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Facile Synthesis and Evaluation of Fe-Metal Organic Framework (Fe-MOF) as Nutrient-Slow-Releasing Agent

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ABSTRACT

Fe-Metal Organic Framework (MOF) was uniquely synthesized hydrothermally at mild conditions from ferric chloride, dipotassium hydrogen phosphate, urea, and oxalic acid (OXA) and duly characterised. The FTIR results showed that -OH of OXA; P-O of phosphate and C=O of OXA participated in the structural formation of the MOF. Whereas, NH_4^+ and K^+ were embedded into the layers of the MOF product. SEM result confirmed the image of the crystalline nature of the Fe-MOF at different magnifications with actual crystal size of 1.1 µm. The x-ray diffraction pattern gave major peaks as (110) and (111) corresponding to 2θ at 28° and 31°, respectively implying the metal-carbonyl linkage for the MOF; as similarly observed in the FTIR absorptions. These results confirmed Face (111) and Body (110) Centered crystals (FCC and BCC).In the results of nutrient-slow-releasing capability of the iron-MOF, the trend of the release was: PO_4^{3-} (2.75 mg/L) < Fe^{3+} (3.30 mg/L) < NH_4^+ (3.36 mg/L) < K^+ (406 mg/L). 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: Food security, Metal Organic Framework (MOF), Nutrient-slow-releasing fertilizer

INTRODUCTION

Metal Organic Frameworks (MOFs)are crystalline materials which can be readily self-assembled from metal ions or metal clusters with organic ligands/linkers (Seetharaj *et al.*, 2016; Mansab and Rafique, 2015).That is, they are formed by strong bonds between metal ions and organic linkers (Yap *et al.*, 2017 and Iswarya *et al.*, 2012).They are also referred to as Porous Coordination Polymers or Coordination Networks. It has been unambiguously demonstrated with high premium that MOFs exhibit very high surface area, large pore volume, structural diversity and excellent chemical stability based on the reagents used and the experimental condition (Seetharaj *et al.*, 2016; Yap *et al.*, 2017 and Iswarya *et al.*, 2012). These have become suitable for them to be tested in wide spectrum of applications including gas capture and storage (Butova *et al.*, 2016), molecule separations, ion exchange, drug delivery, sensing, catalysis, luminescence etc (Seetharaj *et al.*, 2016). Most recently, MOFs are seriously considered as slow release fertilizers, provided the suitable nutrients are built in.

In hydrothermal method for preparing MOFs, the reaction is performed in a closed vessel at elevated temperatures (>100℃) and pressure for several hours or days. Usually, reactants in high boiling, polar solvents such as DMF, DEF, DMSO, H2O, acetone, acetonitrile, alcohols or their mixture are put in Teflon-lined autoclaves. Solution polarity may be tuned leading to more crystal growth. This method offers high solubility of the precursors resulting into generation of high quality MOF crystals suitable for structural characterization (Seetharaj *et al.*, 2016). Mild conditions hydrothermal method was applied for the synthesis MOF using ferric chloride, H_3PO_4, oxalic acid, urea and water at different molar ratios. The solutions in each case were put in a scintillation vials and kept into a preheated oven for the reaction over 24 h at 100℃. Product were collected and dried at 80℃ (Aldren *et al.*, 2018). Increasing the content of the urea from 3 moles to 6 moles did not affect the crystal structure of the MOF (Aldren *et al.*, 2018). In another development, 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 substrates were held in the grinding tank and ground using the planetary micro mill at 600 r/min speed for 12 min. Then, they were heated at 333 K for 10 h. Thereafter, the MOF crystals were collected by filtration and washed (Du *et al.*, 2021). PXRD patterns are used to determine bulk crystallinity of MOFs (Howarth *et al.*, 2016).

