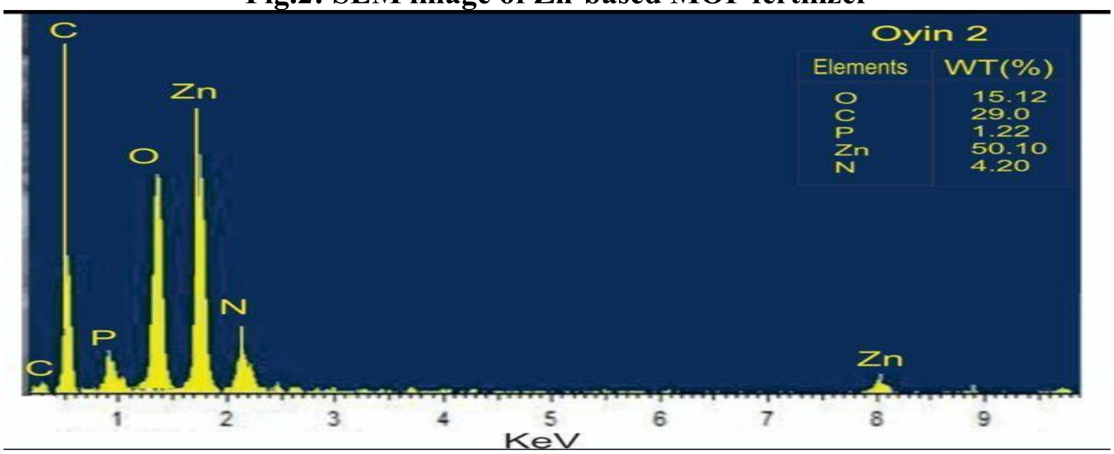


**Fig.3: EDX spectrum of Zn-based MOF fertilizer**

### *3.3 Crystalline phase*

The successful formation of the Zn-based MOF fertilizer was further verified using the X-ray diffraction analysis. The diffractograms of the Zn-based MOF fertilizer is represented in Fig. 4. The 2θ angles around 23.74° and 39.4° indicate a highly crystalline MOF fertilizer material with structural order corroborated by the sharp peaks. This crystalline behaviour presents the Zn-based MOF fertilizer as a good nutrient release and also accounts for its stability in the soil environment (Mohammed et al., 2025 & Zhong-Hong et al., 2021).

### *3.4 Thermal Stability*

The thermal analysis curves for Zn-based MOF fertilizer are shown in Fig. 5 and 6. The TG curve in Fig. 5 shows an initial mass loss within the range of 0 -300 °C, attributed to physically adsorbed moisture and interlayer water molecules losses from the Zn-based MOF fertilizer framework, has been reported. The mass loss recorded at the second degradation temperature was within the range 300 – 570 °C, depicting the degradation of fertilizer framework, which is in agreement with report elsewhere. The nuisance behaviour of the heat on Zn-based MOF fertilizer confirms exothermic reaction curve as shown in Fig. 6 at about 365 °C (More et al., 2023 & Muradiye et al., 2025).

