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ORIGINAL ARTICLE

Synthesis, Characterization and Antifungal Activity of Fe(III) Metal–Organic Framework and its Nano-composite

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Abstract

Metal–organic frameworks (MOFs) have gained developing interest due to their high specific surface area and pore volume, which has been exploited for gas storage, sensors and, drug delivery. This study presents the synthesis of a non-toxic, biocompatible and thermally stable MIL-53(Fe) and the preparation of its silver(I) nitrate nano-composite. This MIL-53(Fe) is a three-dimensional porous solid composed of infinite $FeO_4(OH)_2$ cluster connected by 1,4-benzenedicarboxylate (H_2BDC) ligand using solvothermal method of synthesis and the encapsulation process was also carried out to produce a composite composed of silver nanoparticle (AgNP). The synthesized materials were characterized using Powder X-ray Diffractometer (PXRD), Scanning Electron Microscope coupled with Electron Diffraction X-ray Spectrometer (SEM–EDS) and Fourier Transform Infrared (FT-IR) Spectroscopy. The Ag@MIL-53(Fe) composite exhibits a remarkable antifungal activity against *Aspergillus flavus* using a poison plate method. This can be attributed to the therapeutic nature of nanoparticle with a range of 55–64% growth inhibition rate as the concentration of the Ag@MIL-53(Fe) was increased. Minimum lethal concentrations (MLC) were observed to be 40 µg/mL and 15 µg/mL for the prepared MIL-53(Fe) and the Ag@MIL-53(Fe) composite, respectively.

Keywords Metal–organic frameworks · Nano-composite · *Aspergillus flavus* · Antifungal test

1 Introduction

Metal–organic frameworks (MOFs) are coordination polymers that extend into two, three-dimensional networks [1]. These materials need to be strong bonding metal centers linked by organic ligands to form a geometrically well-defined structure [1]. Metal organic frameworks (MOFs) have received great attention in recent years, due to their fascinating architectures and topologies (low density, high specific surface and pore volume) as well as their increasing properties and potential applications such as functional materials, catalysis, separation (adsorption), gas storage and drug delivery [2–5]. Metal–organic frameworks also known as porous coordination networks and porous coordinated polymers refer to similar but not the same general type of materials [6, 7]. MOFs' well-defined and large pore structure makes it possible for them to be used to stabilize and control the formation of metal nano-particles within their structure [8]. The MIL (*Material Institute Lavoiser*) series of MOFs have been especially reported as versatile materials which have been tested in various applications ranging from

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gas adsorption/separation, gas storage, catalysis, and drug loading. Moreover, there is continued search for materials which can achieve controlled ion release thereby exhibiting antimicrobial properties. MOFs have been proposed as materials which show promising possibility for antimicrobial application. Recently, silver-based MOFs have been reported to show excellent antimicrobial activity, just as two cobalt-imidazolate MOFs were reported to show interesting antibacterial activity against the growth of *Pseudomonas putida* and *Escherichia coli.* The HKUST-1 (i.e. Hong Kong University of Science and Technology metal organic framework (MOF) consisting of copper ion linked by 1,3,5-benzenetricarboxylic acid) has been reported to have a pore system which provides access to the binuclear metal centres. The Cu ion metal centres are capable of been disconnected resulting in the MOF acting as a means of ions which are biologically active [9–11].

Silver nanoparticles (AgNPs) have been presented as broad-spectrum antimicrobial agents that have been widely utilized in products such as personal care and pharmaceutical products. The silver ions present in the core of the nanoparticles are reported to be responsible for the biological activity of the NPs. However, experimental findings reveal that the silver ions alone are not always responsible for the biological action of the NPs [12].

A typical MOF which has found several applications in a variety of processes is the iron−benzenedicarboxylate (MIL-53(Fe)) MOF. This material is constructed from a combination of 1,4-benzenedicarboxylate (BDC) linker and $FeO_4(OH)$. Some potential applications of the MIL-53(Fe) MOF include gas storage/separation, drug loading and delivery, and adsorption. The MIL-53(Fe) has been recently presented as having photocatalytic property in the degradation of organic dyes, and introduction of functionalities into the MIL-53(Fe) material is able to achieve great improvements in their photocatalytic performance [13–15].