More so, even though MOFs have shown high prospect in numerous application, there is paucity of attention as regards their use in agriculture (Du *et al.*, 2021), especially as slow-release fertilizers. Notwithstanding there were some efforts towards the potential application of oxalate phosphate amine (OPA) MOF as a slow-release fertilizer. Hydrothermal method was used in the synthesis of the OPA-MOF with urea as structure-directing agent (SDA). In this studies urea decomposition was found due to high temperature condition (Du *et al.*, 2021). Generation of huge autogenous pressure and longtime were required. The approach was ineffective because of cost of synthesis and processing was still too high as a fertilizer (Du *et al.*, 2021). Again, at present, 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. More so, 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 or coated method. Furthermore, it is still possible to reduce the cost by optimizing or selecting lower cost organic ligands or metal salts (Du *et al.*, 2021).

Furthermore, food security has become more and more topical due to the growth of the world population. Amidst this, it is equally expedient to maintain the harmonious equilibrium between agricultural production, soil, and the environment. It can be recalled that several issues of 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 (Du *et al.*, 2021). Improving efficiency of fertilizers is a plausible path to addressing some of the challenges mentioned above. Therefore, slow-release fertilizer development can enhance soil fertility. Better efficiency in crop fertilization has been reported when release rates of nutrients were delayed or controlled in slow release fertilizer to crops absorptions need (Du *et al.*, 2021). Basic challenges for deployment 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. On the other hand, there is need for sustainable nutrient carriers that would eradicate or alleviate the N and P, or nutrient loss during application of fertilizer to crops. The flexible methods 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 (Du *et al.*, 2021). Plus the linkers in MOFs could become essential to agricultural processes (such as the oxalate) (Aldren *et al.*, 2018). N and P nutrient losses are often because of consistently incongruousness between plant needs and time of application. The best time for P-demand take place from tillering to anthesis (Aldren *et al.*, 2018); whereas, fertilizer-P are normally applied at sowing, especially for wheat crops. Therefore, P-fertilizer rather reacts 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 makes room for substantial gaseous N losses (N_2O, NH_3) and N-leaching (Aldren *et al.*, 2018). Therefore, the research looks at the unique synthesis and Evaluation of Fe-Based MOFs as nutrients Slow-Release Agent.

MATERIALS AND METHODS

Materials/ equipment

All the chemical reagents used were of analytical grade; they include; ferric chloride ($FeCl_3$), potassium hydrogen phosphate (K_2HPO_4), urea [$CO(NH_2)_2$], oxalic acid ($C_2H_2O_4$), distilled Water.

Methods

Preparation of the MOF

This research work employed hydrothermal method of preparing MOFs. The method uses water as a solvent (Seetharaj *et al.*, 2016; Du *et al.*, 2021 and Butova *et al.*, 2016). Ferric chloride, dipotassium hydrogen phosphate, urea, and oxalic acid were weighed out in the molar ratio of 1:3:3:1, respectively and dissolved in 125 mL of distilled water. The solution was stirred for 15 min to homogenization and then heated for 6 h at 90℃. The solution was allowed to cool for 15 min and covered with aluminum foil overnight. The solution was filtered. The filtrates were discarded, and the residue washed with 15 mL of distilled water until the crystals became clear. The retained product was oven dried for 2 h at 50℃. After drying, it was kept in the desiccator. MOF samples of other molar ratios; 1:3:6:1 and 1:6:3:1; were also synthesized from same reagents as stated above. 1:3:3:1, 1:6:3:1 and 1:3:6:1 molar ratio gave % mass yields of 27.27±3.63, 14.93±0.48 and 11.45±2.39, respectively. The MOF (of the composition 1:3:3:1) was characterized by ATR-FTIR, SEM and XRD.

Analysis of the nutrient slow- release ability

About 1.5 g 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 Fe^{3+} 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 to 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 and agitated to mix. 1.0 mL of Nessler reagent was put into each cylinder, stopper and inverted several times to mix. 1 min reaction 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 blank was replaced by the sample. 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

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. The mixture 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. it 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 beeped, the blank was replaced with the sample. 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, urea, and oxalic acid. The equivalent masses for the molar ratio 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). The product is given in Plate 1.

