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Utilization of Polyacrylonitrile Waste Fibers in Metal-Organic Framework Matrix for Forming Bioactive Composites Film

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Abstract

Copper based metal–organic frameworks (Cu-BTC MOFs)/ polyacrylonitrile (PAN) composite films were fabricated by embedding the MOF crystals in soluble polyacrylonitrile (PAN) at different Cu-BTC MOF loadings of 5-40 mass %. The obtained film is highly porous and acts as a house for hosting the bioactive MOF. These Cu-BTC/PAN composite films were then evaluated for antimicrobial application. Data presented herein show that the PAN does not notably interfere with the different strain of bacteria,Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa where the the antimicrobial activity is linearly increase with the increase in Cu-BTC MOF loadings. The results indicated that the best time for elemination of Bacillus subtilize, E. coli , and Candida albicans was 4, 2, and 6 hours respectively.While elimination of Staphylococcus aureus in time (2, 4,and 6 hours) has the same impact. Cu-BTC sheet had the option to eliminate Staphylococcus aureus, Bacillus subtilis, Escherichia coli, and Pseudomonas aeruginosa in both beginning inoculums of 1% and 10% with improved impact on account of 1 %inoculum. Cu-BTC was able to eliminate microorganisms when staying in a mixed co-culture which reduced the cell from 100,000 to 1 CFU/ml.

1. Keywords: Polyacrylonitrile film, Cu-BTC, antimicrobial

1. Introduction

Humans and other kinds of life rely heavily on freshwater supplies to survive and develop. Unfortunately, water contamination has occurred throughout the world as a result of human activities. Water pollutants are defined as physical, chemical, or biological contaminants that alter the physical, chemical, or biological properties of water and have an adverse effect on life. For example, hazardous microbes found in water can cause various diseases in humans and animals[1-3].

Numerous biological water pollution treatment approaches are available, including chlorine, membrane processes, nanotechnology, and layered double hydroxides (LDHs) [4-8]. Antimicrobial weakness testing of nanomaterials made from various metals has been used to investigate the natural highlights of nanomaterials [9-11]. It has been portrayed that metal nanomaterials (Ag, Cu, CuO, and Au) have an immense range of antimicrobial movement in the inconsistency of various sorts of microorganisms, including growths and Gram-positive and Gram-negative bacteria [12]. In

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comparison to natural antibacterial agents, these substances have low poisonousness, adjustment synthetic substances, and warm obstruction [13-15]. The preference for copper nanoparticles linked to silver is due to the minor expense of copper over silver, the physical and synthetic dependability, and the simplicity of blending in with polymers. More modest nanoparticles offer higher action but may bring about bunch development and cause a reduction in fundamental properties [15].Researchers have focused their attention on cellulose fibers (cfs) throughout the last decade. Cfs are hydrophilic, have high porosity and sweat-absorbing characteristics, are affordable, renewable, biodegradable, and flexible, and are frequently utilized [6].In addition, metal surfaces, such as copper, are well-known for their antibacterial properties, as Cu ions have been shown to inhibit bacterial growth[7-14].The presence of copper species and a stable pillar are expected to have a synergistic impact, increasing the antibacterial activity of the modified surface. By combining the antibacterial properties of MOF-199 with the immobilization of these chemicals to cellulose fibers, a cellulose-MOF could provide a novel approach[6, 8].

metal natural systems (MOFs) are described by their permeable construction and photocatalytic action, which makes them profoundly exploitable in their ecological applications like the expulsion of a few perilous materials. Different MOFs, including Cu-MOF, Zr-MOF, Zn-MOF, and Al-MOF, have recently been applied [15–20]. MOFs have been examined to take a gander at their applications like gas stockpiling, gas partitioning of harmful substances, heterogeneous catalysis, energy production, detection, drug conveyance, gadgets, bioreactors, optics, catalysts, the capacity of clean energies, environmental and biological applications [12-14]Many researchers are intrigued by the use of MOFs in wastewater treatment. Metal-organic framework materials (MOFs) are two- or three-dimensional structures made up of metallic ions and bridging organic linkers employed in various applications such as the elimination of microorganisms and hazardous organic compounds. Many researchers are intrigued by the use of MOFs in catalysis[21], sensor [22], hydrogen storage [23], funcrional textile [24] and wastewater treatment [25].MOFs have a huge interior surface area, are very stable, and have well-known properties. MOFs have piqued the interest of researchers in recent years due to their unusual features. The copper-based framework, also known as Cu-BTC, in which dim Eric Cu2+ units are bridged by benzene-1,3,5-tricarboxylate (BTC) linkers, provides a unique and well-studied projecting framework[23-25] .