The incorporation of active metal nano-particles into metal–organic frameworks is relevant for a number of potential applications involving heterogeneous catalysis and gas storage [16, 17]. Intercalation is usually achieved via decomposition of volatile organic precursors although it can be achieved using wetness impregnation, mechanical and co-precipitation methods [16, 18–24]. Palladium and ruthenium nanoparticles have been reportedly incorporated into MOF-5 using the chemical vapour deposition technique [17] while Cu-Pd nanoparticles were successfully intercalated into MIL-101 [24], and both materials were reported to exhibit enhanced catalytic activity in the oxidation of CO than the unincorporated MOFs or the separate nanoparticles, and the incorporation of these nano-particles into the MOFs structure allowed for effective reactions at low temperature. The presence of Pd-Ru and Cu-Pd nanoparticles were confirmed by TEM and XRD analyses [25]. Obtaining catalysts having optimally tuned adsorbate binding property is of great research interest. The study of this category of catalysts involves using density functional theory to determine the ensembles, the ligand, and effects of strain in the close-packed material which has been alloyed using transition metals particularly RhAu, PdAu, and PtAu bimetallic materials. The preparation of Ag–Ir (silver–iridium) alloys as solid-solution nanoparticles and their use as catalysts has been reported. The Ag–Ir NPs were found to have higher selectivity toward the C═O hydrogenation in α,β-unsaturated aldehydes and croton-aldehyde, resulting in crotyl alcohol which has high industrial value. Also, the incorporation of Ag–Ir NPs in the pores of Co_3O_4 leads to about 56% enhancement in selectivity. The performance of bimetallic and single metal surfaces for the reduction of nitrite has been shown to be rapidly enhanced using binding energies of ammonia (NH_3), nitrogen (N), and nitrogen gas (N_2) to describe the reactivity through catalyst modeling using the density functional theory (DFT) calculations [26–28].

There have been reports of preparation of Ag nanoparticles of MOFs such as MIL-101, MIL-53(Al), and silver phosphate composite of MIL-53(Fe), however, to the best of our knowledge, there is no literature report of the antifungal activity of MIL-53(Fe) silver-nanocomposite against the *Aspergillus flavus,* in particular.

The disease *Aspergillosis* is a common fungal infection which is ubiquitous in nature and occurs in birds and occasionally in man by exposure to *Aspergillus* fungi. The genus *Aspergillus* comprises of about 185 species of which 20 species of these have been reported to cause opportunistic infections in man. The species include *Aspergillus fumigatus* which is the most common specie isolated, *Aspergillus flavus* and *Aspergillus niger, Aspergillus clavatus, Aspergillus glaucus group, Aspergillus terreus, Aspergillus oryzae, Aspergillus nidulans.* Less commonly isolated species include the *Aspergillus ustus and Aspergillus versicolor* which have been reported to be less opportunistic pathogens. Disease states associated with aspergillosis include cutaneous aspergillosis, cerebral aspergillosis, meningitis, endocarditis, myocarditis, pulmonary aspergillosis, osteomyelitis, otomycosis, onychomycosis, sinusitis, endophthalmitis, hepatosplenic aspergillosis, and Aspergillus fungemia, disseminated aspergillosis may arise thereof [29, 30].

In this study, we report the synthesis and characterization of MIL-53(Fe), and the incorporation of silver-nanoparticles into its framework. The antifungal activity of the synthesized MOF and its nano-composite were investigated against

Aspergillus flavus using disc diffusion method (poison plate method). The antifungal activity of the MOFs materials, [MIL-53(Fe)] and Ag@MIL-53(Fe), were compared based on the zone of inhibition.

2 Experimental

2.1 Materials

Terephthalic acid (99%), Silver(I)nitrate ($AgNO_3$, 99%), and iron(III)nitrate nonahydrate ($Fe(NO_3)_3{\bullet}9H_2O$, 99%) were obtained from Sigma Aldrich Ltd., Germany. *N*,*N*-dimethylformamide (DMF, 99%) and triethylamine (TEA, 99%) were obtained from was obtained from British Drug House Ltd., England. All chemicals obtained were used as received.

2.2 Synthesis of MIL-53(Fe)

MIL-53(Fe) was prepared by a modification to the procedure described by Zhang et al. [31] Iron(III)nitrate nonahydrate (2 mmol) and terephthalic acid (2 mmol) were dissolved separately in 10 mL dimethyl formamide (DMF), mixed together, and three drops of TEA was added to the mixture, and transferred into a 25 mL Teflon lined hydrothermal reactor, placed in an oven, and heated at 150 °C for 24 h. Thereafter, the reactor was allowed to cool slowly to room temperature. The product formed was recovered by centrifugation (using 80-2 Electronic desktop centrifuge, 1000 rpm, room temp.) for 3 min, and washed with 200 mL distilled water and dried and stored in a desiccator (Scheme 1).

2.3 Characterization of the Synthesized MIL-53(Fe)

The powder X-ray diffraction (PXRD) analysis was carried out on an Empyrean XRD X-ray diffractometer using a CuKα-radiation operating at 30 kV and 40 mA. Fourier transform infrared (FTIR) spectrum was measured using a Shimadzu 8400 s spectrophotometer with KBr. The samples were mixed with KBr in the ratio 1:10 and pelletized, and the spectra were recorded over a range of 400–4000 cm^{-1}. Scanning electron microscopy (SEM) images and energy-dispersive X-ray (EDX) analysis of the synthesized MOFs were obtained using a TESCAN Vega 3 XMU scanning electron microscope.