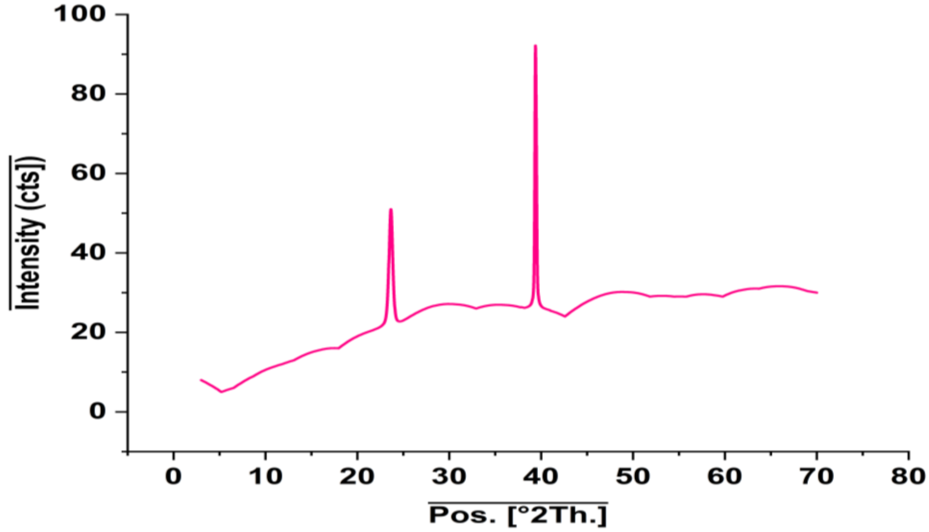


**Fig. 4: XRD spectrum of Zn-based MOF fertilizer**

### *3.5 Nutrient Release*

The nutrient release behaviour of the Zn-based MOF fertilizer under different pH conditions is presented in Fig. **7 (a–c)**. As shown in **Fig. 7a**, nitrogen was released in the form of ammonium-nitrogen ($NH_4^+$–N). The cumulative percentage release of nitrogen at pH 5.5 and 7.5 over three weeks indicated a slow and sustained release, with values of 21.12, 26.19, and 49.87% at pH 5.5 and 22.79, 22.14, and 27.25% at pH 7.5 for weeks 1–3, respectively. This nitrogen release pattern is consistent with previously reported MOF-based fertilizers and is beneficial for early crop establishment and continued growth (Yaxiao et al., 2021 & Suganathan and Suganthy, et al., 2025).

The cumulative release of phosphorus as phosphate, shown in Fig. 7b, exhibited a distinctly slow and controlled release profile, with 8.57, 9.52, and 10.47% release at pH 7.5 for weeks 1, 2, and 3, respectively. Finally, the cumulative release of zinc, presented in Fig. 7c, reached 31.66, 34.29, and 46.00% at pH 7.5 over the same period. Overall, these controlled release profiles for nitrogen, phosphorus, and zinc are favourable for supporting crop growth and enhancing potential yield (Ke et al., 2019).

