Jagua Publication

www.jpub.org

Current Research in Interdisciplinary Studies 3(1) (2024): 1 –10

Research Article

Assessment of Fe-Based Organic Framework (Fe-MOF) as Nutrient-Slow-Releasing Material

Kaana Asemave[1]*, **Denen Cletus Lubem**[1]

[1] Department of Chemistry, Benue State University, Makurdi, Nigeria.
*Corresponding email: kasemave[@]gmail.com

How to cite:
Asemave et al 2024. "Assessment of Fe-Based Organic Framework (Fe-MOF) as Nutrient-Slow-Releasing Material". *Current Research in Interdisciplinary Studies* 3(1): 1 – 10. https://doi.org/10.58614/cris311

Received: November 25, 2023
Accepted: March 1, 2024
Published: March 11, 2024

Abstract:
There has been serious focus about improving the efficiency of fertilizers so as to substantially ease the problem of food security, deficit of trace elements, soil degradation, groundwater, and air pollution. Hence, assessment of Fe-Based Organic Framework (Fe-MOF) as Nutrient-Slow-Releasing Material (slow-releasing fertilizer); synthesized hydrothermally from ferric chloride, dipotassium hydrogen phosphate, diammonium hydrogen phosphate, urea, and oxalic acid (OXA) is herein studied. From the FTIR results, -OH & C=O (OXA) and NH_2 (urea) participated in the structural formation of the MOFs. Crystals of the Fe-MOFs at different magnifications with pores sizes of ~1.10 µm were observed from the SEM results. The major peaks are (110) and (111) corresponding to 2θ at 28° and 31°, respectively, as given in MOF_1. For MOF_2 the peaks of (110), (111), and (121) correspond to 2θ at 22.12°, 27.15°, and 33°, respectively. These indicate that the metal-carbonyl linkage for the MOF. These results agreed with the face and body centered crystals. In the results of nutrient-slow-releasing capability of the iron-MOF, the trend of the release at the end of the 3-week is: PO_4^{3-} (2.75 mg/L) < Fe^{3+} (3.30 mg/L) < NH_4^+ (3.36 mg/L) < K^+ (406 mg/L) for MOF_1 and PO_4^{3-} (2.75 mg/L) < Fe^{3+} (3.30 mg/L) < NH_4^+ (3.36 mg/L) for MOF_2. Therefore, the synthesized MOF is recommended for real-life tests as slow-releasing fertilizer. The use of such products would also ensure food security, soil sustainability, and lessen pollution against the fast-releasing fertilizers. More so, the synthesis is handy and utilizes inexpensive reagents.

Keywords: Metal Organic Framework (MOF), Nutrient-slow-releasing fertilizer, Food security.

Introduction

Metal Organic Frameworks (MOFs) may be defined as crystalline materials which can be readily self-assembled from metal ions or metal clusters in the presence of organic ligands/linkers [1-4]. MOFs are also referred to as Porous Coordination Polymers or Coordination Networks. There is much attention about MOFs due to their high surface area, large pore volume, structural diversity and excellent chemical stability based on the reagents used and the experimental condition [1,3,4]. Hence they have found uses in gas capture and storage [5], molecule separations, ion exchange, drug delivery, sensing, catalysis, luminescence etc [1]. In another development, MOFs are demonstrated as slow release fertilizers, when the rightful nutrients are used in the framework development.