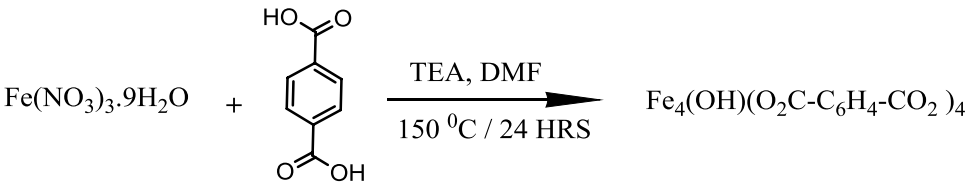
2.4 Preparation of MIL-53(Fe) Silver-nanoparticles (Ag@MIL-53(Fe))

The Ag@MIL-53(Fe) was prepared by a modification to the procedure reported by Liang et al. [32]. Anhydrous ethylene glycol (15 mL) was heated in the oven at 160 °C for 1 h. Degassed MIL-100(Fe) (100 mg) was dispersed in 6 mL of ethylene glycol solution containing 28 mg $AgNO_3$ by ultrasonication for 10 min and a separate ethylene glycol solution (6 mL) containing 30 mg of polyvinylpyrrolidone (PVP) surfactant was also prepared. Polyvinylpyrrolidone (PVP) was utilized to guard against framework degradation. These two suspensions were simultaneously added slowly to the heated ethylene glycol and the mixture further heated at 160 °C for 20 min. The silver-nanoparticle loaded MIL-53(Fe) was thereafter allowed to cool to room temperature and centrifuged at 14,000 rpm for 5 min, washed with 50 mL acetone five times to remove unincorporated nano-particles (Scheme 2).

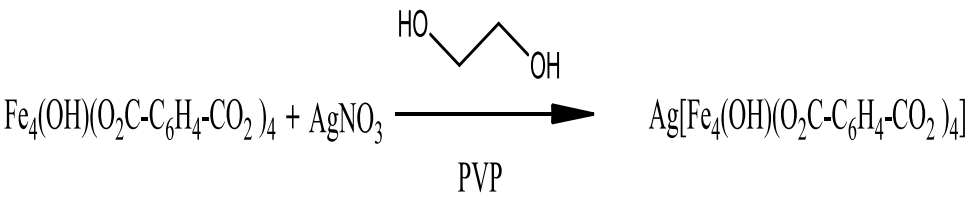
2.5 Antifungal Activity

The inhibitory or stimulatory activity of the synthesized MIL-53(Fe) and its composites, Ag@MIL-53(Fe), on micro-organisms was determined by following the procedure described by Obaleye et al. [33]. The antifungal activity was studied using a potato dextrose agar on which 1.0 cm diameter walls was punched and three different concentrations (5%, 10%, 15% *m/v* in distilled water) of the MOFs and its composite were utilized.

Scheme 1 Equation showing the solvothermal synthesis of MIL-53(Fe)



Scheme 2 Equation showing the preparation of the Ag@MIL-53(Fe)



2.6 Determination of Minimum Lethal Concentration (MLC)

The procedure described by Obaleye et al. [33] was adopted in order to determine the MLC. Sterile stoppered test tubes were utilized and the growth medium for the *Aspergillus flavus* added. This was followed by subsequent addition of 0.05 mL aliquots of MIL-53(Fe) and its composites, Ag@MIL-53(Fe), from a volume of 0.1 mL to 5.0 mL. This represented 10 to 500 µg/mL, in a final mixture of 10 mL. Standard volume to represent the inoculum (0.2 mL each of the test), in which the MIL-53(Fe) and its composites, Ag@MIL-53(Fe), are omitted, and another in which the *Aspergillus flavus* test organism is omitted was also prepared. The tubes were all incubated at a temperature of 35 °C for a period of 24 h and evidence of growth observed. The MLC was thus noted.

3 Results and Discussion

3.1 Fourier Transform Infrared (FT-IR) Spectra

The FTIR spectra of the synthesized MIL-53(Fe), in its hydrated form and after immersing in ethylene glycol solution accompanied by heat treatment (MIL-53(Fe)@et), and the Ag@MIL-53(Fe) composite are presented in Fig. 1. The ν(C=O) vibrations in the carboxyl group was observed at 1660 cm^{-1} in the three products which is consistent with reported values for coordinated C=O in

