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Metal Organic Framework for Removal of Cu (II) Ion from Aqueous Solution

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Abstract

Copper is a heavy metal that is utilized in a variety of sectors and is renowned for its severe environmental and health effects. With varied starting Cu+2 concentrations and pH levels, 5mg of MOF was applied to measure its ability in Cu+ 2 removals (5, 7 and 9). For starting concentrations of 5, 10, 15, and 20 ppm, the prepared MOF was able to remove Cu with 94.6 percent, 93 percent, 91.5 percent, and 92.5 percent, respectively. It also worked well at pH 5 and 7, with average removal rates of 93.9 percent and 95 percent for pH 5 and 7, respectively, for starting concentrations of 5, 10, and 15, indicating that the produced MOF has a strong capacity to remove Cu^{+2}.

Keywords: Metal Organic Framework; Cu (II) ion- industrial wastewater; pH; time.

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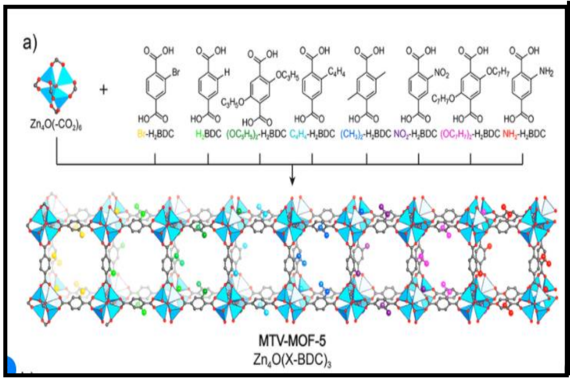
1. Introduction

The ongoing increase in human population and industrial growth is contributing to worldwide environmental contamination. Waste resources, through contaminating land, water, and air, are harmful to the environ-ment and human health [1, 2, 3]. In recent years, industrial activities had resulted in an increase in toxic contaminants in wastewater, such as copper (II) ion (Cu2+). Electroplating, battery manufacture, mining, and textile manufacture are all primary emitters of copper ions [4, 5]. Although cop-per is an aspect of the environment, too much of it can cause liver and re-nal issues in humans. Cu2+ levels in drinking water must not exceed 1.3ppm, according to EPA (2021) [6, 7]. Contamination elimination using adsorbents with high adsorption [8-10] capacity is one of the most promising technologies owing to its ease of use, high removal effectiveness, and application to a wide range of contaminants [11]. Metal-organic frameworks (MOFs) are a novel class of porous inorganic organic hybrid materials that have piqued the interest of academics and industry in recent years [12, 13]. MOFs often have a high degree of tenability, which may be done by a variety of metal ions and organic linkers, as well as post-synthesis surface changes. Because of their porous nature, they may be used for a variety of purposes, including nat-ural gas and hydrogen storage [14, 15] gas separation and recently in heavy metal removals from water and more [16, 17, 18]. Heterogeneity is introduced into MOFs as showed in Figure (1). Heterogeneity can be es-tablished by designing a framework with numerous linkers that share the same topicality and metrics but have different functionality attached to them. MTV-MOF-5 is made up of basic zinc carboxylate SBUs and a va-riety of various BDC derivatives. These derivatives are interchangeable in their crystal structure, and crystallography cannot pinpoint their specific placement. Heterogeneity is discovered using the multi-SBU technique for SBUs that may be made from a variety of metals as Figure (2). This is observed in [(MA, MB)3OL3] (TCPP-MC)3 where two scenarios are dis-tinguished; well-mixed [M3OL3] (−COO)6 SBUs are observed in [(Fe, Ni)3OL3] (TCPP-MC)3 whereas a domain-arrangement is found for [(Mn, Fe)3OL3] (TCPP-MC)3. Color code: M, blue/ orange/pink; C, gray; N, green; O, red. All hydrogen atoms are omitted for clarity [19].



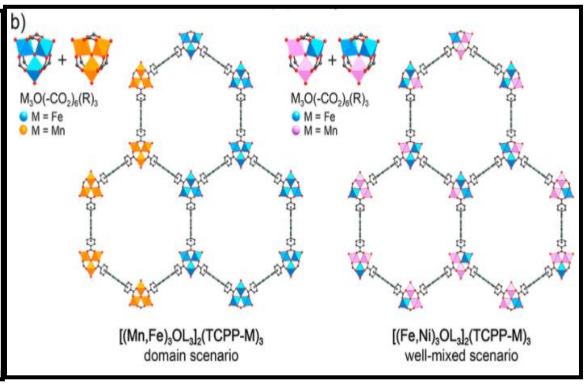


Figure 1: Framework with **multiple** linkers **Figure 2:** Secondary building units (SBU**)**

2. Materials and Methods

Recent reaches have been utilizing MOF as an organic – inorganic structure in removal of heavy metal ions from wastewater [20,21] The chemicals and materials used to prepare the MOF, and tests performed for copper removal are presented in the following subsections.

Table 1: Chemicals used in MOF Preparation

Number	Name	Chemical formula
1	Phathelic acid	$C_8H_6O_4$
2	O-phenelyne diamine	$C_6H_8N_2$
3	Zinc acetate	$Zn\ (CH_3CO_2)_2$
4	Copper Sulphate penta-hydrate	$CuSO_4.5H_2O$

2.1 Characteristic of MOF analysis

The morphology of the synthesized adsorbent was investigated by scanning electron microscopy (Zeiss EVO-10 microscopy). Structural properties of MOF-5 were determined with N2 adsorption/desorption isotherm at 77.3 K (NOVA Station: A). Also, for the crystalline charac-terization, X-ray diffraction (XRD, Shimadzu XD-l) was used. The in-struments used for studying the MOF structure are presented in Table (2) and demonstrated in **Figures 3-6**.