The hydrothermal method for preparing MOFs makes use of high temperatures (>100 ℃) and pressure for several hours or days; plus, the Teflon-lined autoclaves vessel. Polar solvents such as DMF, DEF, DMSO, H_2O, acetone, acetonitrile, alcohols or their mixture are mostly used. The yield of the MOF can be enhanced by tuning the polarity of the solvents. Again hydrothermal method makes precursors highly soluble resulting into excellent crystals quality the MOF [1]. In addition, ferric chloride, H_3PO_4, oxalic acid, urea and water at mild condition were employed for the synthesis of MOF using scintillation vials at 100 ℃ over 24 h [6]. By doubling the amount of the precursor (urea) had no influence on the crystal structure of the MOF [6]. On the otherhand, mechanochemical method was used for the synthesis of MOFs from the following precursors: $FeCl_3.6H_2O$, $(NH_4)_2HPO_4$, $H_2C_2O_4.2H_2O$ (molar ratio: 1: 2: 1, respectively); $FeCl_3.6H_2O$, $K_2HPO_4.3H_2O$, $H_2C_2O_4.2H_2O$ (molar ratio: 1: 2: 1, respectively); and $FeCl_3.6H_2O$, $K_2HPO_4.3H_2O$, $H_2C_2O_4.2H_2O$, CH_4N_2O (molar ratio: 1: 2: 1: 2, respectively). The reaction was carried out in a planetary micro mill at 600 r/min speed for 12 min. Then, they were heated at 333 K for 10 h. Then, the MOF crystals formed were filtered, washed and collected [7]. PXRD patterns are used to determine bulk crystallinity of MOFs [8].

There is dearth of use of MOFs in agriculture, especially as slow-release fertilizers; even though MOFs have shown high prospect in numerous application [7]. Notwithstanding there are some efforts towards the potential application of MOF as a slow-release fertilizer. The drawback about these is the high cost of synthesis of the slow-release fertilizer-MOF [7]. Subsequently, MOF- fertilizers were mechanochemically synthesized from reactants containing N, K, P, and Fe. The cost of this method was greatly reduced compared with that of the hydrothermal method earlier reported or from the membrane-coated fertilizers. Again the cost could further be mitigated by selecting lower cost organic ligands or metal salts [7]. Presently, the slow/controlled release fertilizers in the market are mainly coated fertilizers, which are composed of an internal fertilizer and a membrane material. The release of nutrients is controlled by an insoluble or hydrophobic coating. Most importantly, food security has ever been societal concern due to the growth of the world population. Amidst this, it is equally expedient to maintain an equilibrium between agricultural production, soil, and the environment. It can be recalled that several issues about soil and environment were brought by persistent large-scale food production involving high quantum of fertilizer input; which resulted in a deficit of trace elements, soil degradation, groundwater, and air pollution [7]. Enhancing efficiency of fertilizers can eradicate some of the challenges mentioned above. Hence slow-release fertilization has been considered to be used in improving soil fertility. Crop fertilization efficiency has been demonstrated when release rates of nutrients were delayed or controlled in slow-releasing manner to crops absorptions need [7]. Basic hinderances of slow release fertilizer are; the potential negative impact of membrane material or carrier residue, insufficient initial nutrient release rate, the unstable quality of nutrients release, and high synthesis and processing costs. Thus, there is need for sustainable and efficient nutrient carriers that would mitigate the N and P, or nutrient loss during application of fertilizer to crops. The methodically and versatile routes of syntheses and unique properties of metal-organic frameworks (MOFs) - such as various ligands, high porosity, and a flexible and adjustable structure - could make them suitable carriers of nutrients for the slow release [7]; even so the linkers in MOFs could become essential to agricultural processes (such as the oxalate) [6]. N and P nutrient losses are often because of persistent disharmony of time of application and plant needs. The best time for P-demand take place from tillering to anthesis [6]. Whereas, in real-life the fertilizer-P are normally applied at sowing (especially for wheat crops). Therefore, P-fertilizer rather interferes with soil instead of being used by crops. More so, the application of rapid-release N-fertilizer such as urea at sowing or pre-sowing allows significant gaseous N losses (N_2O, NH_3) and N-leaching [6]. Therefore, the research looks at the assessment of Fe-Based Organic Framework (Fe-MOF) as Nutrient-Slow-Releasing Material.

Material and Methods

Materials/ equipment

All the chemical reagents used were of analytical grade; they include; ferric chloride ($FeCl_3$), potassium hydrogen phosphate (K_2HSO_4), diammonium hydrogen phosphate ($(NH_4)_2HPO_4$), urea [$CO(NH_2)_2$], oxalic acid ($C_2H_2O_4$), and distilled Water (H_2O).