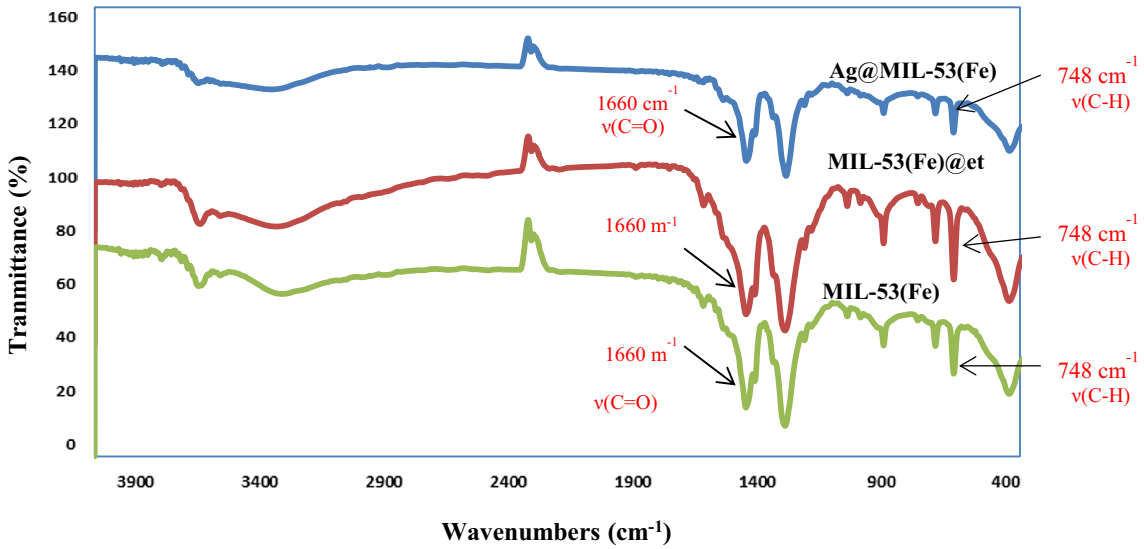


Fig. 1 FTIR spectra for MIL-53(Fe) and its nano-composite

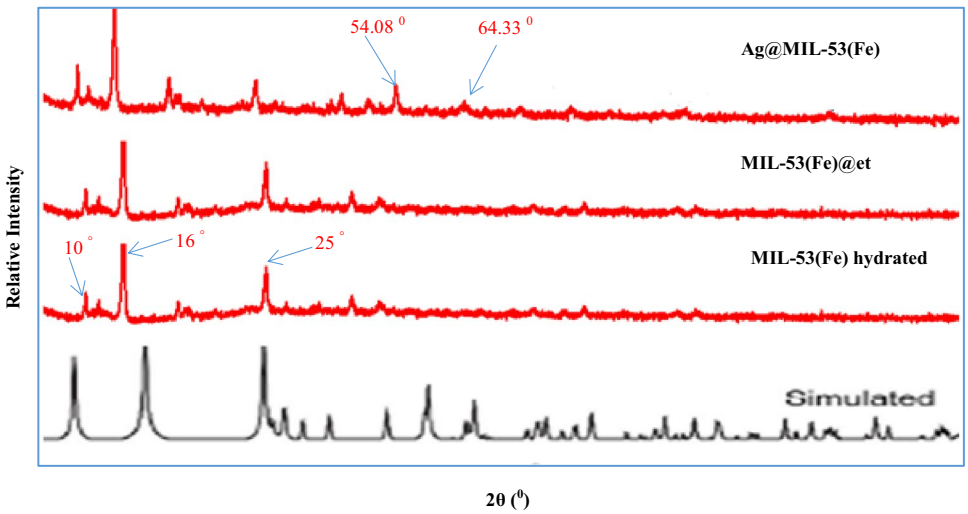


Fig. 2 Comparison PXRD pattern of the MOFs and its nano-composite

literature [34]. A value of 160 cm^{-1} was obtained for the $\Delta(\upsilon_{asymm}(COO–) - \upsilon_{sym}(COO–))$, which indicates a bidentate coordination mode of the carboxyl group to the metal ion [35, 36] while the ν(C–H) bending vibrations of the benzene rings was observed at 748 cm^{-1} [37].

The FTIR spectra of the synthesized MIL-53(Fe) and that of the Ag@MIL-53(Fe) showed similar peaks indicating that the incorporated silver nano-particles did not alter the structure of the MIL-53(Fe) [38].

3.2 Powder X-ray Diffraction (PXRD) Analysis

PXRD patterns of the synthesized MIL-53(Fe) and the Ag@MIL-53(Fe) composite (Fig. 2) showed good