Plate 1: Product of the MOF (for ratio, 1:3:3:1)

ATR-FTIR Results

The synthesized product (MOF) and other reagents such as dipotassium hydrogen phosphate, urea and oxalic acid were characterized for their ATR-FTIR absorptions. The striking ATR-FTIR spectra results are shown in Figure 1.

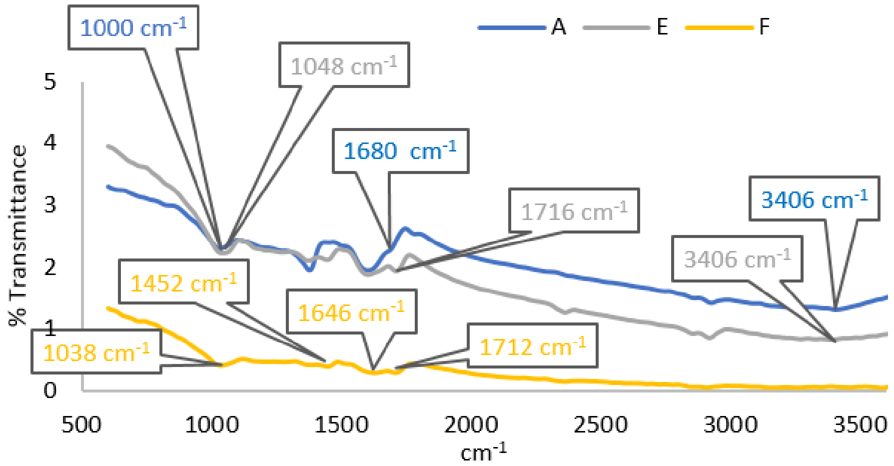

Figure 1: ATR-FTIR spectra of the MOF (A), urea (F) and the oxalic acid (E)

For the free oxalic acid, OXA (Figure 1) we observed asymmetric stretching for C=O at 1716 cm^{-1}. There was decrement of this value to 1680 cm^{-1} (a very tiny shoulder) in the ATR-FTIR spectrum of the MOF; it has become broaden because of the incorporation of the Fe(III) into the framework. This implied the involvement of the C=O of the OXA in bonding with the Fe(III) in the formation of the MOF. In addition, OXA in free form and in MOF produced a broad ATR-FTIR absorption at about 3406 cm^{-1}for -OH stretch. This -OH group of OXA also is being established that it often participates in bonding to the central metal ions in these kinds of 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 MOF. Furthermore, the MOF showed P-O stretch at 1029 cm^{-1}; while the free phosphate gave the value of 1034 cm^{-1}. 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)and P-O (of phosphate) got participated in the formation of the MOF. 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, C-N or N-H stretching, and C-O stretching (Isik *et al.*, 2023; Asemave *et al.*, 2015 and Asemave *et al.*, 2019). Similarly, peaks at 3292.6 cm^{-1}, 1609.6 cm^{-1}, 1515.9 cm^{-1}and 1024.1 cm^{-1} correspond to the -OH stretching, C=O stretching, C-N or N-H stretching and C-O stretching, respectively (Shah *et al.*, 2021 and Jawad *et al.*, 2018). 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 in Plate 2 was obtained from the synthesized product at magnification of 9000x.The MOF crystals has varying sizes of about 1.1 µm.The crystal sizes of some MOFs have been previously established via SEM in the range of 1-6 µm (Mansab and Rafique 2015); which is similar to the one reported here. More so, MOFs are also known to be mesoporous crystalline materials (Mansab and Rafique 2015).