Methods

Preparation of the MOF

This research work employed hydrothermal method of preparing MOFs. The method used water as solvent [1][7][5]. Ferric chloride, dipotassium hydrogen phosphate or diammonium hydrogen phosphate, urea, and oxalic acid (OXA) were weighed out in the molar ratio of 1: 3: 3: 1, respectively and dissolved in 125 mL of dissolved water. The solution was stirred for 15 min for homogenization. The solution was heated for about 6 h at a temperature of 90 ℃. The solution was allowed to cool for 15 min and covered with aluminum foil overnight. The solution was filtered using Whatman filter paper and a funnel. The filtrates were discarded, and the residue was washed with 15 mL of distilled water until the crystals became clear. The retained product was oven dried for 2 h at a temperature set at 50 ℃. After drying had taken place, it was kept in the desiccator. The same experiment was repeated twice. Same procedure was used to prepare MOFs from other molar ratios such as 1: 3: 6: 1 and 1: 6: 3: 1; ferric chloride, dipotassium hydrogen phosphate or diammonium hydrogen phosphate, urea, and oxalic acid, respectively. The weight of the dried product was taken, and hence the mass % yield was calculated. With dipotassium hydrogen phosphate (MOF_1) at 1:3:3:1, 1:6:3:1, or 1:3:6:1 molar ratio gave % mass of 27.27±3.63, 14.93±0.48 and 11.45±2.39, respectively. The experiment using diammonium hydrogen phosphate (MOF_2) yielded 38.19±4.40%, 17.62±1.02% and 15.13±4.79% for 1:3:3:1, 1:6:3:1, 1:3:6:1 molar ratio, respectively. These MOFs were characterised with ATR-FTIR, SEM and XRD.

Analysis of the nutrient slow- release ability

About 1.5 g of MOF_1 or MOF_2 was taken into a beaker containing 100 mL of distilled water and the mixture/ suspension was allowed to stand for 3 weeks. For every week, 20 mL of the solution was removed and diluted to 100 mL with distilled water for the determination of the available nutrient using the UV-Visible spectrophotometer.

Determination of Fe3+ using the Ferrover method

The stored program number for Fe was entered (265) on the UV-Visible spectrophotometer. The wavelength was set to 510 nm, for mg/L Fe FV. The cell was filled with 25 mL of the sample. One Ferrover iron reagent; a powder pillow was added to the sample in the cell; swirled and mixed for homogenization. The solution was allowed to stand for 3 min. Thereafter, the solution was placed into the cell holder and closed. The result in mg/L iron was displayed and recorded against the blank.

Determination of Nitrogen Ammonia using the Nessler Method.

The stored program number for ammonia nitrogen (NH_3-N) was inserted (380) on the Uv-visible spectrophotometer. The wavelength dial was rotated until the small display showed 425 nm, and the unit in mg/L of N-NH_3 Ness displayed. A 25-mL mixing graduated cylinder was filled with the prepared sample to the mark. Another 25-mL mixing graduated cylinder of the blank was also filled with deionized water. The three drops of mineral stabilizer were added to each cylinder and was inverted several times to homogenized. Three drops of polyvinyl alcohol dispersing agent were also added to each cylinder by holding the dropping bottle straight and inverting several times to mix. Pipettes 1.0 mL of Nessler reagent into each cylinder, stopper and invert several times to mix. One-minute reaction time was observed. Each solution was poured into a sample cell. when the timer beeped, the display showed the unit in mg/L N-NH_3 Ness. The blank was placed into the cell holder to reset the Uv-visible spectrophotometer. After some time, the prepared sample was replaced by the blank in the cell holder and closed. Light shielded and the result displayed on the screen and recorded. NH_3 = N-NH_4 × factor (1.33)

Determination of phosphorus using the Phosver 3 method.

The stored program for reactive phosphorus-powder pillows (490) was entered on the UV-Visible spectrophotometer. The wavelength was adjusted to 890 nm (for mg/L PO_4^{3-} PV). The sample cell was filled with a sample solution and one phosver-3 phosphate powder was added. It was swirled immediately to mix. A 2-min reaction period was observed and sample was placed into the cell holder and closed. The results in mg/L PO_4^{3-} PV were displayed and recorded against the blank.

Determination of Potassium using the Tetraphenylborate Method, using Acid or Fluoride Extraction.