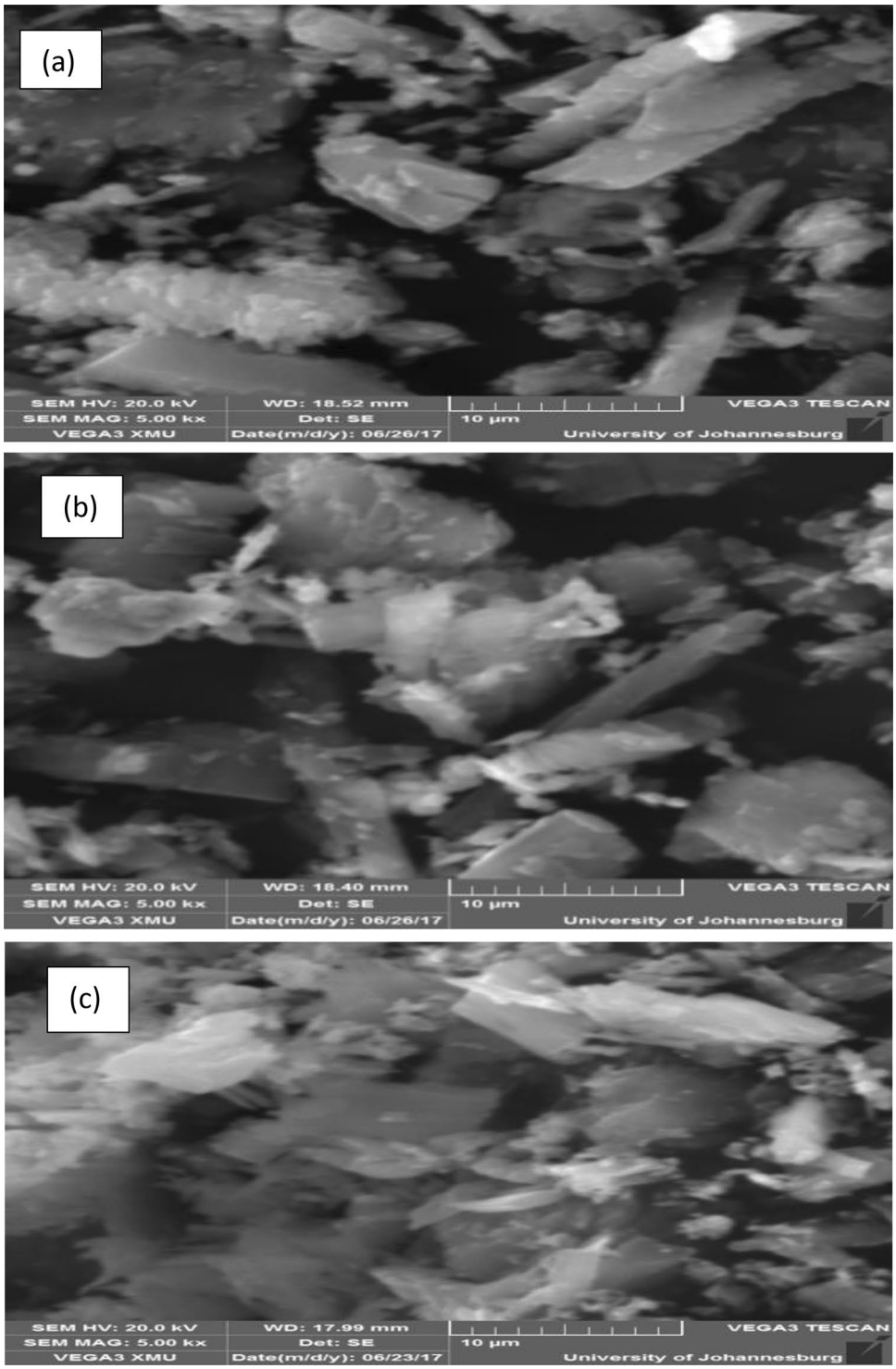


Fig. 3 SEM image of **a** MIL-53(Fe); **b** MIL-53(Fe)@et; **c** Ag@MIL-53(Fe) Composite

agreement with that reported in literature [32, 33] which confirms the successful synthesis of the material. Furthermore, the incorporation of silver nano-particles was observed to not alter the framework of the MOF compared to the report of framework decomposition during solution based infiltration of metal ions into MOFs [19, 38]. Characteristic 2θ peaks at 54.08° and 64.33° observed in the PXRD pattern of the prepared Ag@MIL-53(Fe) was absent in the MIL-53(Fe). This indicates the successful incorporation of silver nano-particles in the MIL-53(Fe) framework at the same time retaining the integrity of the MOF structure. Furthermore, there was no observed changes in the PXRD patterns of the synthesized MIL-53(Fe) and the ethylene glycol treated MIL-53(Fe) (i.e. MIL-53(Fe)@et), indicating that treatment of MIL-53(Fe) in hot ethylene glycol does not alter the structural framework of the prepared MOF.

3.3 SEM–EDX Analysis

SEM images of the prepared compounds were obtained at a magnification of 5000 ×. This was selected in order to clearly observe the phases of the compounds and the possible phase changes. It was observed from the SEM images at a magnification of 5000 × that the surfaces remained rough-like in the MIL-53(Fe) and MIL-53(Fe)@et. The MIL-53(Fe) showed non-homogeneous, stick-like particle shapes (Fig. 3) which was retained in the MIL-53(Fe)@et (Fig. 3). The particles of the Ag@MIL-53(Fe) composite was observed to be bulky having rough surfaces (Fig. 3) compared to the MIL-53(Fe) particles. This can be attributed to the presence of silver-nanoparticles in the framework [39].

Elemental composition of MIL-53(Fe) and the Ag@MIL-53(Fe) composite are presented in Fig. 4a, b, respectively. The EDX spectrum of the selected region in the SEM images of the Ag@MIL-53(Fe) composite (Fig. 4b) shows the Ag-rich region of spheres and the carbon-rich smooth surface of the micro-rods revealing the presence of Ag nanoparticles on the surface of the MIL-53(Fe) and the uniform distribution of carbon and oxygen atoms in the nano-composite.