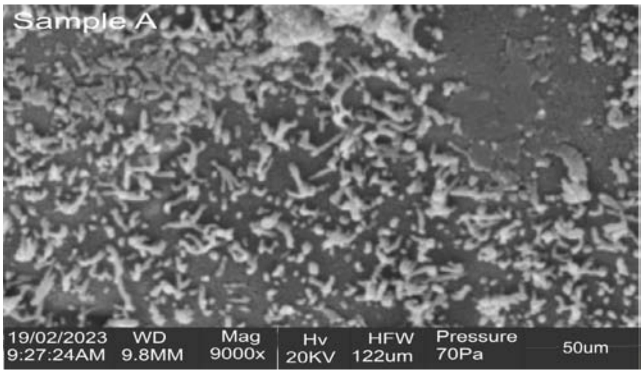

Plate 2: SEM morphology of MOF

Results of the XRD

The x-ray diffraction pattern below in Figure 2 was obtained from the synthesized MOF product. The major peaks are (110) and (111) corresponding to 2θ at 28° and 31°, respectively. From the results obtained, closed pack face-centered cubic (111) and body-centered cubic (110) crystals are found for the product. Again, such XRD diffraction peaks implied metal-carbonyl (-C=O - M) linkage. Previous reports of XRD of MOF similarly found 2θ at 27-29°(Aldren *et al*., 2018 and Lei *et al*., 2013). This is likely a single phase with other minor crystalline compounds; or that at least 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 (Christina *et al*., 2020). Evidence to support our findings in accordance to Mansab and Rafique (Mansab & Rafique 2015) is that, metal to carbonyl linkage diffraction peaks of MOF are observed 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 (Du *et al*., 2021). The P and Fe were loaded into MOF as the structural elements along oxalate, whereas NH_4^+ and K^+ were then embedded into the layers among the MOF frameworks. Urea addition mainly functioned in the structure formation of the MOF (Du *et al*., 2021). See the structure of the MOF as presented in Plate 3.

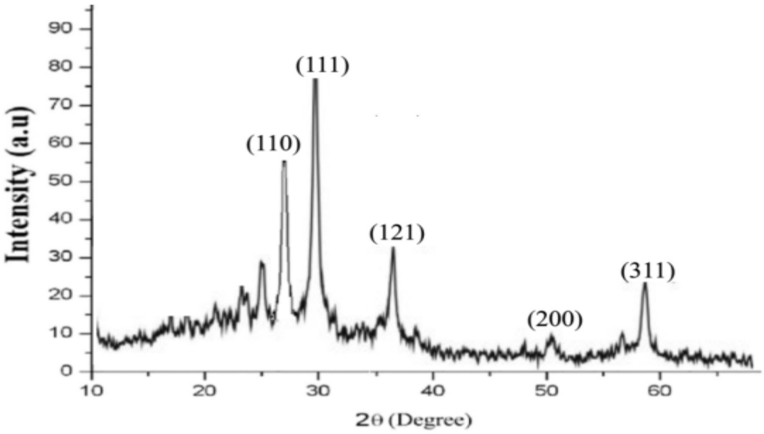

Figure 2: XRD of the synthesized MOF

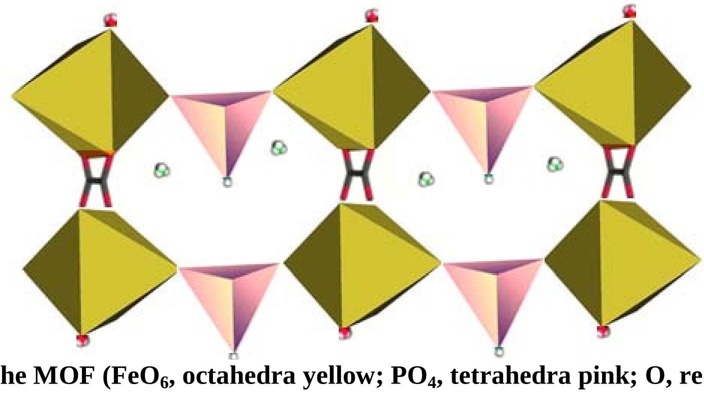

Plate 3: Structure of the MOF (FeO_6, octahedra yellow; PO_4, tetrahedra pink; O, red; C, black; N, green; H, white)