The user stored program number for potassium was inserted (581) on the uv-visible spectrophotometer. The wavelength dial was rotated until the small display showed 650 nm and the unit in ppm K A/Fs displayed. A 25-mL sample cell was filled with the prepared sample. The content of one potassium-1 powder pillow and that of one potassium-2 powder pillow were added. Was stopper and inverted several times. The contents of one potassium-3 powder pillow was also added to the sample cell containing the prepared solution. Was stoppered and shaken for 30 sec. A 3 min reaction time was observed. After the timer beeped, the sample cell was filled with water (the blank) and placed into the sample holder and closed. Within 7 min after the timer beeps, the sample cell containing the prepared sample was replaced by the blank into the cell holder and closed. The result displayed and recorded accordingly.

Results and Discussion

Product of the Synthesized Fe-based-MOF

The results of the hydrothermal synthesis of metal organic framework (MOF) employed various compounds such as ferric chloride, dipotassium hydrogen phosphate or diammonium hydrogen phosphate, urea, and oxalic acid. The equivalent masses for the molar ratios of 1:3:3:1, 1:6:3:1 and 1:3:6:1, respectively were obtained, dissolved in distilled water and heated at 90 ℃ for 6 h. Eventually, the ratio, 1: 3: 3: 1 had the higher % mass yield (27.27±3.63) than the ratios 1:6:3:1 (14.93±0.48) and 1:3:6:1 (11.45±2.39) in the case of dipotassium hydrogen phosphate. Similar trend was found with diammonium hydrogen phosphate, as 38.19±4.40% (1:3:3:1), 17.62±1.02% (1:6:3:1) and 15.13±4.79% (1:3:6:1) was observed.

MOF$_1$ MOF$_2$

Table 1. Figure 1. Products; MOF$_1$ and MOF$_2$

ATR-FTIR Results

The synthesized products (MOF$_1$ & MOF$_2$) and other reagents such as dipotassium hydrogen phosphate, diammonmium hydrogen phosphate, urea and oxalic acid were characterized for their ATR-FTIR absorptions. The ATR-FTIR spectra results are shown in Figure 2.

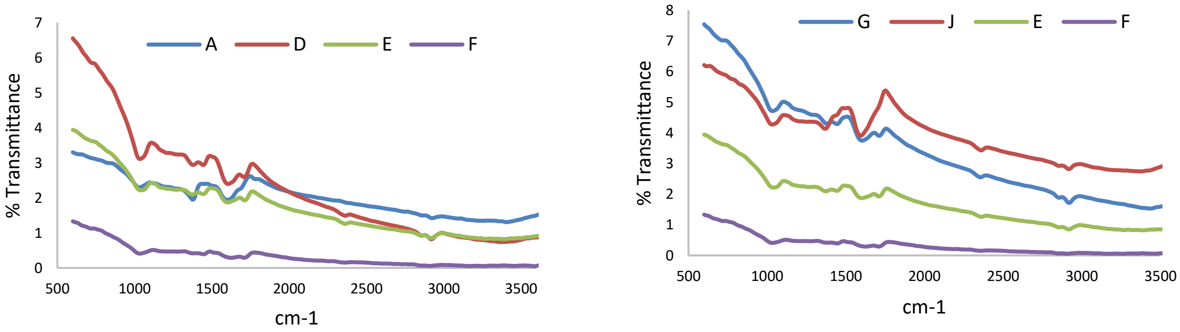

Figure 2. ATR-FTIR spectra of the MOF_1 (A) and MOF_2 (G) along urea (F), oxalic acid (E), dipotassium hydrogen phosphate (D), and diammonium hydrogen phosphate (J)