One of the most fascinating applications for cellulose is as the platform for composites, chiefly as fiber, cotton, layer, or film. Cellulose filaments have found an expansive application in the clinical material field attributable to their one-of-a-kind trademark; for example, fluid adsorption and high dampness, low debasement, and great mechanical properties notwithstanding, cellulose strands give a brilliant surface to microorganisms' development, which is their weakness [17–20].

It was discovered that Cu-BTC MOFs could limit and prevent the development and spread of bacteria on agar dishes, resulting in a deadly effect on bacteria, whether Gram-positive like Staphylococcus aureus, Bacillus spp., or Gram-negative like Escherichia coli, Pseudomonas aeruginosa[8].This study focused on the possible of use Cu-BTC MOFs to eliminate microbial impurities in water. Finally, estimating the optimum conditions to deactivate pathogens wasinverstigated [26-29]..

2. Experimental:

Chemicals and Materials

Copper nitrate (Cu (NO3).3H2O, 99%), trismic acid (C9H6O6, 99%), N,N-dimethylformamide (DMF, C3H7NO, 99.9%), ethanol (C2H6O, 99.9%), methanol (CH4O, 99.9%), and benzoic acid (C7H6O2, 99.5%), all purchased from Sigma-Aldrich and used without purification. Acrylic fabric wastes as source for polyacrylonitrile were purchased from Miser El-Mahalla for Spinning and Weaving, Egypt.

Synthesis of Cu-BTC

Cu-BTC MOF was prepared as the described techniques [30, 31]. Copper (II) trinitrate (2.077 g) was added in water (15 ml) and a solution of 1,3,5-benzenetricarboxylic acid (1.0 g) in a 1:1 mixture of ethanol/N,N-dimethylformamide (DMF) (30 ml) was added to prevous solution and stirred for 10 minutes. The resulting mixture was then transferred to a Teflon-lined stainless steel autoclave and heated at approximately 100 °C for 10 h. The reaction vessel was cooled to room temperature and the resulting blue crystals were isolated by filtration and extracted with methanol overnight using a Soxhlet extractor to remove DMF. The product was then dried at room temperature.

Process

Polyacrylonitrile film (PAN) was synthesized from acrylic fabric wastes as follows: 10 g of acrylic fabric wastes were dissolved in 100 mL DMF at 60 °C for 2 h. The colloid was added and casted on glass slide via a membrane applicator. The film was formed by impregnation in distillate H2O as coagulating bath of for 1 h at room temperature. The obtained PAN film was taken out and dried at ambient conditions prior to be used. For making porous polyacrylonitrile (PAN) film was obtained in two step processes. Acrylic fabric wastes (10 g) were solubilized in dimethyl formamide (100 mL) at 60 °C for 2 h, then 0.5 g of benzoic acid was added. The colloid was stirred for 2 h at 60 °C to be casted by membrane applicator. The film was completely formed by doping in the coagulation water bath. The immobilized benzoic acid was eliminated from the obtained film by formation of water-soluble sodium benzoate form through doping in 100 mL of 5 N sodium hydroxide for 1 h. The PAN film was taken out, washed with distilled H2O and then dried at ambient conditions.

Copper-based coordination polymer (Cu-BTC) was individually synthesized and then immobilized within the synthesized PAN film with two different percentage weights (10% & 30%).The freshly synthesized Cu-BTC was firstly dispersed in 50 mL ethanol and then PAN film was immersed under stirring conditions for half hour. The resulted Cu-BTC/PAN film was removed, rinsed with distilled H2O and consequently dried prior to analysis and application.

Bacterial assays

Bacterial cells (Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa) were cultured in 50 brain-heart broth at37 °until reaching a stationary phase of growth. Bacterial cultures were centrifuged at 2000 rpm for 15minutesto precipitate the bacteria and then the precipitated bacteria were washed with deionized water to ensure absence of any growth medianutrients.The bacterial pellets were re-suspended in 50 mL deionized water.In50 mL falcon tubes, 500 µL of each bacterial culture was placed in 45 ml sterilized water containing0.88 g from Cu-BTC MOFs, then shaken for4 hours at room temperature. This experiment was repeated to study the effect of starting microbial inoculum load,co-culture, different incubation times, and temperature to estimate the functionalities of Cu-BTC MOFs under different conditions. A viable bacterial count technique was performed by diluting and spreading 1 mL of each bacterial culture before and after shaking with the Cu-BTC MOFs on brain-heart infusion agar plates and incubated overnight at37°C.Each experiment was repeated in triplicates

Sensitivity test

Overnight culture of microorganisms (Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa) were diluted to 0.5 McFarland standard and distributed on brain heart in fusion agar plates using sterile cotton swabs. The hand sheet samples were placed in the center of the agar plates and incubated at 37 °C for 24 hours. The zone of inhibitions were monitored and measured [16].