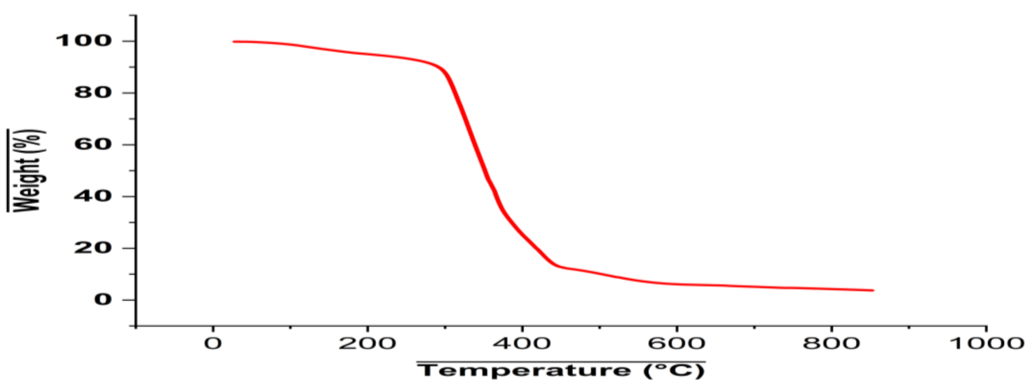


**Fig. 5: TGA curve of Zn-based MOF fertilizer**

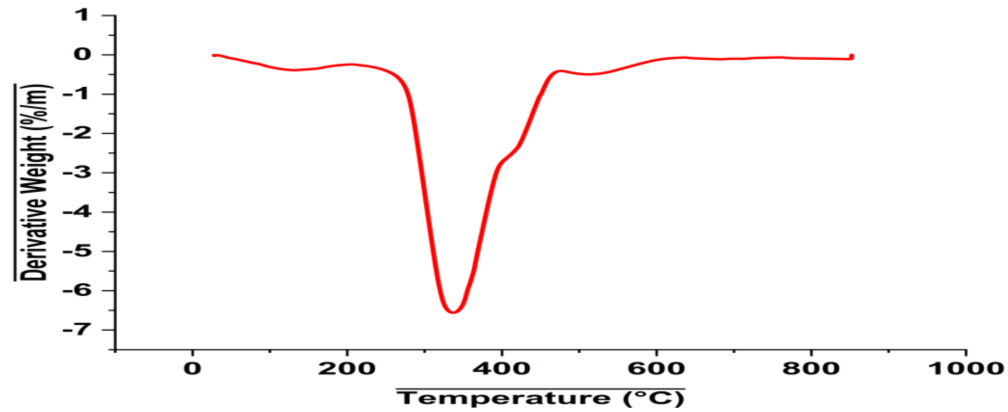


**Fig. 6: DTG curve of Zn-based MOF fertilizer**

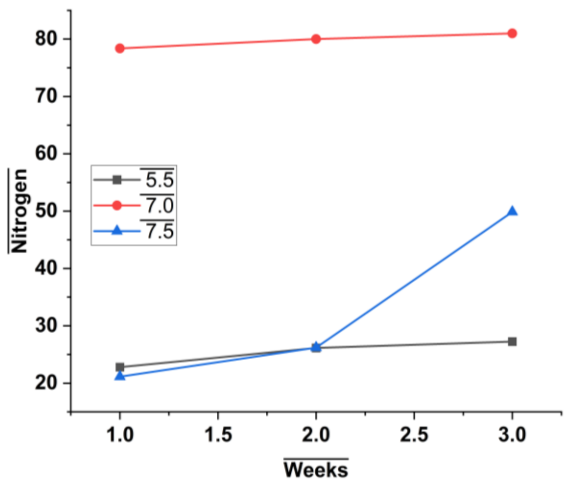


**Fig. 7a: Nitrogen release profile from Zn-based MOF fertilizer**

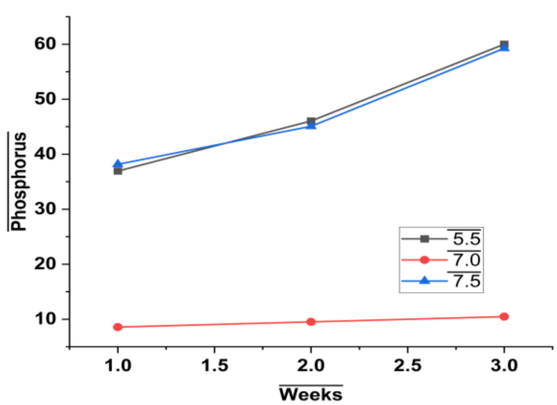


**Fig. 7b: Phosphorus release profile from Zn-based MOF fertilizer**

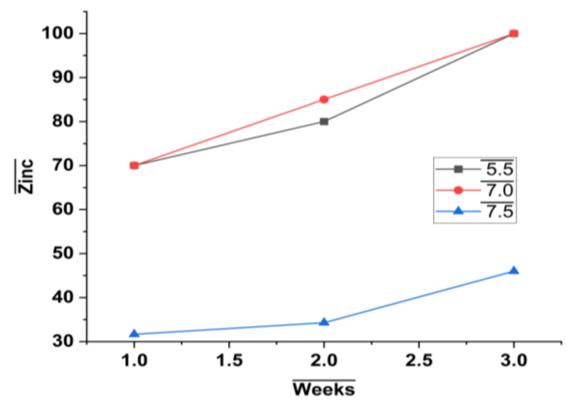


**Fig. 7c: Zinc release profile from Zn-based MOF fertilizer**

The Korsmeyer-Peppas model verified the nutrient release mechanisms from Zn-based MOF fertilizer, as illustrated in Fig. 8 (a-c). Fig. 8a depicts the nitrogen release profiles across varying pH environments, all conforming to the Korsmeyer-Peppas equation as shown to equ. 5, with the highest $R^2$ value of 0.99994 at pH 7.0. At pH 7.0 and 5.0 (n = 0.029522 and 0.16664 respectively. $n<0.43$ signifies Fickian diffusion, driven by nitrogen diffusion through the framework matrix due to concentration gradients, whereas at pH = 7.5 n = 0.96924 > 0.85 indicates super Case II transport, attributed to framework erosion. Fig. 8b illustrates the phosphorus release mechanism, achieving a maximum $R^2$ of 0.98549 at pH 7.0, with Fickian diffusion dominating across all tested pH environments (Ke et al., 2022). Similarly, Fig. 8c depicts the zinc release profile, yielding a maximum $R^2$ of 0.95442 at pH 7.0 and consistently following Fickian diffusion(Chunli et al., 2023).

