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Cu- organic framework modified by diatomite: synthesis, characterization and antimicrobial studies

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Abstract

This work is concerned with the studies of the bioactivities of the prepared Cu-MOF compound and its modification with diatomite. This work aims to preparation and characterization of Cu-MOF nano-particles and evaluation against some organisms. Otherwise, the structure of the Cu-MOF was modified and the effects of modification on the bioactivity were investigated. Cu-MOF/diatomite was prepared and their characterizations by using different methods were carried out. The characterization by flourier transforms Infrared red (FTIR), X-ray diffraction (XRD), transmission electron microscope (TEM) and thermal degradation analysis (TGA) indicates that Cu-MOF incorporated onto the diatomite unit. The thermo-gravimetric studies showed that as the diatomite particles coated with the organic fragments prevent their thermal decomposition at low temperature. The bioactivity of Cu-MOF/diatomite was studied by using the agar diffusion technique; it is found that incorporated Cu-MOF onto diatomite increases the bioactivity of Cu-MOF.

Keywords**:** Metal organic framework (MOF); Antimicrobial; Characterization; Diatomite; Fungi; Yeast.

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Introduction

Because the bacterial contamination causes various losses in the economic and the human [1-6], several works were devoted to reduce the effects of these contaminations. The efforts of the researchers directed in two direction, the first one is take different protection and the second is using different materials to restrict the spread of the bacterial effects. In this field, different attempts were done using organic, inorganic, organometallic materials [7-9] and ores [10] to minimize the damage effects of the bacterial. The main effects of the researches focused on low cost materials and simply application as well as have high efficiency to reduce the growth of the bacterial. For these reasons, the first part of our works devoted to use the metal organic frame work (MOF) compound as antibacterial materials because it have many advantages in this field such as it found in a frame works shape, high surface area, high pore size, low density and have different active functional group [11, 12]. The results of antibacterial evaluation against pathogenic Gram-positive bacteria (*Bacillus subtilis* ATCC6633, *Lactobacillus cereus* ATCC 14579 and *Staphylococcus aureus* ATCC29213), Gram-negative bacteria (*Escherichia coli* ATCC 25922 and *Salmonella enterica* ATCC 25566) also gram negative against some bacteria indicate that among the antibacterial materials, the Cu-MOF have a good antibacterial effects. Moreover, the bioactivity an effect of MOFs increases by improvement its structural through incorporated some melamine molecules. The antibacterial effects of the MOFs and that improved return to the nature of the chemical and morphological structures.

On the other hand, through our attention with the reducing the antimicrobial effects, diatomite were used as a raw material or that incorporated with some cations [10]. Also, the diatomite unit shows antibacterial effects against some bacteria and fungi. These effects were explained in the light of chemical and structure of the diatomite. Due to the properties of the diatomite such as large specific surface area, porosity and surface hydroxyl group, it can be as superstation to the MOFs for uses in the antibacterial effects. It is noteworthy that several modifications for MOFs or diatomite by using physical, chemical, radiation and other treatments were used [11-24]. For

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the above reasons, the present work is devoted to study the effects of the incorporated materials, MOFs and diatomite on the resistivity of some bacteria and fungi.

Experimental

Materials

Natural diatomite without purification except washing with distilled water was used. Diatomite samples were exposed to chemical analysis and characterized with different techniques as described elsewhere [13]. It contains ~ 83.6% SiO_2 and 4.24 Al_2O_3, 1.07 % Fe_2O_3, 6.17% CaO, and others oxides 4.86 % and it is free from TiO_2, Na_2O, K_2O and MgO. Cu-MOF was prepared as described previously [11]. Absolute ethanol and other chemicals were supplied from Sigma Aldrich without further purification.

Synthesis of Cu-MOF/Diatomite

1.0 g Cu-MOF which prepared previously [11] and 2.0 g diatomite were dispersed in 150 ml anhydrous ethanol separately to prepare solution A and solution B. After mixing the two solutions, the mixture was sonicated for 2 h and transferred to a flask equipped with condensed reflux at 100 °C for 12 h. The suspension was centrifugally washed three times with absolute ethanol and dried under vacuum at 70 °C overnight to obtain a Cu-MOF/Diatomite powder.

The Characterization Techniques

X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) patterns were performed with power D8 ADVANCE diffractometer (Germany) using CuKa radiation (1.542°A, 40 KV, 40mA) in the 2Ө range of 4–80. The acquisition parameters were as: a step size of 0.02 and a step time of 0.4s.

Fourier transforms infrared (FTIR) spectroscopy

FTIR spectra of the samples were obtained using a KBr disk and FTIR 6500 spectrometer (JASCO, Japan) in the range of 400-4000cm^{-1}

The thermal analysis

The thermal analysis (TGA, DTA) were performed by USA Berkin – Elmer thermogravimeter samples of approximately 10 mg was heated from 50ºC to 800ºC with heating rate 10/min under a nitrogen atmosphere, and the flow of nitrogen was 50 ml/min.

Transmission Electron Microscope (TEM)

To identify the morphology and the particle size of the prepared samples was examined by using a transmission electron microscope (TEM) quanta FEG working at 100 keV.