3. Results and Discussion

Porous PAN film was firstly synthesized to act as the porous structure. The immobilized benzoic acid was removed by sodium hydroxide thereby forming porous structure PAN film. The film of Cu-BTC /PAN was obtained with 5% to40% MOF contents. The proposed mechanism for Cu-BTC /PAN synthesis is depicted in Figure. 1. Beside the physical deposition of Cu-BTC within the PAN films, the nitrile groups of PAN molecules could be chemically interacted with the Cu-BTC P through coordination between nitrogen atom of nitrile groups in PAN and the copper atom Cu-BTC

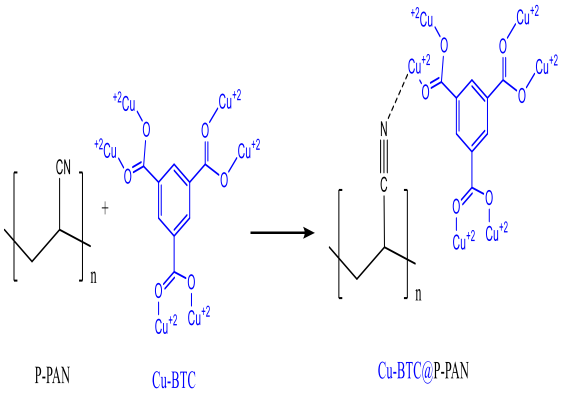


Figure 1. The schematic preparation of Cu-BTC /PAN film

The content of copper within the PAN films was estimated and the evaluated contents of copper were 101.2, 276.7, 315, 420 mg/g for 5%, 20%, 30% and 40%Cu-BTC/PAN film, this quantity is quite close to that theoretically added. The synthesized films (PAN, 20% Cu-BTC/PAN) were examined under the electronic microscope. Figureure 2 showed that highly porous structure was observed for PAN after removing of organic acid[30]. The diameter of the seen pores was measured and was ranged in 8.5–51.2 µm, which confirmed the macro porous structure of the produced film. For Cu-BTC/PAN film, crystalline Cu-BTC was densely distributed over the surface of the PAN film and filled the small pores. Moreover, the observed pore is quite small than the parent film. The EDX analysis showed the signals of C and N for PAN film. While, the signals of oxygen and copper were both recorded besides those of C & N in case of Cu-BTC/PAN film, which further confirmed the incorporation of Cu-BTC within the film.

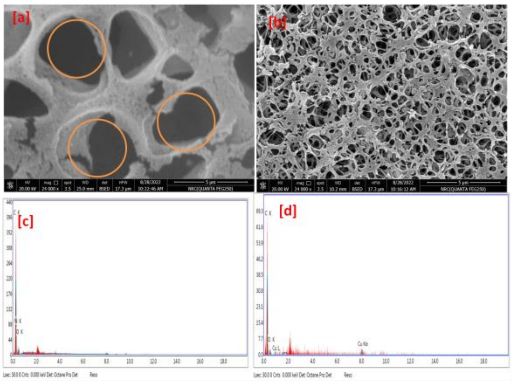


Figure 2.SEM images of [a] PAN film, [b]Cu-BTC/PAN, EDX of [c] PAN film, [d]Cu-BTC/PAN

The XRD for the as-synthesized films were shown in Figure. 3 for more confirmation to the successive preparation of the as-required films. For PAN film, two diffractions at 2θ° = 17.2° (strong) and 29.3° (weak) characterized for (100) and (110) crystalline indices of PAN. Cu-BTC powder showed many characterized diffractions at 2θ° = 6.6°, 9.8° and 11.7°, 15.3°, 16.7°, 18.0°, 19.6° 21.6°, 22.7° and 25.4°, which were strongly matched with the diffractions in literature. For Cu-BTC/PAN films, the diffraction patterns of Cu-BTC were obtained beside those of PAN, which is further confirming the successive immobilized of Cu-BTC in the PAN film.

The intensity of Cu-BTC diffraction was higher in case of impregnation higher Cu-BTC contents.

