Synthesis and characterization of manganese-L-arginine framework (MOF) for antibacterial and antioxidant studies

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Due to their unique properties, metal-organic frameworks (MOF-2) have demonstrated significant potential for various biomedical applications. In this research, a manganese-L-arginine framework (MOF-2) was synthesized and characterized using techniques such as X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The MOF-2's antibacterial activity against selected bacteria was evaluated via the agar-well diffusion method, and it was found to be more effective against *E. coli* than *S. aureus*. Furthermore, the MOF-2's potential as an antioxidant was investigated using the spectrophotometric method against ABTS and DPPH free radicals, with the MOF-2 displaying higher antioxidant activity against DPPH. The obtained results indicate that the synthesized MOF-2 possesses potent antibacterial and antioxidant activities, making it a promising candidate for various biomedical applications.

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1. Introduction

The search for new and effective antibacterial and antioxidant agents has become imperative due to the emergence of drug-resistant bacterial strains and the increasing concerns over the detrimental effects of free radicals on human health. The evolution of resistant bacterial strains has outpaced the development of new antibiotics, making antibiotic resistance a significant global health challenge [1,2]. Moreover, free radicals are known to cause oxidative damage to cellular components, leading to various diseases such as cancer, diabetes, and neurodegenerative disorders. To address these issues, researchers have turned to MOFs as potential candidates for developing new antibacterial and antioxidant agents. MOFs are the porous materials that consist of organic ligands connecting metal ions, and they possess numerous benefits such as high surface area, adjustable pore size, and thermal stability [3,4].

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In recent years, the unique properties of MOFs have gained significant attention and have the potential to be applied in a variety of fields such as gas storage, separation, catalysis, and drug delivery [5]. The MOFs are porous structures made up of metal ions or clusters that are interconnected by organic ligands, resulting in a high surface area and customizable properties [6]. The MOFs are emerged as promising candidates for antibacterial and antioxidant applications due to their tunable pore size, high surface area, and chemical stability [7]. Among various MOFs, manganese-based MOFs have been shown to possess antibacterial and antioxidant properties due to the redox-active nature of manganese ions [8]. Previous studies have reported the synthesis and characterization of manganese-based MOFs for various applications, including drug delivery and catalysis [9,10].

In this study, we report the synthesis and characterization of a manganese-L-arginine framework (MOF) for antibacterial and antioxidant studies. The synthesized MOF was characterized using various techniques such as XRD, FTIR, and SEM. L-arginine is a common amino acid with known antibacterial and antioxidant activities, and its incorporation into the MOF structure can potentially enhance its antibacterial and antioxidant properties. In this study, we aimed to assess the potential of the synthesized MOF as a novel antibacterial and antioxidant agent. To evaluate its antibacterial activity, we tested it against both Gram-positive (GPB) and Gram-negative bacteria (GNB), while its antioxidant activity was assessed through DPPH and ABTS assays.

2. Experimental section

2.1. Reagents used

The chemicals utilized in this study were manganese chloride, L-arginine, dimethyl sulfoxide, 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid), and 2,2-diphenyl-1-picrylhydrazyl, all of which were acquired from Sigma-Aldrich and utilized without any additional purification.

2.2. Synthesis of MOF-2

The manganese-L-arginine framework was synthesized by dissolving 10 mmol (1.61 g) $MnCl_2.2H_2O$ and 10 mmol (1.74 g) L-arginine in distilled water. The reaction mixture was subjected to reflux for 14 hours. The dark brown solid product was washed multiple time with distilled water and dried in oven at 70 ℃.

2.3. Instrumentation

In this study, we used several analytical techniques to investigate the properties of the synthesized manganese-L-arginine framework (MOF-2). The XRD model Xpert Pro, with copper as the radiation source, to study the crystalline nature of the sample. XRD analysis is a powerful tool to determine the crystal structure and phase purity of the MOF-2. The SEM model 5910 made in Japan to examine the surface morphology of the synthesized MOF-2. SEM is a high-resolution imaging technique that provides information about the surface morphology and topography of materials. The FTIR (Nicolet-6700) to study the chemical composition of the MOF-2 using KBr pellets and was run in the range of 4000 to 400 cm^{-1}. FTIR analysis is a powerful tool to determine the functional groups present in a material, and it is commonly used to identify and quantify the chemical bonds in organic and inorganic compounds.