3.4 Antifungal Activity

The antifungal activity study of the synthesized MOFs revealed that the Ag@MIL-53(Fe) composite has better antifungal activity at concentrations of 50, 100, and 150 ppm

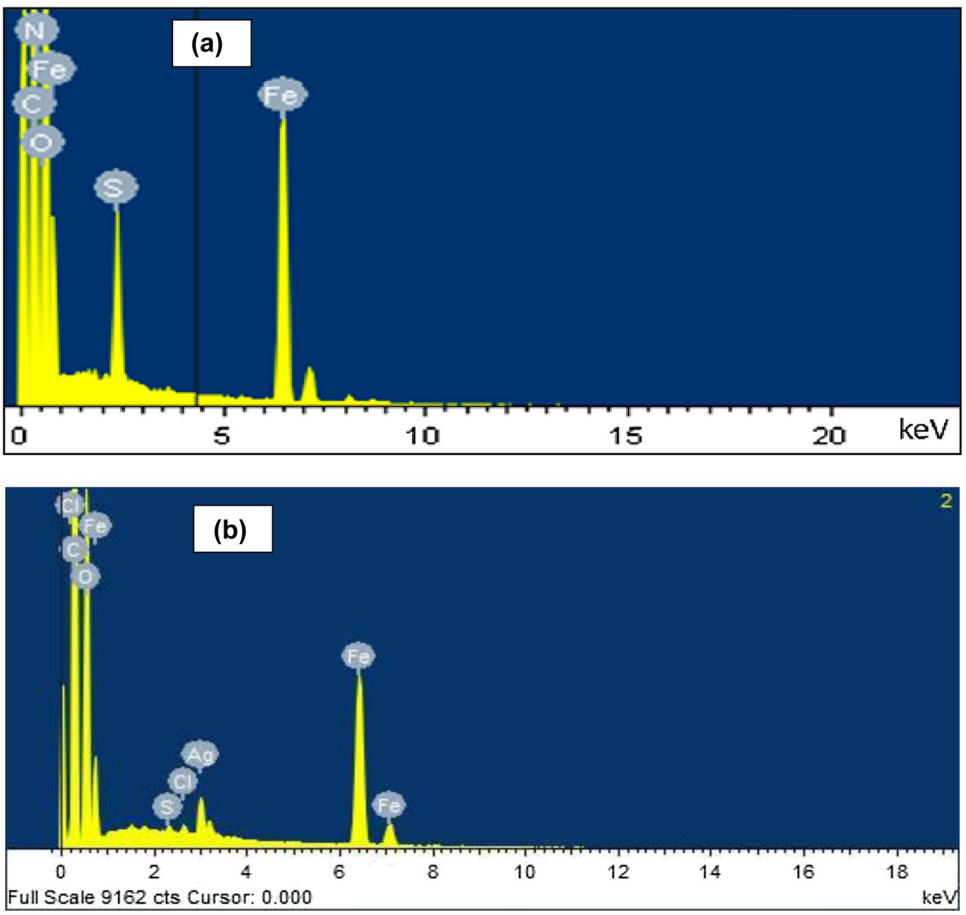


Fig. 4 EDS spectrum of **a** MIL-53(Fe); and **b** Ag@MIL-53(Fe)

Table 1 Antifungal activity of MOFs and its nano-composite against *Aspergillus flavus*

S/N	Concentrations (ppm)	Sample code	% inhibition
1.	50	M_A	23.60
		M_B	39.75
		M_C	55.27
2.	100	M_A	43.47
		M_B	54.65
		M_C	59.62
3.	150	M_A	59.62
		M_B	60.86
		M_C	63.97

Significant increase in zone of inhibition as the concentrations of the MOFs increases is observed in Table 1

M_A hydrated MIL-53(Fe), M_B dehydrated MIL-53(Fe), M_C Ag@MIL-53(Fe)

(Table 1), compared to the MIL-53(Fe). This can be attributed to the presence of Ag nanoparticles in the nano-composite which improves its antifungal activity [40] and the small particle size of the nano-composite which enables ease of penetration into the cell wall of the *Aspergillus flavus* thereby affecting the cell membrane and growth of the cell. The capping agent polyvinylpyrrolidone (PVP) surfactant was observed to enhance the dispersion of the nanoparticles thereby improving the performance of the material. It was observed that the PVP capping agent properly encapsulated the Ag@MIL-53(Fe) nanoparticles thereby enhancing its stability. The MLC of the prepared MIL-53(Fe) and the Ag@MIL-53(Fe) composite was observed to be 40 µg/mL for the MIL-53(Fe) and 15 µg/mL for the Ag@MIL-53(Fe), giving % inhibition values of 17.92% and 16.37% respectively. The Ag@MIL-53(Fe) exhibited better activity against the fungi tested, and this can be attributed to the presence of the silver ions in the composite [9, 12].

4 Conclusion

MIL-53(Fe) was synthesized and its Ag@MIL-53(Fe) composite successfully prepared using polyvinylpyrrolidone (PVP) surfactant. The antifungal activity of the MOFs and its composite was tested against *Aspergillus flavus* and the activities of the MOFs were compared based on the zone of inhibition. The Ag@MIL-53(Fe) was observed to have better antifungal activity against the *Aspergillus flavus* fungi at the various concentrations used which may be due to the therapeutic nature of the silver nanoparticles present in the framework. This work thus presents the Ag@MIL-53(Fe) as an effective antifungal agent against *Aspergillus flavus*. This indicates the capability of the Ag@MIL-53(Fe) to be used as an antifungal agent in the treatment of fungal infections arising from the *Aspergillus flavus*.