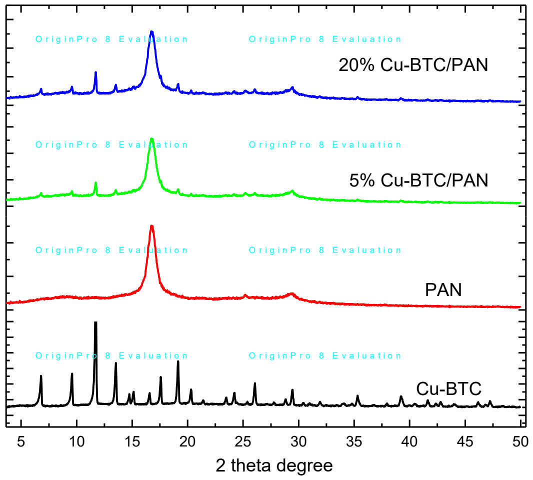


Figure 3. PXRD pattern of Cu-BTC, PAN film, and Cu-BTC/PAN

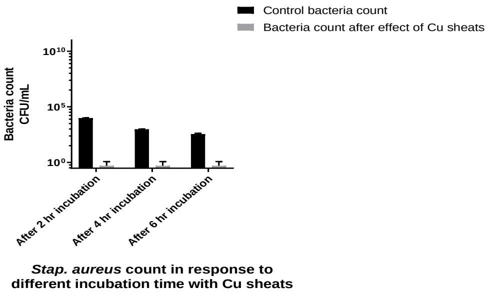
Stability of Cu-BTC and Cu-BTC/PAN in water

Cu-BTC MOF and Cu-BTC/PAN were tested toward water by mixing 200 mg of synthesized Cu-BTC or a piece of Cu-BTC/PAN in the tube have 10 mL water at room temperature. The materials were eliminated from the mixture by centrifugation and/or filtration. The materials were ovened at 75°C overnight. Cu-BTC and Cu-BTC/PAN samples were identified by PXRD to illustrate any structural mutation. The data show an unmutated diffraction pattern over the period of 5 h; this means both Cu-BTC and Cu-BTC/PAN are stable in the presence of water.

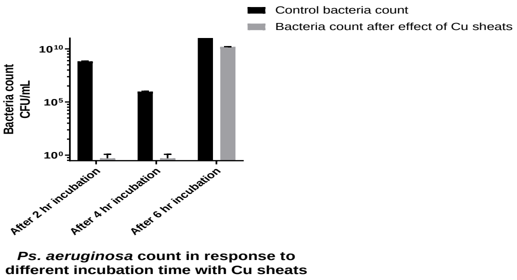
It is known that copper's antimicrobial applications are multidimensional and numerous. The copper (II) antimicrobial activities are probably caused by interaction with the cell membrane by oxidation of membrane proteins and fatty acids or trans membrane possible alteration leading to cell lysis. Applying the oxidized state of copper in the Cu-BTC structure combined with the scarcity of open metal sides could cause the lysisof the membrane. This special situation in the Cu-BTC structure could enhance and increase the antimicrobial potential of copper[27,29].

In the present study, both Gram-positive and Gram-negative grow well on the surface of brain-heart infusion agar. Reaction time (Figure.4) had almost no effect on the growth ratio, which signified that the reaction of Cu-BTC was very rapid [27].

As shown in Figure (4a), Cu-BTC could eliminate Staphylococcus aureus in time (2, 4,and6 hours) with no different effect. Also, Cu-BTC was able to eliminate Pseudomonas aeruginosa in time 2 and 4 hours, as seen in Figure (4b),while there was no effectafter6 hours that could be attributed to the capability of such microbe to overcome the adsorption effect of Cu-BTC after 6 hrs. In Figure (4c), a substantial effect of Cu-BTC was noticed for the treatment of Bacillus subtilisat the best time after 4 hours. The elimination of E. coli was distinguished at the shortest time after 2 hours, as seen in Figure (4d). The best time to remove Candida albicans was after6 hours, but there is a slight reduction at 2 and 4 hours, as seen in Figure (4e).



(a)



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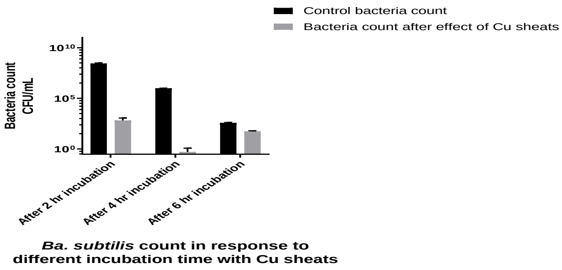

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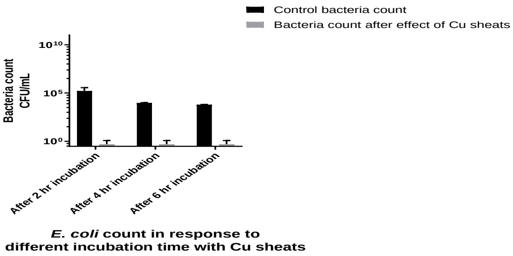

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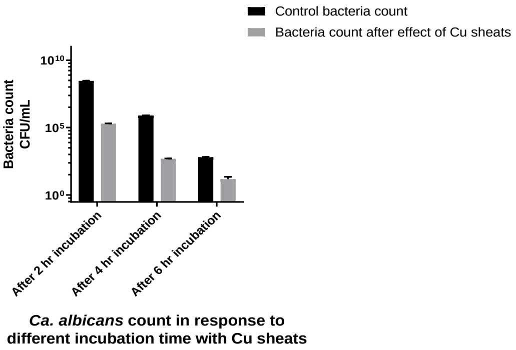