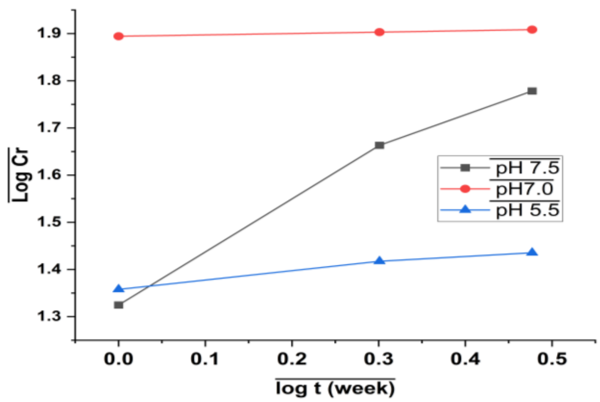


**Fig. 8a: Korsmeyer-peppas model for Nitrogen release**

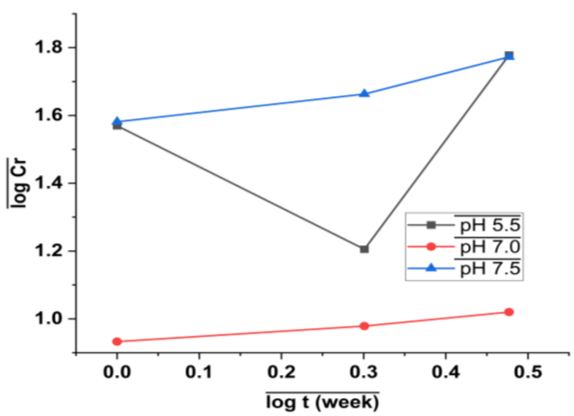


**Fig. 8b: Korsmeyer-peppas model for phosphorus release**

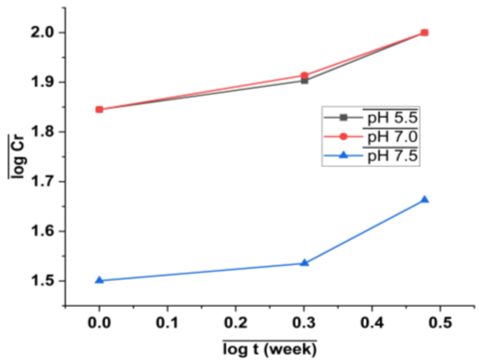


**Fig. 8c: Korsmeyer-peppas model for zinc release**

## 4.0 Conclusion

Zn-based MOF fertilizer was successfully synthesized using an co-crystallization microwave-assisted technique. SEM analysis showed a rough, flaky-like surface morphology, while the EDX spectrum and AAS analysis confirmed the presence of essential Zn, N and P nutrients. Thermal analysis indicated that the MOF fertilizer remained stable up to 300 °C, exhibiting an exothermic behaviour in the TG/DTG curves. XRD patterns confirmed the crystalline nature of the fertilizer, as indicated by a prominent peak indexed at 39.4°. FTIR-ATR spectrum demonstrated coordination of $Zn^{2+}$ centre to the ligand components in the framework. Furthermore, the nutrient release profile showed a slow, controlled release mechanism. Therefore, Zn-based MOF fertilizer has the potential for scale-up production and subsequent field trials as an effective N and P fertilizer.


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**Declaration**

**Conflict of interest**

No conflict of interest declared by the authors

**Ethical Consideration**

Not applicable

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**Availability of Data**

Data shall be made available upon request

**Author contributions statement**

Afamefuna E. Okoronkwo and Emmanuel O. Adeyemi conceptualized the study, designed experiments, and supervised the research. S. A. Adejoro contributed to soil and nutrient analysis. A. O. Adebisi, O. P. Damilola, and I. A. Ukamaka performed synthesis, characterization, and data analysis. All authors contributed to manuscript writing, interpretation of results, and approved the final version for publication.