For the free oxalic acid, OXA (see Figure 2) we observed asymmetric stretching for C = O (1710 cm^{-1}). There was decrement of this value in the ATR-FTIR spectra of the MOF_1 and MOF_2. This implied the involvement of the C = O of the OXA in bonding with the Fe (III) in the formation of the MOFs. In addition, OXA in free form and in the MOFs produced a broad FTIR absorption at about 3406 cm^{-1} for -OH stretch. This -OH group of OXA also is bonded to the central metal ion of the MOF products. For the urea spectrum, we observed the following absorption peaks; 1452 cm^{-1} for C-N stretch, 1646 cm^{-1} for N-H stretch, and 1712 cm^{-1} for C = O stretch. The peak 1646 cm^{-1} disappeared in the MOFs. Considering the results obtained from the ATR-FTIR spectra, it can be said that -OH (of OXA), NH_2 (of urea), C=O (of OXA) are responsible for the structural formation of the MOFs. Elsewhere, it has been reported that, the ATR-FTIR peaks at 3341.3 cm^{-1}, 1603.3 cm^{-1}, 1507.8 cm^{-1}, and 1033.5 cm^{-1} are related to -OH stretching, C = O stretching [9], C - N or N - H stretching, and C-O stretching [10][11][12][13]. Similarly, peaks at 3292.6 cm^{-1}, 1609.6 cm^{-1}, 1515.9 cm^{-1} and 1024.1 cm^{-1} corresponded to the -OH stretching, C=O stretching, C-N or N-H stretching and C-O stretching, respectively [14][15]. Relatedly, in our hands, it was found that the ATR-FTIR absorptions of urea, MOF and OXA for C – O stretching were; 1038 cm^{-1}, 1000 cm^{-1} and 1048 cm^{-1}, respectively.

Scanning Electron Microscopy (SEM)

The SEM micrographs in Figure 3 were obtained from the synthesized products with morphologies at different magnifications. In general, the MOF crystals are variable with somewhat rough surfaces and average crystal size of about 1.1 µm. The MOF_1 and MOF_2 synthesized are mesoporous. The crystal size of some MOFs had been previously established via SEM as Ni-OX (1-5 µm, Ox= oxalate), Ni -T (1.47-6 µm, T= trimesic acid) [2]. Whereas, the composite MOF (NiTOX) size was determined of the range 24-840 nm. The study concludes that synthesized MOFs are mesoporous with definite crystalline geometry [2]. The framework of oxalic acid and trimesic acid complexed with nickel shows beautifully arranged particles with well-defined geometrical shapes. Agglomerates of cubic shapes stacked one above other defined

Ni-OX crystals. Meanwhile, cubic geometry with tetrahedral arrangement of Ni-Ox was observed [2].

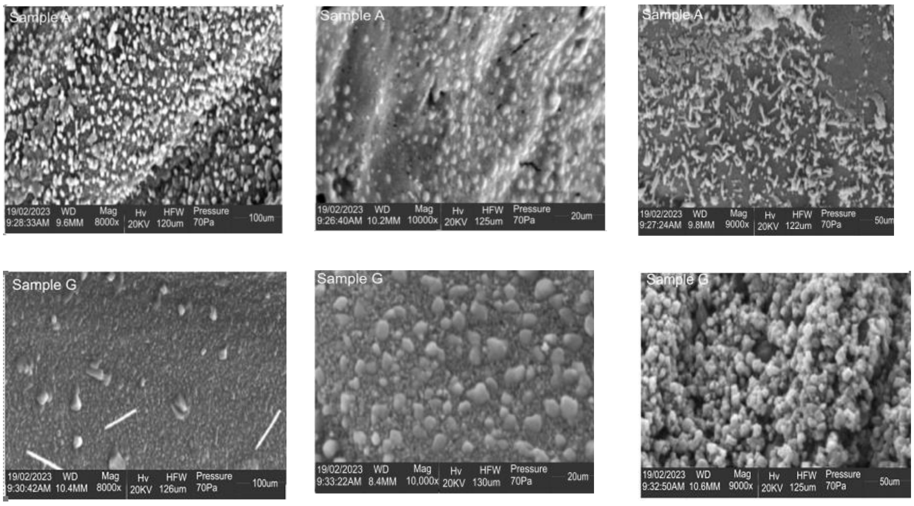

Figure 3. SEM morphology of MOF$_1$ (in the first row) and MOF$_2$ (in the second row)