(e)

Figure4. Effect of the incubation time with Cu-BTC (15%) on the elimination of(a)Staphylococcus aureus,(b) Pseudomonasaeruginosa,(c) Bacillus subtilis,(d) E-coli,(e)Candida albicans

Cu-BTC was able to remove microorganisms (Staphylococcus aureus, Bacillus subtilis,Escherichia coli, Pseudomonas aeruginosa, Candida albicans) when they were applied as a mixed co-culture at which the viable cells were reduced from 100,000to 1CFU/mlas observed in Figure (5). In addition, the composite of Cu-BTChad significant antibacterial activity against Staphylococcus aureus, Bacillus subtilis, Escherichia coli, Pseudomonas aeruginosa, and Candida albicans [29-32].

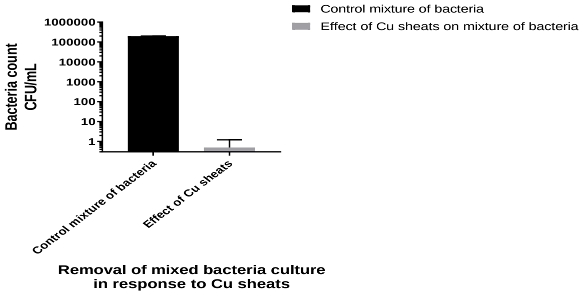
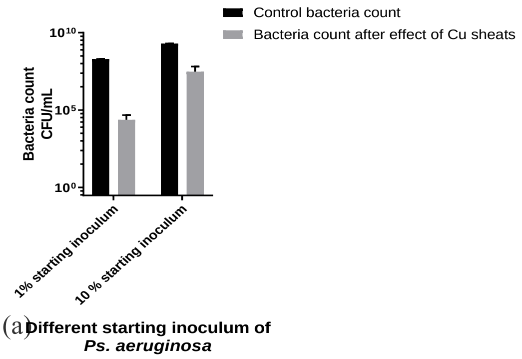
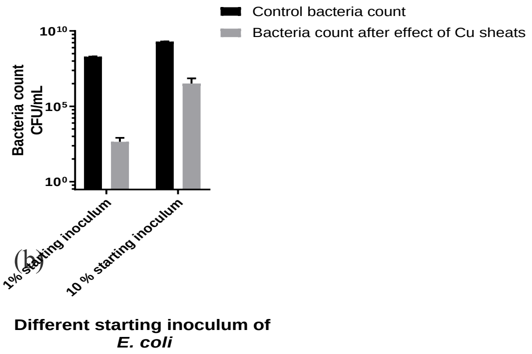
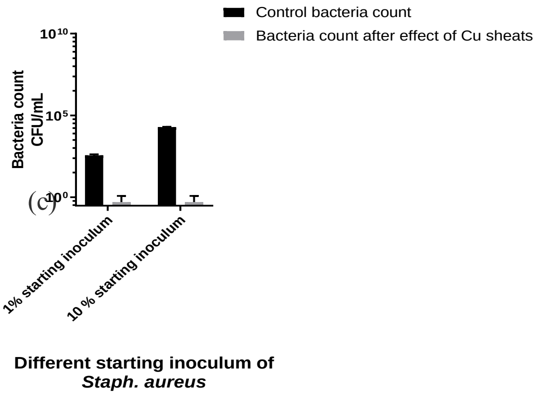


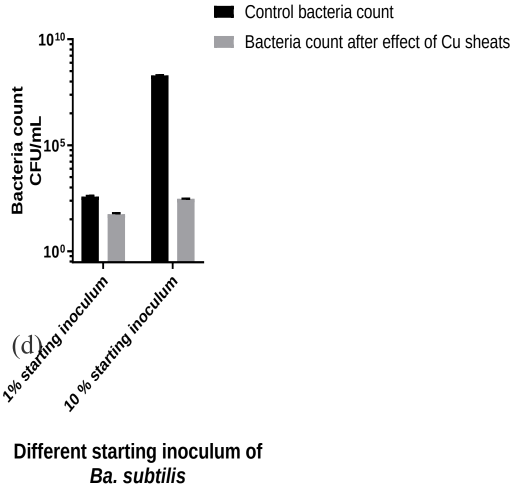
Figure 5.Elimination of mixed bacterial species using Cu-BTC.