Antibacterial activity assays

Antimicrobial activity of selected compounds were evaluated against pathogenic Gram-positive bacteria (*Bacillus subtilis* ATCC6633 and *Staphylococcus aureus* ATCC29213), Gram-negative bacterium (*Escherichia coli* ATCC 25922 and *Salmonella enterica* ATCC 25566), yeast fungi (*Candida albicans* NRRL-Y477 and *Candida tropicalis* ATCC750) and fungus (*Aspergillus niger* NRC53) by the agar diffusion technique. Bacteria were obtained from the American Type Culture Collection and Northern Regional Research laboratories while the fungal isolates were obtained from the culture collection of the Department of Chemistry of Natural and Microbial Products, National Research Centre, Cairo, Egypt. The microorganisms were passage at least twice to ensure purity and viability. The bacteria were maintained on nutrient agar medium and fungi were maintained on potato dextrose agar medium. About 50 mg of the prepared powder samples were applied on the inoculated agar plates and incubated for 24 h at 37 ºC for bacteria and 72 h at 28 ºC for fungi. The antimicrobial effect was evaluated by measuring the inhibition zone diameter around samples in (mm).

Results and Discussion

It is noteworthy that the Cu-MOF sample was prepared and characterized elsewhere [11]. Then the prepared diatomite and Cu-MOF/diatomite were characterized by using the following Techniques:

FTIR of prepared sample

On the FTIR curves, Fig. 1, it is observed that three small specific bands at 1096, 796 and 472 cm-1 were appeared. The first one corresponds to the Si-O-Si anti-symmetric band while that observed at 794 and 472 cm-1 are corresponding the bending and rocking respectively. These findings are in agreement with that observed by Gulturk et al [25] and Singho et al [26]. Moreover, two absorption peaks were observed at 1620 and 1700 cm-1 and attributed to the Si-OH bending. By comparison the obtained results with that suggested by other works, it is clear that a peak corresponds to the OH of the moisture content was absent. This may due the diatomite sample was very dry.

For the Cu-MOF/diatomite coupled, the IR spectrum shows that:

i) The peaks corresponding to Si-OH of the diatomite molecules were disappeared.
ii) A flat bottom peak at 3400 cm^{-1} was observed and that attributed to the Cu-MOF.
iii) At 488 cm $^{-1}$ a specific peak characterized the Cu–O bonding was observed while

another one at 721 cm^{-1} attributed to the stretching modes of Cu–O.

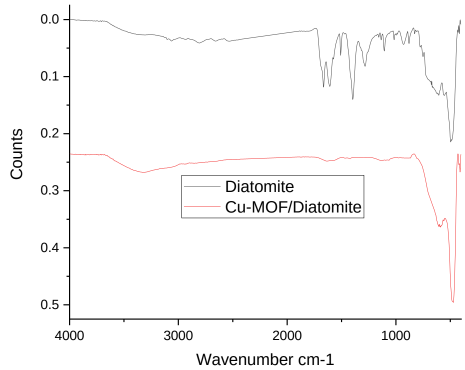


Fig. 1 FTIR of diatomite and Cu-MOF/diatomite

X-ray diffraction (XRD) analysis

Fig. 2 represents the X-ray diffraction of diatomite powder and that incorporated with Cu-MOF. It observed that 2 theta equal 18-40 on the X-Pattern; this means that the main component of diatomite is silica [27]. For the sample Cu-MOF/diatomite, the X-ray pattern exhibits a main peak at 2-theta equals to 22 was appeared while the main peak at 18 for the diatomite only was disappeared. This may due to the compound formation was happened between the diatomite and Cu-MOF.

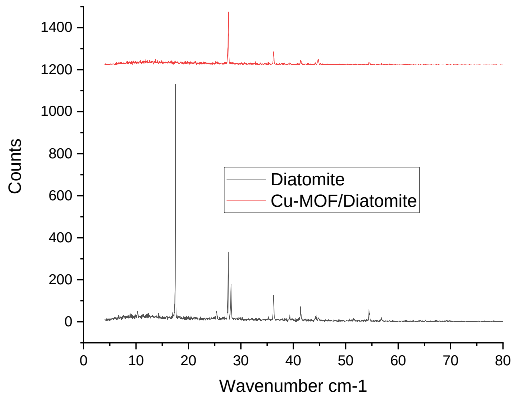
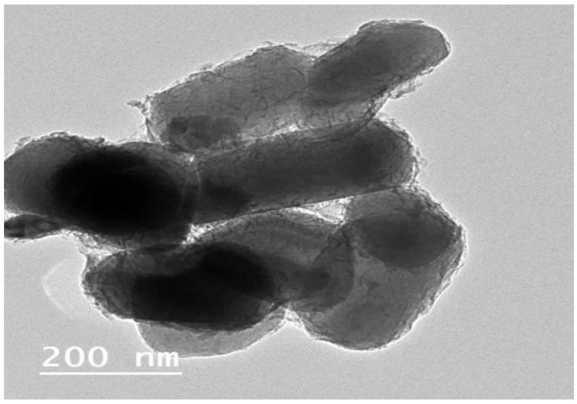