Results of the XRD

The x-ray diffraction patterns below were obtained from the synthesized MOF products. The major peaks are (110) and (111) corresponding to 2θ at 28° and 31°, respectively, as given in MOF$_1$. For MOF$_2$ the peaks of (110), (111), and (121) correspond to 2θ at 22.12°, 27.15°, and 33°, respectively. Such XRD diffraction peaks implied the metal-carbonyl (-C=O-M) linkage. Previous reports of XRD of MOF similarly found 2θ at 27-29° [6][16]. This is likely a single phase with other minor crystalline compounds; or that at least that the product is crystalline in nature. More so, the synthesized product is insoluble in various solvents such as H_2O, ethanol, DMF, and DMSO, which gives an indication that the product has the framework structure of MOF, not just a metal-ligand complex. In addition, the presence of a sharp diffraction peak in the XRD spectrum also confirms the formation of the crystalline structure [17]. Evidence to support our findings in accordance to Mansab and Rafique [2] is that, metal to carbonyl linkage diffraction peaks of MOF is often in the range, 29° -31° for 2θ. Therefore, iron-phosphate-oxalate frameworks were successfully synthesized at lower temperature using unique composition of the starting reagents, though similarly reported in [7]. Thus, P and Fe were loaded into MOF as the structural elements, and NH_4^+ and K^+ were loaded into the layers among the MOF frameworks, while urea addition mainly functioned in the structure formation of MOF [7]. The XRD showed the MOFs as face/ or body centered cubic (FCC/ BCC) crystals.

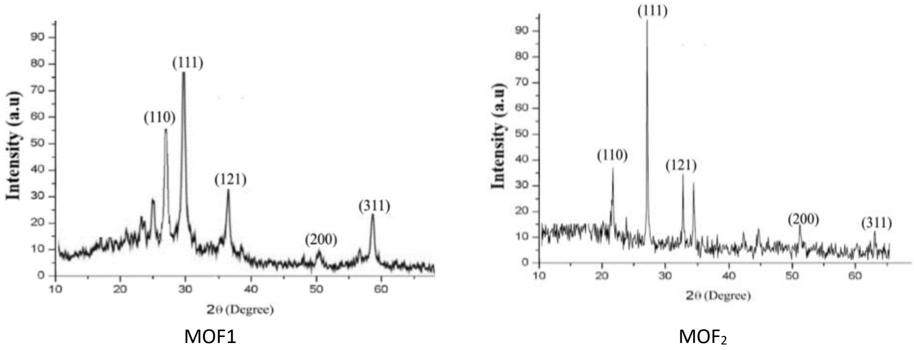

Figure 4. XRD of the MOFs

Results of Slow-Nutrient-Releasing Potentials

A prelim slow nutrient releasing potential of the MOFs were also determined as follows. The products were weighed (1.5 g) and placed into a beaker containing 100 mL of distilled water. The reacting mixture was allowed to stand for 3 weeks to assess their slow-nutrient-releasing potentials. At the end of every week (wk), 20 mL of the solution was taken and diluted to 100 mL with distilled water for the determination of the nutrients using the UV-Visible Spectrophotometric technique. The results obtained from this experiment are presented in Table 1 as follow:

Table 1. Results of slow-nutrient-releasing potentials (mg/L)

Parameters	Week One		Week Two		Week Three	
	MOF_1	MOF_2	MOF_1	MOF_2	MOF_1	MOF_2
Fe^{3+}	0.89	1.74	2.73	2.74	3.30	3.30
K^+	406	-	406	-	406	-
PO_4^{3-}	2.55	2.17	2.68	2.35	2.75	2.75
NH_4^+	0.90	1.16	1.78	1.86	3.36	3.36

The PO_4^{3-} release rate in the first week was fastest. More so, the PO_4^{3-}, Fe^{3+}, and NH_4^+ were slowly released (for MOF_1 and MOF_2), whereas the concentration of the K^+ remained constant over the 3-week period; in the case of MOF_1. The trend of the release of nutrients (PO_4^{3-} , Fe^{3+}, and NH_4^+) in general were comparative; whereas, the rate of K^+ release was fastest. Hence, the trend of the release (in terms of amount) at the end of the 3-week is: PO_4^{3-} (2.75 mg/L) < Fe^{3+} (3.30 mg/L) < NH_4^+ (3.36 mg/L) < K^+ (406 mg/L) for MOF_1 and PO_4^{3-} (2.75 mg/L) < Fe^{3+} (3.30 mg/L) < NH_4^+ (3.36 mg/L) for MOF_2 as similarly reported by Asemave *et al.* [18]. Du *et al*. [7] also submitted that the Iron-based Metal-Organic Frameworks (MOFs) could be applied as high-grade compound fertilizer. They similarly and previously demonstrated in conformity to our research that such iron-based MOF released P, Fe, NH_4^+ and K^+ slowly from the MOF structure. They observed also that the release rates of P and Fe were relatively lower, while the release rates of NH_4^+ and K^+ were faster. However, unlike our results; their release rates of K^+ was lower than that of NH_4^+ [7]. The mechanism of the slow release of nutrients by these MOFs is via cation exchange;