As shown in Figure(6), the Cu-BTC could imply its effects against different starting bacterial inoculum loads, but it has high efficiency at starting lower inoculum. Cu-BTC sheet was able to eliminate Pseudomonas aeruginosa and E-coli in both starting inoculums of 1% and 10% with better effect in the case of 1 %inoculum as seen in Figure 6a and 3b, respectively. These results had been reported in the previous work.









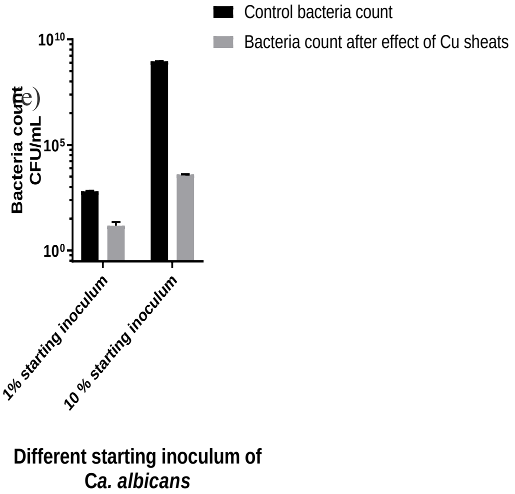
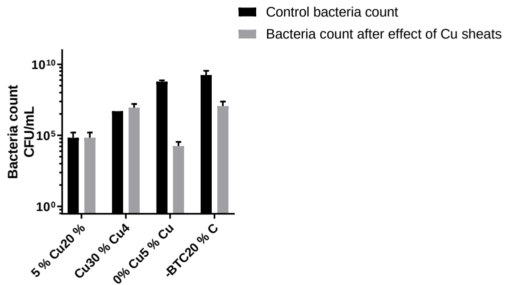


Figure 6.Efficacy of Cu-BTC in presence of different starting microbial inoculum load of(a) Pseudomonas aeruginosa,(b)E. coli,(c)Staphylococcus aureus,(d)Bacillus subtilis,(e)Candida albicans.

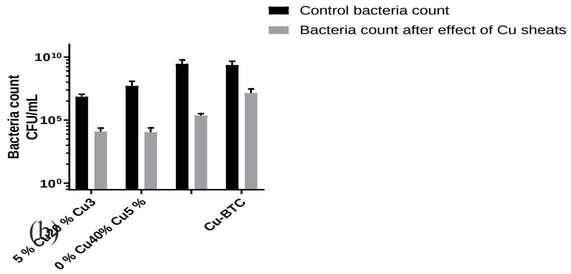
A qualitative test was performed under stationary conditions at which no microbial growth was noticed on or lowers the Cu-BTC fabric. These results designate that the Cu-BTC crystals show antibacterial activity against microbes [32.33].

Effect of Cu concentration



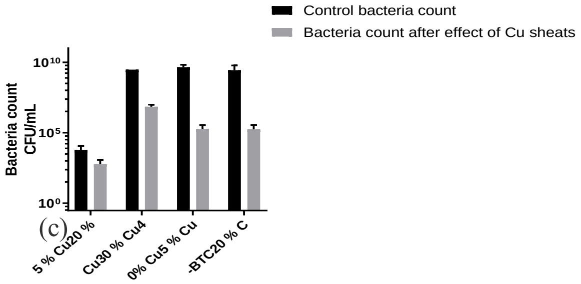
(a)

Effect of different Cu-BTC concentrations on elimination of *Ba. subtilis*



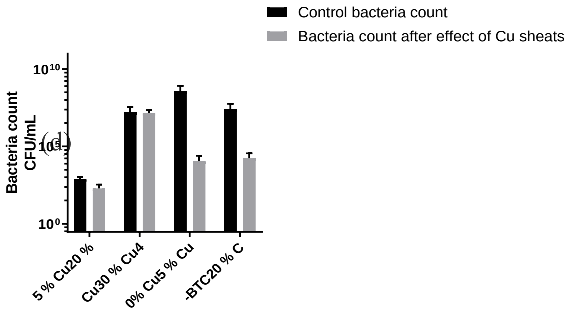
(b)

Effect of different Cu-BTC concentrations on elimination of *Stap. aureus*



(c)

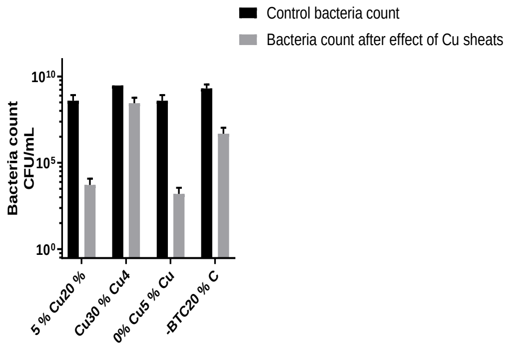
Effect of different Cu-BTC concentrations on elimination of *E. coli*



(d)

Effect of different Cu-BTC concentrations on elimination of *Candida albicans.*

(e)



Effect of different Cu-BTC concentrations on elimination of *Pseudomonas* sp.