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Compliance with Ethical Standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

1. Roswell JLC, Yaghi OM (2004) Metal-organic frameworks: a new class of porous material. Microporous Mesoporous Mater 73:3–14
2. Kuppler RJ, Timmons DJ, Fang Q-R, Li JR, Makal TA, Young MD, Yuan D, Zhao D, Zhuang W, Zhou HC (2009) Potential applications of metal-organic frameworks. Coord Chem Rev 253:3042–3066
3. Huxford RC, Rocca JD, Lin W (2010) Metal-organic frameworks as potential drug carriers. Curr Opin Chem Biol 14(2):262–268
4. Liu Y, Ng Z, Khan EA, Jeong HK, Ching CB, Lia Z (2009) Synthesis of continuous MOF-5 membranes on porous α-alumina substrates. Microporous Mesoporous Mater 118:296–301
5. Linares N, Silvestre-Albero AM, Serrano E, Silvestre-Albero J, Garcıa-Martınez J (2014) Mesoporous materials for clean energy technologies. Chem Soc Rev 43:7681–7717
6. Hirscher M, Panella B, Schmitz B (2010) Metal-organic frameworks for hydrogen storage. Microporous Mesoporous Mater 129:335–339
7. Tella AC, Isaac AY (2012) Syntheses and applications of metal-organic frameworks materials: a review. Acta Chim Pharm Indica 2(2):75–81
8. Hermes S, Schröter MK, Schmid R, Khodeir L, Muhler M, Tissler A, Fischer RW, Fischer RA (2005) Metal@MOF: loading of highly porous coordination polymers host lattices by metal organic chemical vapor deposition. Angew Chemie Int Ed 44(38):6237–6241
9. Chiericatti C, Basilico JC, Basilico MLZ, Zamaro JM (2012) Novel application of HKUST-1 metal–organic framework as antifungal: biological tests and physicochemical characterizations. Microporous Mesoporous Mater 162:60–63
10. Lu X, Ye J, Zhang D, Xie R, Bogale RF, Sun Y, Zhao Q, Ning G (2014) Silver carboxylate metal–organic frameworks with highly antibacterial activity and biocompatibility. J Inorg Biochem 138:114–121
11. Firouzjaei MD, Shamsabadi AA, Sharifian GhM, Rahimpour A, Soroush M (2018) A novel nanocomposite with superior antibacterial activity: a silver-based metal organic framework embellished with graphene oxide. Adv Mater Interfaces 5:1701365
12. Xiu Z, Zhang Q, Puppala HL, Colvin VL, Alvarez PJJ (2012) Negligible particle-specific antibacterial activity of silver nanoparticles. Nano Lett 128:4271–4275
13. Liang R, Shen L, Jing F, Qin N, Wu L (2015) Preparation of MIL-53(Fe)-reduced graphene oxide nanocomposites by a