2.4. Antibacterial assay

Bacteriostatic activity of the MOF-2 was securitized against the selected bacteria using standard procedure [11]. Bacterial culture was uniformly spread onto agar plates using sterile swabs, and wells were created with sterile borers. A stock suspension (1mg in 1mL) of MOF-2 was prepared in distilled water and a determine volume was added in each wells and were incubate at 37 °C. The clear zones of inhibition (in millimeter) was considered as the activity of MOF-2.

2.5. Antioxidant assay

The DPPH and ABTs assays were followed to examine the antioxidant potential of MOF-2, where different concentrations (10-40 mg/mL) were dissolved in DMSO. The mixture of ABTs and $K_2S_2O_8$ in DMSO were incubate for sixteen hours to generate $ABTs^{\bullet+}$ and then mixed with MOF-2 solutions followed by UV-Vis analysis at 734 nm. In the second assay, DPPH was dissolved DMSO and the UV analysis was done after thirty min at 517 nm. The percent scavenging activity in both cases was determined.

3. Results and discussion

3.1. XRD study

The crystallographic parameters of the MOF-2 consist of of L-arginine and manganese were studied through XRD and the pattern is given in Fig. 1. The sharp signals at 2 theta positions with the d-spacing values in parenthesis are 15.69(5.69), 18.13(4.84), 19.61(4.62), 21.66(4.15), 24.10(3.70), 24.91(3.66), 26.14(3.41), 28.98(3.09) and 32.53(2.72). The listed data is matched with reference card no. 00-019-1546, confirm the presence of unknown crystal of L-arginine in the sample with crystallite size of 35.1 nm with 0.354 percent lattice strain. Other set of diffraction peaks at 2 theta position are 36.18, 44.61, 58.73, 59.94, 64.97 correspond the miller planes of (220), (222), (331), (421) and (422) are exactly matched with reference card no. 00-021-0547. These peaks confirm the presence of manganese with cubic crystal structure (space group of P), where the length of all three coordinates is 7.00 Å. The calculated crystallite size is 35.4 nm with 0.315 percent lattice strain.

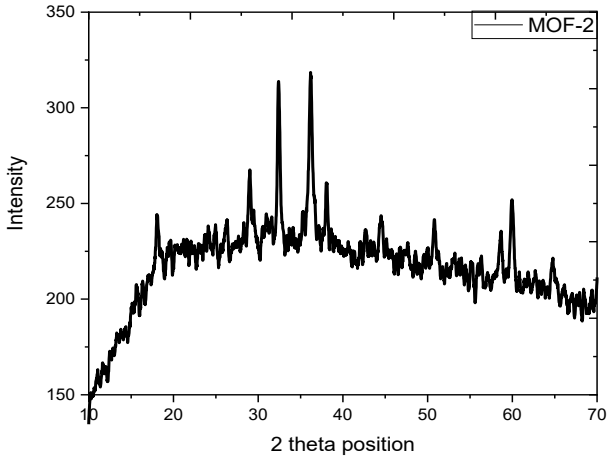

Fig. 1. XRD pattern of the synthesized MOF-2.

3.2. FTIR study

The FTIR spectrum of the synthesized MOF-2 (Fig. 2) exhibit a clear band at 1612 cm^{-1} seems due to carbonyl shift that is an indication for metal carbonyl interaction [12]. However, two more possibilities that can contribute to this band are azomethine functionality of arginine and primary amine (N–H bend) that usually lies in 1350-1000 cm^{-1}.

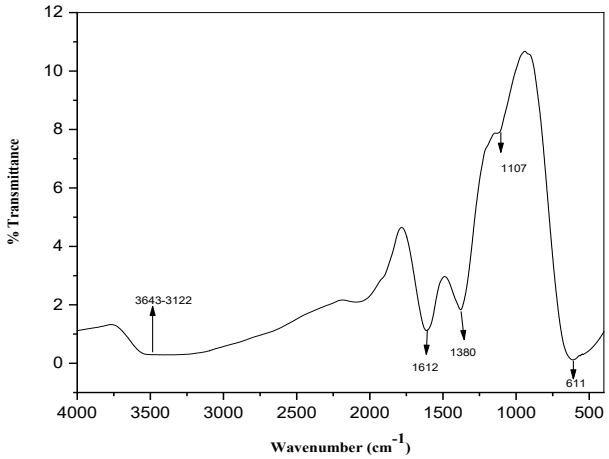

Fig. 2. FTIR spectrum of the synthesized MOF-2.

But for N-H there is no evident band in 3500-3300 cm^{-1} range that might be obscured due to presence of water (3623-3128 cm^{-1}, a broad band). The band at 611 cm^{-1} are likely to be due to metal linker bond [13]. Vibrational band at 1380 cm^{-1} appeared due to either O-H bend, C-H bend or COO^- (asymmetric stretching) [12].