Figure 7. Effect of Cu conc .on elimination of microorganism [a] Ba. Subtilis, [b] Stap. aureus, [c] E. coli, [d] candida and [e] Pseudomonas sp

4. Conclusions

In the present study, the Cu-BTC system was effectively synthesized, and its antibacterial properties against both gram-positive and gram-negative bacteria can be quantified. The consequences refer to the cellulose MOF system showing great antibacterial activity and inhibiting microorganism growth on solid cultures. Experimental results also indicate that reaction time had nearly no effect on statement proportion, which signifies that the reaction of CU-BTC was very rapid and also it could affect different bacterial inoculum loads. CU-BTC was able to remove microorganisms when they were applied as a mixed co-culture in different inoculum loads. CU-BTC could extend the fabric's lifespan and aid in the resolution of environmental issues associated with the release of antibacterial compounds.

5. Conflicts of interest

No conflicts to declare.

6. Formatting of funding sources

No funding sources

7. Acknowledgments

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References

[1] P. Goel, Water pollution: causes, effects and control, New age international2006.

[2] P. Servais, G. Billen, P. Bouillot, Biological colonization of granular activated carbon filters in drinking-water treatment, Journal of Environmental Engineering 120 (1994) 888-899.

[3] P. Servais, P. Laurent, G. Randonl, Mesure de la biomasse et de l'activité bactérienne dans l'eau de distribution, Revue des sciences de l'eau/Journal of Water Science 5 (1992) 473-488.

[4] M. Amin, A. Alazba, U. Manzoor, A review of removal of pollutants from water/wastewater using different types of nanomaterials, Advances in Materials Science and Engineering 2014 (2014).

[5] L. Wu, M. Shamsuzzoha, S. Ritchie, Preparation of cellulose acetate supported zero-valent iron nanoparticles for the dechlorination of trichloroethylene in water, Journal of Nanoparticle Research 7 (2005) 469-476.

[6] C. Wang, X. Qian, X. An, In situ green preparation and antibacterial activity of copper-based metal–organic frameworks/cellulose fibers (HKUST-1/CF) composite, Cellulose 22 (2015) 3789-3797.

[7] S.Y. Park, S.-Y. Ryu, S.-Y. Kwak, Antibacterial metal-fiber hybrid with covalent assembly of silver and palladium nanoparticles on cellulose fibers, Environ. Chem 1 (2011) 183-186.

[8] H.S. Rodríguez, J.P. Hinestroza, C. Ochoa-Puentes, C.A. Sierra, C.Y. Soto, Antibacterial activity against Escherichia coli of Cu-BTC (MOF-199) metal-organic framework immobilized onto cellulosic fibers, Journal of Applied Polymer Science 131 (2014).

[9] Usman, M. S., Zowalaty, M. E. E., Shameli, K., Zainuddin, N., Salama, M., & Ibrahim, N. A. (2013). Synthesis, characterization, and antimicrobial properties of copper nanoparticles. International journal of nanomedicine, 4467-4479

[10] Bhattacharyya S, Kudgus RA, Bhattacharya R, Mukherjee P. Inorganic
nanoparticles in cancer therapy. Pharm Res. 2011;28:237–259.

7. Lim ZZ, Li JE, Ng CT, Yung LY, Bay BH. Gold nanoparticles in cancer therapy. Acta Pharmacol Sin. 2011;32:983–990.

[11] Hirsch LR, Stafford R, Bankson J, et al. Nanoshell-mediated nearinfrared thermal therapy of tumors under magnetic resonance guidance. Proc Natl Acad Sci U S A. 2003;100:13549–13554

[12] Chatterjee AK, Sarkar RK, Chattopadhyay AP, Aich P, Chakraborty R, Basu T. A simple robust method for synthesis of metallic copper
nanoparticles of high antibacterial potency against E. coli. Nanotechnology. 2012;23:1–11

[13] Mohammadi, F., Montazer, M., Mianehro, A., Eslahi, N., & Rad, M. M. (2022). Preparation of Antibacterial Cellulose Fabric via Copper (II) Oxide and Corn Silk (Stigma Maydis) Nanocomposite. Starch‐Stärke, 2200156.

[14] Jrad, A., Damacet, P., Yaghi, Z., Ahmad, M., & Hmadeh, M. (2022). Zr-based metal–organic framework nanocrystals for water remediation. ACS Applied Nano Materials, 5(8), 10795-10808.