and the eventual degradation of the framework, accompany by release of phosphates and iron-oxalate complexes [6]. The MOF structure and the nutrients release mechanism are described as follows (see Fig. 5).

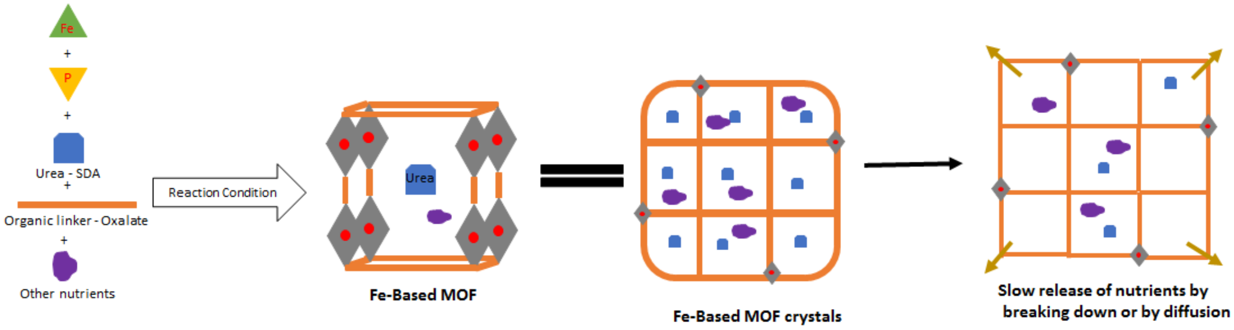

Figure 5. Structure and nutrients release mechanism of the MOF

Conclusion

There has been serious focus about improving the efficiency of fertilizers so as to substantially ease the problem of food security, deficit of trace elements, soil degradation, groundwater, and air pollution. Hence, assessment of Fe-Based Organic Framework (Fe-MOF) as Nutrient-Slow-Releasing Material (slow-releasing fertilizer); synthesized hydrothermally from ferric chloride, dipotassium hydrogen phosphate, diammonium hydrogen phosphate, urea, and oxalic acid (OXA) is here reported. From the FTIR results, -OH & C=O (OXA) and NH_2 (urea) participated in the structural formation of the MOFs. Crystals of the Fe-MOFs at different magnifications with pores sizes of ~1.10 µm were observed from the SEM results. The XRD peaks agreed with the face and body centered crystals. In the results of nutrient-slow-releasing capability of the iron-MOF, the trend of the release at the end of the 3-week is: $PO_4^{3-} < Fe^{3+} < NH_4^+$. Therefore, the synthesized MOF is recommended for real-life tests as slow-releasing fertilizer. The use of such products would also ensure food security, soil sustainability, and lessen pollution against the fast-releasing fertilizers. More so, the synthesis is handy and utilizes inexpensive reagents.

Acknowledgements

The authors are thankful to the Department of Chemistry, Benue State University, Makurdi for making their facilities available for use for this research work.

References

[1] R. Seetharaj, P. V. Vandana, P. Arya, and S. Mathew, “Dependence of solvents, pH, molar ratio and temperature in tuning metal organic framework architecture,” Arab. J. Chem., pp. 295–315, 2016.
[2] S. Mansab and U. Rafique, “Synthesis of MOFs from Carboxylate Ligands and Its Industrial Application,” Int. J. Sci. Eng. Res., vol. 6, no. 3, pp. 45–53, 2015.
[3] M. H. Yap, K. L. Fow, and G. Z. Chen, “Synthesis and applications of MOF - derived porous nanostructures,” Green Energy Environ., pp. 1–68, 2017.