Fig. 2 XRD of diatomite and Cu-MOF/diatomite

Transmission Electron Microscope (TEM)

To study the morphology, the diatomite and Cu-MOF/diatomite samples were exposed to TEM investigation. Fig. 3 shows that the diatomite particles consist of well-defined homogeneous cubic particles. In the case of incorporated with Cu-MOF, the particles goes to rounded shape. This change in the structure may due to the accumulation the organic fragments on the surface of the diatomite units.

a



b

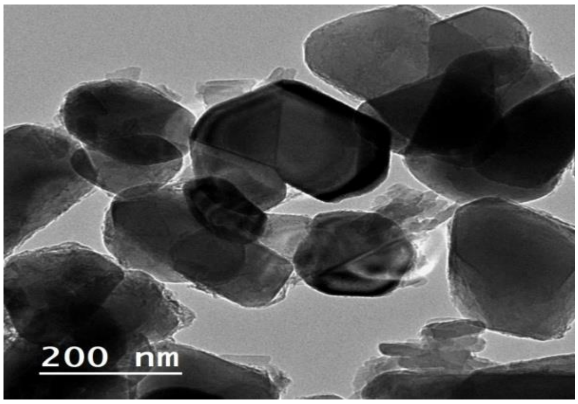


Fig. 3 TEM of a) diatomite and b) Cu-MOF/diatomite

The thermal analysis (TGA)

Fig. 4 represents the TG curves of diatomite and that incorporated with Cu-MOF. The TG profile of the diatomite indicates that it is thermally degraded by heating from room temperature till 900 ºC. After this degradation, the weight loss decreased sharply, this may due to convent the diatomite to like glass structure. For the Cu-MOF/diatomite, the TG profile shows that the weight loss is nearly constant till 800 ºC, this indicates that the incorporated sample doesn't contain any volatile materials and still thermally stable. Above 800 ºC it is observed that a sharp weight loss occurred, this means that the organic parts which coated the diatomite units as indicated from the morphology examination prevent the thermal degradation of diatomite at low temperature. This findings means that the incorporation of Cu-MOF onto diatomite which increases the thermal stability even at high temperature.

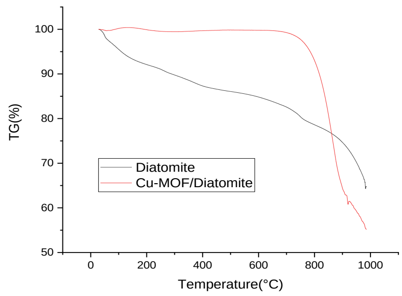


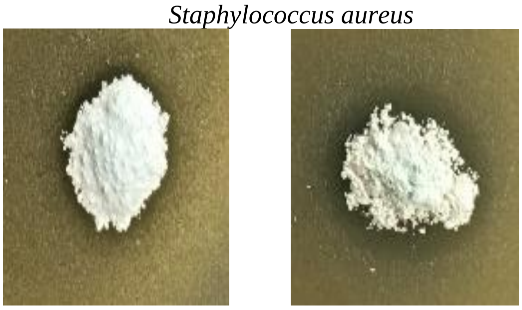
Fig. 4 TGA of diatomite and Cu-MOF/diatomite.

Bioactivity test

Results of antimicrobial testing of the Cu-MOF/diatomite are shown in (Table 1) and Figs. (5-8). Cu-MOF/diatomite showed a potent antimicrobial activity against all tested microorganisms.

a b

Fig. 5 Antibacterial activity of Cu-MOF/Diatomite on Gram positive bacteria a) *Bacillus subtilis and b) Staphylococcus aureus*



a b

Fig. 6 Antibacterial activity of Cu-MOF/Diatomite on Gram negative bacteria a) *Escherichia coli* and b) *Salmonella enteric*

a b

Fig. 7 Anti-yeast activity of Cu-MOF/Diatomite on Yeast a) *Candida albicans* and b) *Candida tropicalis.*

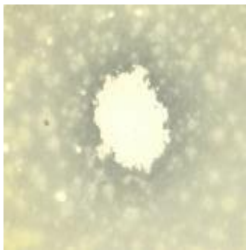


Fig. 8 Antifungal activity of Cu-MOF/Diatomite on Aspergillus niger Fungi

Table 1. Antimicrobial activity of Cu-MOF/diatomite.

Microorganism		Inhibition zone (mm)
		Cu-MOF/Diatomite
Gram positive bacteria	*Bacillus subtilis*	9
	Staphylococcus aureus	10
Gram negative bacteria	*Escherichia coli*	15
	Salmonella enterica	12
Fungi	*Aspergillus niger*	16
Yeast	*Candida albicans*	15
	Candida tropicalis	**13**

Conclusion

Through the work about the antimicrobial of some compounds, it may conclude that:

1) Cu-MOF/diatomite due to their properties and structure exhibit a potent on the all microorganisms.

2) The improvement of Cu-MOF by diatomite as source of silica leads to increase the efficiency of antimicrobial activity.

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Declarations

Conflict of interest: All authors declare that, there is no competing of interests.

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