[15] Abdelhameed, R. M., Abdel-Gawad, H., & Emam, H. E. (2021). Macroporous Cu-MOF@ cellulose acetate membrane serviceable in selective removal of dimethoate pesticide from wastewater. Journal of Environmental Chemical Engineering, 9(2), 105121.

[16] Bag, P. P., Singh, G. P., Singha, S., & Roymahapatra, G. (2020). Synthesis of metal-organic frameworks (MOFs) and their biological, catalytic and energetic application: a mini review. Engineered Science, 13(2), 1-10.

[17] Emam, H. E., Ahmed, H. B., Gomaa, E., Helal, M. H., & Abdelhameed, R. M. (2020). Recyclable photocatalyst composites based on Ag3VO4 and Ag2WO4@ MOF@ cotton for effective discoloration of dye in visible light. Cellulose, 27(12), 7139-7155.

[18] Emam, H. E., El-Shahat, M., & Abdelhameed, R. M. (2021). Observable removal of pharmaceutical residues by highly porous photoactive cellulose acetate@ MIL-MOF film. Journal of Hazardous materials, 414, 125509.

[19] Xie, Y., Lyu, S., Zhang, Y., & Cai, C. (2022). Adsorption and Degradation of Volatile Organic Compounds by Metal–Organic Frameworks (MOFs): A Review. Materials, 15(21), 7727.

[20] Abdelhameed, R. M., Alzahrani, E., Shaltout, A. A., & Emam, H. E. (2021). Temperature-controlled-release of essential oil via reusable mesoporous composite of microcrystalline cellulose and zeolitic imidazole frameworks. Journal of Industrial and Engineering Chemistry, 94, 134-144.

[21] Emam, H. E., Darwesh, O. M., & Abdelhameed, R. M. (2020). Protective cotton textiles via amalgamation of cross-linked zeolitic imidazole frameworks. Industrial & Engineering Chemistry Research, 59(23), 10931-10944.

[22] E.A. Dolgopolova, A.M. Rice, C.R. Martin, N.B. Shustova, Photochemistry and photophysics of MOFs: steps towards MOF-based sensing enhancements, Chemical Society Reviews 47 (2018) 4710-4728.

[23] Abdelhameed, R. M., El-Shahat, M., & Emam, H. E. (2020). Employable metal (Ag & Pd)@ MIL-125-NH2@ cellulose acetate film for visible-light driven photocatalysis for reduction of nitro-aromatics. Carbohydrate polymers, 247, 116695.

[24] H.E. Emam, R.M. Abdelhameed, Anti-UV radiation textiles designed by embracing with nano-MIL (Ti, In)–metal organic framework, ACS applied materials & interfaces 9 (2017) 28034-28045.

[25] H.E. Emam, R.M. Abdelhameed, H.B. Ahmed, Adsorptive performance of MOFs and MOF containing composites for clean energy and safe environment, Journal of Environmental Chemical Engineering (2020) 104386.

[26] Ruangpan, L., & Tendencia, E. (2004). Laboratory manual of standardized methods for antimicrobial sensitivity tests for bacteria isolated from aquatic animals and environment. Aquaculture Department, Southeast Asian Fisheries Development Center..

[27] Esteban-Cubillo, A., Pecharromán, C., Aguilar, E., Santarén, J., & Moya, J. S. (2006). Antibacterial activity of copper

monodispersed nanoparticles into sepiolite. Journal of materials science, 41(16), 5208-5212.

[28] Son, W. K., Youk, J. H., Lee, T. S., & Park, W. H. (2004). Preparation of antimicrobial ultrafine cellulose acetate fibers with silver nanoparticles. Macromolecular rapid communications, 25(18), 1632-1637.

[29] Santo, C. E., Quaranta, D., & Grass, G. (2012). Antimicrobial metallic copper surfaces kill Staphylococcus haemolyticus via membrane damage. Microbiologyopen, 1(1), 46-52.

[30] Abdelhameed, R. M., Taha, M., Abdel-Gawad, H., & Emam, H. E. (2022). Purification of soybean oil from diazinon insecticide by iron-based metal organic framework: Effect of geometrical shape and simulation study. Journal of Molecular Structure, 1250, 131914

[31] Abdelhameed, R. M., & Emam, H. E. (2022). Modulation of metal organic framework hybrid cotton for efficient sweeping of dyes and pesticides from wastewater. Sustainable Materials and Technologies, 31, e00366.

[32]Mathews, S., Kumar, R., & Solioz, M. (2015). Copper reduction and contact killing of bacteria by iron surfaces. Applied and environmental microbiology, 81(18), 6399-6403.

[33] Meyer, Travis J., et al. "Antimicrobial properties of copper in gram-negative and gram-positive bacteria." International Journal of Pharmacological and Pharmaceutical Sciences 9.3 (2015): 274-278.