[4] N. Iswarya, M. G. Kumar, K. S. Rajan, and J. B. B. Ryappan, “Metal Organic Framework (MOF-5) for sensing of volatile organic compounds,” J. Appl. Sci., vol. 12, no. 16, pp. 1681–1685, 2012.

[5] V. V Butova, M. A. Soldatov, A. A. Guda, K. A. Lomachenko, and C. L. A, “Metal-organic frameworks: structure, properties, methods of synthesis and characterization,” Russ. Chem. Rev., vol. 85, no. 3, pp. 280–307, 2016.

[6] U. K. S. Aldren, S. C. J. Buenviaje, Y. D. G. Edanol, M. T. Conato, and L. M. J. Payawan, “Facile fabrication of a potential slow-release fertilizer based on oxalate-phosphate-amine metal-organic frameworks (OPA-MOFs),” Mater. Sci. Forum, vol. 936, pp. 14–19, 2018.

[7] Y. Du, X. Xu, F. Ma, and C. Du, “Solvent-Free Synthesis of Iron-Based Metal-Organic Frameworks (MOFs) as Slow-Release Fertilizers,” Polymers (Basel)., vol. 13, no. 561, pp. 1–10, 2021.

[8] A. J. Howarth et al., “Best Practices for the Synthesis, Activation, and Characterization of Metal−Organic Frameworks,” Chem. Mater., p. A-N, 2016.

[9] K. Asemave, A. J. Hunt, T. J. Farmer, and J. H. Clark, “Modification of Biobased Lipophilic Β-diketone,” Org. Med. Chem IJ, vol. 7, no. 1, pp. 001–006, 2018.

[10] B. Isik, S. Avci, F. Cakar, and O. . Cankurtaran, “Adsorptive removal of hazardous dye (crystal violet) using bay leaves (Laurus nobilis L.): surface characterization, batch adsorption studies, and statistical analysis,” Env. Sci Pollut Res, vol. 30, pp. 1333–1356, 2023.

[11] K. Asemave, B. A. Anhwange, and T. J. Anom, “Antibacterial studies of leucine complexes of Fe (III) and Cu (II),” Int. J. Sci. Res., vol. 4, no. 1, pp. 1527–1529, 2015.

[12] K. Asemave, F. P. Byrne, J. H. Clark, T. J. Farmer, and A. J. Hunt, “Modification of bio-based β-diketone from wheat straw wax: synthesis of polydentate lipophilic super-chelators for enhanced metal recovery,” RSC Adv., vol. 9, no. 7, 2019.

[13] K. Asemave, “Biobased Lipophilic Chelating Agents and their Applications in Metals Recovery,” University of York, UK, 2016.

[14] S. S. Shah, T. Sharma, B. A. Dar, and R. K. Bamezai, “Adsorptive removal of methyl orange dye from aqueous solution using populous leaves: Insights from kinetics, thermodynamics and computational studies,” Env. Chem Ecotoxicol, vol. 3, pp. 172–181, 2021.

[15] A. H. Jawad, S. H. Mallah, and M. S. Mastuli, “Adsorption behavior of methylene blue on acid-treated rubber (Hevea brasiliensis) leaf,” Desalin Water Treat, vol. 124, pp. 297–307, 2018.

[16] B. LEI, G. ZHOU, T. CHENG, and J. DU, “Synthesis of Potassium Ferrate by Chemical Dry Oxidation and Its Properties in Degradation of Methyl Orange,” Asian J. Chem., vol. 25, no. 1, pp. 27–31, 2013.

[17] L. C. Christina, J. Gunlazuardi, and A. Zulys, “Synthesis and characterization of lanthanide metal-organic framework with perylene 3,4,9,10-tetracarboxylate ligand,” Mater. Sci. Eng., vol. 902, pp. 1–11, 2020.

[18] K. Asemave, D. C. Lubem, and G. T. Buluku, “Facile Synthesis and Evaluation of Fe-Metal Organic Framework (Fe-MOF) as Nutrient-Slow-Releasing Agent,” ChemSearch J., vol. 14, no. 2, pp. 67 – 73, 2023.