3.3. SEM study

The SEM analysis was done in order the examined the morphology of the MOF-2. The SEM Image of the synthesized MOF is given in the Fig. 3 shows that the formation of an irregular shaped particles, where compact solids are seen in the background, which are due to high degree of agglomeration. The individual particles are present on the surface of the larger solid structures, were of irregular shape and morphology. Both the larger structures and the small particles on the surface are randomly distributed leading the formation of cavities. It has been seen in the high magnified SEM image, the smaller particles combine to a bit larger aggregates, where the size is dependent on the number of the combining particles. The size of the individual compound is difficult to identify due to high degree of agglomeration.

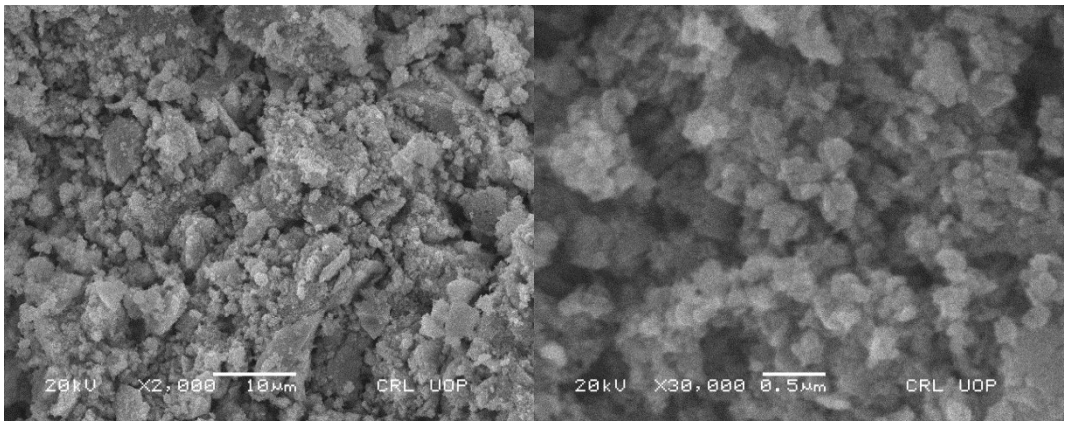

Fig. 3. Low (a) and high (b) magnification SEM images of the synthesized MOF-2.

3.4. Antibacterial study

The antibacterial activity of the synthesized MOF-2 was evaluated against two bacterial strains, *E. coli and S. aureus*, using the agar well diffusion method. The results showed that the synthesized MOF-2 exhibited higher antibacterial activity against *E. coli* compared to *S. aureus* (Fig. 4). One possible mechanism of action for the antibacterial activity of the MOF is that the metal ions

in the MOF may interact with the bacterial cell wall or membrane, disrupting its structure and function. This could lead to the leakage of essential cellular components and ultimately, the death of the bacteria [11].

The difference in the bacteriostatic activity of MOF-2 against *S. aureus* and *E. coli* can also be attributed to the differences in the cell wall composition of both bacteria. The cell walls of GNP like *E. coli* are thinner and more complex than GPB like *S. aureus*. The thinner cell wall in GNP is made up of a thin layer of peptidoglycan, which is surrounded by an outer membrane consisting of lipopolysaccharides and proteins. On the other hand, the thicker cell wall of GPB is mainly composed of a thick layer of peptidoglycan [14].

It has been observed that antibiotics and antibacterial agents can have different effects on GNB and GPB due to the differences in their cell wall composition. In the case of MOF-2, it is possible that the thinner cell wall of *E. coli* allows for easier penetration of the MOF-2 particles, leading to a higher antibacterial activity as compared to *S. aureus* [15,16].