simple self-assembly strategy for increasing interfacial contact: efficient visible-light photocatalysts. ACS Appl Mater Interfaces 7(18):9507–9515
14. Ai L, Zhang C, Li L, Jiang J (2014) Iron terephthalate metal organic framework: revealing the effective activation of hydrogen peroxide for the degradation of organic dye under visible light irradiation. Appl Catal B Environ 148–149:191–200
15. Millange F, Guillou N, Medina ME, Ferey G, CarlinSinclair A, Golden KM, Walton RI (2010) Selective sorption of organic molecules by the flexible porous hybrid metal–organic framework MIL-53(Fe) controlled by various host–guest interactions. Chem Mater 22:4237–4245
16. Zlotea C, Campesi R, Cuevas F, Leroy E, Dibandjo P, Volkringer C, Loiseau T, Férey G, Latroche M (2010) Pd nanoparticles embedded into a metal-organic framework: synthesis, structural characteristics, and hydrogen sorption properties. J Amer Chem Soc 132(9):2991–2997
17. Esken D, Zhang X, Lebedev OI, Schröder F, Fischer RA (2009) Pd@MOF-5: limitations of gas-phase infiltration and solution impregnation of [Zn4O(bdc)$_3$] (MOF-5) with metal–organic palladium precursors for loading with Pd nanoparticles. J Mater Chem 19(9):1314–1319
18. Schröder F, Esken D, Cokoja M, Van-Den-Berg MWE, Lebedev OI, Van-Tendeloo G, Walaszek B, Buntkowsky G, Limbach HH, Chaudret B, Fischer RA (2008) Ruthenium nanoparticles inside porous [$Zn_4O(bdc)_3$] by hydrogenolysis of adsorbed [Ru(cod)(cot)]: a solid-state reference system for surfactant-stabilized ruthenium colloids. Amer Chem Soc 130(19):6119–6130
19. Houk RJ, Jacobs BW, Gabaly FE, Chang NN, Talin AA, Graham DD, Allendorf MD (2009) Silver cluster formation, dynamics, and chemistry in metal–organic frameworks. Nano Lett 9(10):3413–3418
20. Jacobs BW, Houk RJ, Anstey MR, House SD, Robertson IM, Talin AA, Allendorf MD (2011) Ordered metal nanostructure self-assembly using metal–organic frameworks as templates. Chem Sci 2(3):411–416
21. Ishida T, Kawakita N, Akita T, Haruta M (2009) One-pot N-alkylation of primary amines to secondary amines by gold clusters supported on porous coordination polymers. Gold Bull 42(4):267–274
22. Ishida T, Nagaoka M, Akita T, Haruta M (2008) Deposition of gold clusters on porous coordination polymers by solid grinding and their catalytic activity in aerobic oxidation of alcohols. Chem A Euro J 14:8456–8460
23. Opelt S, Türk S, Dietzsch E, Henschel A, Kaskel S, Klemm E (2008) Preparation of palladium supported on MOF-5 and its use as hydrogenation catalyst. Catal Comm 9(6):1286–1290
24. Gu X, Lu ZH, Jiang HL, Akita T, Xu Q (2011) Synergistic catalysis of metal-organic framework-immobilized Au-Pd nanoparticles in dehydrogenation of formic acid for chemical hydrogen storage. J Amer Chem Soc 133(31):11822–11825
25. El-Shall MS, Abdelsayed V, Abd-El-Rahman SK, Hassan HMA, El-Kaderi HM, Reich TE (2009) Metallic and bimetallic nanocatalysts incorporated into highly porous coordination polymer MIL-101. J Mater Chem 19(41):7625–7631
26. Guo H, Li H, Jarvis K, Wan H, Kunal P, Dunning SG, Liu Y, Henkelman G, Humphrey SM (2018) Microwave-assisted synthesis of classically immiscible Ag–Ir alloy nanoparticle catalysts. ACS Catal 8:11386–11397
27. Li H, Shin K, Henkelman G (2018) Effects of ensembles, ligand, and strain on adsorbate binding to alloy surfaces. J. Chem. Phys. 149:174705
28. Li H, Guo S, Shin K, Wong MS, Henkelman G (2019) Design of a Pd–Au nitrite reduction catalyst by identifying and optimizing active ensembles. ACS Catal. 9(9):7957–7966
29. Pattron DD (2006) Aspergillus, health implication and recommendations for public health food safety. Internet J. Food Safety 8:19–23
30. Arikan S, Lozano-Chiu M, Paetznick V, Rex JH (2001) In-vitro susceptibility testing methods for caspofungin against Aspergillus and Fusarium isolates. Antimicrob Agents Chemother 45:327–330
31. Zhang C, Ai L, Jiang J (2015) Solvothermal synthesis of MIL–53(Fe) hybrid magnetic composites for photoelectrochemical water oxidation and organic pollutant photodegradation under visible light. J Mater Chem A 3:3074–3081
32. Liang R, Jing F, Shen L, Qin N, Wu L (2015) M@MIL-100(Fe) (M = Au, Pd, Pt) nanocomposites fabricated by a facile photodeposition process: efficient visible-light photocatalysts for redox reactions in water. Nano Res 8(10):3237–3249
33. Obaleye JA, Adediji JF, Adebayo MA (2011) Synthesis and biological activities on metal complexes of 2,5-Diamino-1,3,4-thiadiazole derived from semicarbazide hydrochloride. Mol. 16:5861–5874
34. Tama SK, Dusseault J, Polizu S, Menard M, Halle JP, Yahia LH (2005) Physicochemical model of alginate–poly-L-lysine microcapsules defined at the micrometric/nanometric scale using ATR-FTIR, XPS, and ToF-SIMS. Biomater 26:6950–6961
35. Yılmaz E, Sert E, Atalay FS (2016) Synthesis, characterization of a metal organic framework: MIL-53(Fe) and adsorption mechanisms of methyl red onto MIL-53(Fe). J Taiwan Inst Chem Eng 000:1–8
36. Nguyen DTC, Le HTN, Do TS, Pham VT, Tran DL, Ho VTT, Tran TV, Nguyen DC, Nguyen TD, Bach LG, Ha HKP, Doan VT (2019) Metal-organic framework MIL-53(Fe) as an adsorbent for ibuprofen drug removal from aqueous solutions: response surface modeling and optimization Hindu. J Chem Article ID. https://doi.org/10.1155/2019/5602957
37. Banerjee R, Gokhale S, Bhatnagar J, Jog M, Bhardwaj B, Lefez B, Hannoyer B, Ogale S (2012) MOF derived porous carbon–Fe_3O_4 nano-composite as a high performance, recyclable environmental super-adsorbent. J Mater Chem A 22:19694–19699
38. Li B, Chen X, Yu F, Yu W, Zhang T, Sun D (2014) Luminescent response of one anionic metal–organic framework based on novel octa-nuclear zinc cluster to exchanged cations. Cryst Growth Des 14(2):410–413
39. Sabo M, Henschel A, Frode H, Klemm E, Kaskel S (2007) Solution infiltration of palladium into MOF-5: synthesis, physisorption and catalytic properties. J Mater Chem 17(36):3827–3832
40. Obaleye JA, Caira MR, Tella AC (2008) Crystal structure of dichlorobis (N-{4-[(2-pyrimidinyl-κN-amino)-sulfonyl]phenyl}acetamide)copper(II). Anal Sci X-ray Struc Anal Online 24:x63–x64