Results of Slow-Nutrient-Releasing Potentials

The slow-nutrient-releasing potentials of the MOF was determined using the UV-Visible Spectrophotometric technique. The results obtained from this experiment are presented in Table 1:

Table 1: Results of slow-nutrient-releasing potentials (mg/L) of the MOF

Parameters	Week 1	Week 2	Week 3
Fe^{3+}	0.89	2.73	3.30
K^+	406	406	406
PO_4^{3-}	2.55	2.68	2.75
NH_4^+	0.90	1.78	3.36

PO_4^{3-}, Fe^{3+}, and NH_4^+ were slowly released, whereas the concentration of the K^+ remained constant over the 3-week period. More so, the release of PO_4^{3-} and Fe^{3+} were relatively lower, while the release rates of NH_4^+ and K^+ were faster. In a nutshell the rate of K^+ release was fastest. Hence, the trend of the release at the end of the 3-weekis: PO_4^{3-} (2.75 mg/L) < Fe^{3+} (3.30 mg/L) < NH_4^+ (3.36 mg/L) < K^+ (406 mg/L). Thus the MOF could be used as slow release fertilizer. Du *et al*. (2021) also submitted that the Iron-Based Metal-Organic Frameworks (MOFs) could be applied as high-grade compound fertilizer. They previously demonstrated in conformity to our research that such iron-based MOF released P, Fe, NH_4^+ and K^+slowly as structural elements. 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^+; that the addition of urea delayed the release of K^+ (Du *et al*., 2021). Furthermore, potential slow release fertilizer material from oxalate-phosphate-amine metal organic framework was synthesized from hydrothermal treatment of $FeCl_3.6H_2O$, H_3PO_4, $H_2C_2O_4.2H_2O$ and $(CO(NH_2)_2)$. The MOF was intended to slowly release urea via cation exchange and eventually facilitate the degradation of the framework, with eventual release of phosphates and iron-oxalate complexes (Aldren *et al*., 2018).

CONCLUSION

Therefore, Fe-based metal organic framework MOF was uniquely synthesized hydrothermally at mild temperature and time conditions with varying ratios (1:3:3:1, 1:6:3:1 and 1:3:6:1) of ferric chloride, dipotassium hydrogen phosphate, urea, and oxalic acid, respectively. Thereafter, the 'MOF' was characterised by the ATR-FTIR, XRD and SEM. Also, the nutrient-slow-releasing capability of the iron-based MOF was evaluated. The ATR-FTIR results showed that -OH (of OXA), NH_2 (of urea), C=O (of OXA) got participated in the structure formation of the MOF along phosphate. For the SEM results, the MOF gave average crystal size of 1.1 µm. The x-ray diffraction pattern gave major peaks are (110) and (111) corresponding to 2θ at 28° and 31°, respectively implying the metal-carbonyl linkage for the MOF. For the nutrient release experiment, the rate of K^+ release was fastest. Hence, the trend of the release at the end of the 3-week: PO_4^{3-} (2.75 mg/L) < Fe^{3+} (3.30 mg/L) < NH_4^+ (3.36 mg/L) < K^+ (406 mg/L). 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 utilized inexpensive reagents.

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REFERENCE

Aldren, U. K. S., Buenviaje, S. C. J., Edanol, Y. D. G., Conato, M. T. and Payawan, L. M. J. (2018). Facile fabrication of a potential slow-release fertilizer based on oxalate-phosphate - amine metal - organic frameworks (OPA-MOFs). *Materisl Science Forum*, *936*, 14–19.

Asemave, K., Anhwange, B. A. and Anom, T. J. (2015). Antibacterial studies of leucine complexes of Fe (III) and Cu (II). *International Journal of Science and Research*, *4*(1), 1527–1529.