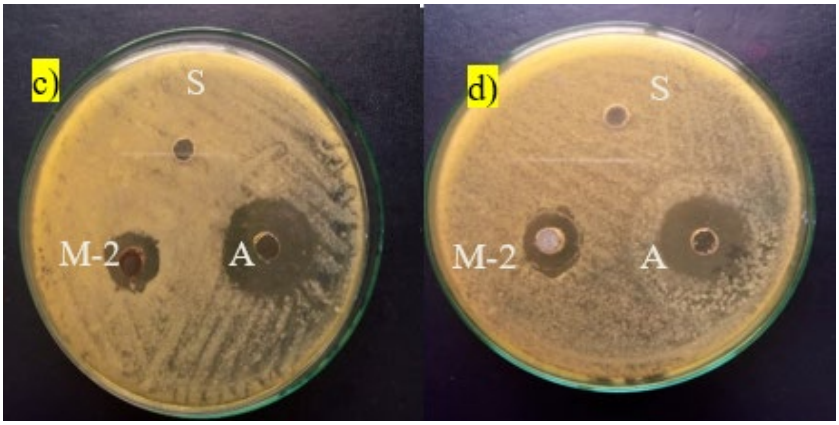

Fig. 4. Antibacterial activity photographs of the synthesized MOF-2; (c) = E. coli; (d) = S. aureus; A = standard antibiotic; M-2 = synthesized MOF; S = solvent (DMSO).

3.5. Antioxidant study

The dose-dependent antioxidant potential of the synthesized MOF was evaluated against ABTS and DPPH free radicals. For this purpose, 10, 20, 30, and 40 mg of the MOF were dissolved in DMSO and introduced into the free radical solutions, and the absorbance was checked at their respective wavelengths. In the case of both free radicals, the activity was seen to increase with increasing the concentration of MOF in the reaction. The IC50 values listed in tables 1 and 2 reveal that the antioxidant potential of the MOF is higher against DPPH free radicals as compared to ABSTS free radicals. The possible reaction for the antioxidant action is given as:

$$MOF + ABTS^{\bullet+} \rightarrow MOF^{\bullet+} + ABTS \qquad \text{(eq. 1)}$$

Here, MOF is the antioxidant compound in the reaction which reacts with ABTS•+ (a blue-green chromophore) and converts it into a non-radical form ABTS, resulting in the reduction of the color intensity of the solution. The extent of this reaction is used to measure the antioxidant activity of MOF against ABTS free radicals [17].

In this case, the MOF acts as an antioxidant by donating an electron to the ABTS•+ free radical, which stabilizes the radical and prevents it from reacting with other molecules in the body. This donation of an electron converts the ABTS•+ radical to a non-radical form, which is colorless and does not absorb light at the specific wavelength used in the measurement. Therefore, the decrease in absorbance over time indicates the antioxidant activity of the MOF-2 [18].

Table 1. ABTS radical scavenging activity of the synthesized MOF-2.

Concentration (mg/mL)	A_o	MOF-2		
		A_i	%RSA	IC_{50}
10	0.208	0.129	37.98	16.11
20	0.208	0.083	60.09	
30	0.208	0.059	71.63	
40	0.208	0.016	92.3	

The reaction for the antioxidant activity of manganese-L-arginine framework against DPPH free radicals is:

$$MOF + DPPH^{\bullet} \rightarrow MOF(H) + \text{DPPH(H)} \quad \text{(eq. 2)}$$

In this reaction, the DPPH radical is a stable free radical that is violet in color, and reacts with the antioxidant MOF-2 to form a stable MOF-H and a reduced DPPH-H. The reduction of DPPH by MOF-2 is indicated by the change in color from violet to yellow [19].

The antioxidant mechanism of MOF-2 against DPPH free radicals is similar to that of ABTS. The manganese ion in MOF-2 can donate electrons to the DPPH radical, which has an unpaired electron, thus neutralizing it and making it stable. The amino acid L-arginine also plays a role in the antioxidant activity by donating hydrogen atoms to the free radicals. The antioxidant activity of MOF-2 against DPPH free radicals can be measured by monitoring the absorbance at 517 nm, which decreases as the concentration of reduced DPPH-H increases [20].

Table 2. DPPH radical scavenge activity of synthesized MOF-2.

Concentration (mg/ml)	A_o	MOF-2		
		A_i	%RSA	IC_{50}
10	0.341	0.147	56.8	4.68
20	0.341	0.113	66.86	
30	0.341	0.097	78.59	
40	0.341	0.036	91.23	

4. Conclusion

In conclusion, the synthesis and characterization of the manganese-L-arginine framework (MOF-2) for antibacterial and antioxidant studies have been successfully performed in this study. The synthetic method for MOF-2 was found to be simple and efficient, resulting in mixed morphological shaped MOFs. The MOF-2 exhibited potent antibacterial activity against *E. coli* and *S. aureus*, with higher activity noted against *E. coli*. Furthermore, the MOF-2 showed significant activity against examined free radicals, with the percent scavenging found higher against ABTS. However, the lost IC_{50} value demonstrated that the MOF-2 is highly active against DPPH radicals. These results suggest that the synthesized MOF-2 possesses promising potential as a new antibacterial and antioxidant agent for various biomedical applications.

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