Asemave, K., Byrne, F. P., Clark, J. H., Farmer, T. J. and Hunt, A. J. (2019). Modification of bio-based β-diketone from wheat straw wax: synthesis of polydentate lipophilic super-chelators for enhanced metal recovery. *RSC Advances*, *9*(7). https://doi.org/10.1039/c8ra09426h

Butova, V. V., Soldatov, M. A., Guda, A. A., Lomachenko, K. A. andLamberti, A. C. (2016). Metal-organic frameworks: structure, properties, methods of synthesis and characterization. *Russian Chemical Reviews*, *85*(3), 280–307. https://doi.org/10.1070/RCR4554

Christina, L. C., Gunlazuardi, J. and Zulys, A. (2020). Synthesis and characterization of lanthanide metal-organic framework with perylene 3,4,9,10-tetracarboxylate ligand. *Materials Science and Engineering*, *902*, 1–11. https://doi.org/10.1088/1757-899X/902/1/012046

Du, Y., Xu, X., Ma, F. and Du, C. (2021). Solvent-Free Synthesis of Iron-Based Metal-Organic Frameworks (MOFs) as Slow-Release Fertilizers. *Polymers*, *13*(561), 1–10. https://doi.org/10.3390/polym13040561

Howarth, A. J., Peters, A. W., Vermeulen, N. A., Wang, T. C., Hupp, J. T. and Farha, O. K. (2016). Best Practices for the Synthesis, Activation, and Characterization of Metal−Organic Frameworks. *Chemistry of Materials (ACS),* A-N. https://doi.org/10.1021/acs.chemmater.6b02626

Isik, B., Avci, S., Cakar, F. and Cankurtaran, O.(2023). Adsorptive removal of hazardous dye (crystal violet) using bay leaves (Laurus nobilis L.): surface characterization, batch adsorption studies, and statistical analysis. *Environ Sci Pollut Res*, *30*, 1333–1356. https://doi.org/10.1007/s11356-022-

22278-4

Iswarya, N., Kumar, M. G., Rajan, K. S. and Ryappan, J. B. B. (2012). Metal Organic Framework (MOF-5) for sensing of volatile organic compounds. *Journal of Applied Sciences*, *12*(16), 1681–1685.

Jawad, A. H., Mallah, S. H. and Mastuli, M. S. (2018). Adsorption behavior of methylene blue on acid-treated rubber (Hevea brasiliensis) leaf. *Desalin Water Treat*, *124*, 297–307. https://doi.org/10.5004/dwt.2018.22915

Lei, B., Zhou, G., Cheng, T. and Du, J. (2013). Synthesis of Potassium Ferrate by Chemical Dry Oxidation and Its Properties in Degradation of Methyl Orange. *Asian Journal of Chemistry*, *25*(1), 27–31.

Mansab, S. and Rafique, U. (2015). Synthesis of MOFs from Carboxylate Ligands and Its Industrial Application. *International Journal of Scientific & Engineering Research*, *6*(3), 45–53.

Seetharaj, R., Vandana, P. V., Arya, P. and Mathew, S. (2016). Dependence of solvents, pH, molar ratio and temperature in tuning metal organic framework architecture. *Arabian Journal of Chemistry*, 295–315. https://doi.org/10.1016/j.arabjc.2016.01.003

Shah, S. S., Sharma, T., Dar, B. A. and Bamezai, R. K. (2021). Adsorptive removal of methyl orange dye from aqueous solution using populous leaves: Insights from kinetics, thermodynamics and computational studies. *Environ Chem Ecotoxicol*, *3*, 172–181. https://doi.org/10.1016/j.enceco.2021.05.002

Yap, M. H., Fow, K. L. and Chen, G. Z. (2017). Synthesis and applications of MOF - derived porous nanostructures. *Green Energy and Environment*,1–68. https://doi.org/10.1016/j.gee.2017.05.003