Table 2: Instrumentation Used in MOF characterization

Number	Name	Model
1	Powder X-ray diffraction	PXRD, Shimadzu XD-l
2	FTIR	FT/IR 4100
3	SEM/EDX	Zeiss EVO-10 microscopy
4	ICP	Model 7700

(a) (b) (c) (d)

Figure 3: Equipment used to test for the prepared MOF: (a) SEM (b) ICP (c) FTIR (d) XRD

2.3 Experimental Procedure

Several parameters were considered in the scope of work, some of those were constant while others were variable. The temperature of the Lab used to perform the experimental analyses was maintained at 25oC.Variable parameters included different concentrations of copper, the contact time with the adsorbent material and the pH of water used in testing.

2.3.1 Preparing synthetic water solution with the designed initial concentration of copper

A set of 76 water samples were prepared at different concentration, taking a sample of 100ml in beaker and then adding a 5mg of MOF-Powder in each sample. According to the designed time table, sam-ples were taken after 24 hr. A sample of 100ml was collected from different concentrations in a flask and then a drop of sodium hydroxide was added to increase the al-kalinity of water and in another flask a drop of Sulphuric acid was added to increase the acidity of water, then 5mg of powder was added in each flask with different Cu+2 concentration, samples were collected after 5 hours.

Three factors were examined during these experiments:

Effect of time (the change in removal percentages corresponding to the duration of the contact time, the results of this experiment was im-portant to determine the breakthrough curve). Effect of initial Cu+ 2 concentrations (The experiment was conduct-ed with synthetic copper solution of 100 ppm concentration separately. The various concentration of copper tested included in the previous ex-periment were: 5, 10, 15 and 20 ppm.) Effect of different pH to test the effect of prepared MOF on copper removal in case of acidic, neutral and alkaline water solutions (pH: 5, 7 and 9). The testing phase was executed over four phases. Phase I included the study of MOF characterization prepared in the lab. Phase II was done to determine the ability of MOF to eliminate the copper with different concentrations. In Phase III, samples were collected over 24 hours to de-termine the optimum time for adsorption with different pH media (acidic, neutral and alkaline) for the 15ppm copper initial concentration. Lastly in Phase IV, copper removal was examined for initial concentrations of 5, 10, 15 mg/l.

3. Results and discussion

The characterization and the adsorption capabilities of the prepared MOF to eliminate copper metal ions possibly from industrial wastewater are demonstrated.

3.1 Phase I Copper Removal with different concentrations over 24 hours

It was vital to test the performance of the MOF prepared concerning adsorption. Henceforth, synthetic solution with initial concentrations of 5, 10, 15, 20 ppm was prepared for copper. The effect of initial copper con-centration on the copper adsorption rate was studied in the range of 5-20mg/L at pH 7 at room temp over a 24hr contact time. The results are presented Figure 8. Results show that the percentage removal is directly proportional with the initial copper concentration. Moreover, from the at-tained effluent levels of Cu+2, results show that for initial copper concen-tration up to 10 ppm and possibly 15 ppm or less, the used amount of MOF would be sufficient to fulfill the WHO requirements for Copper present in surface water (1.3 mg/l) as previously mentioned, in case of treatment. However for higher concentrations more MOF material could be required for better removals. The results also revealed a uniform ad-sorption of CuSO4 by the MOF prepared; the percentage removal ranged between 91.5% to 94.6.

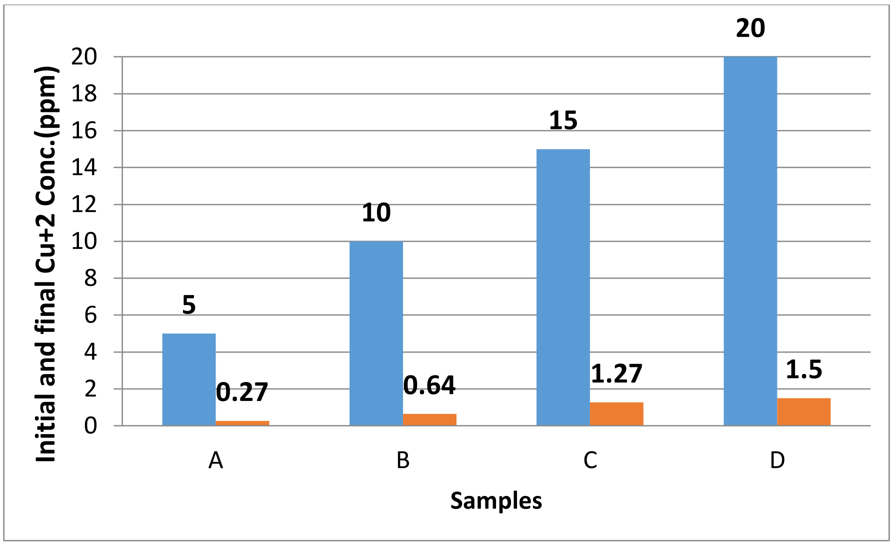


Figure 8: Effect of MOF on Cu II ion adsorption

3.2 Phase II: Testing adsorption rate of MOF for Cu+2 with con-centration of 15 mg/l against acidic, neutral and alkaline media

Samples were collected over 24 hours with 4-hour interval duration to test the optimum time required for Cu+2 adsorption to attain acceptable limits. An initial 15ppm of copper solution was prepared. Figure 9 demonstrates the results for the performance of the MOF for Cu+ 2 re-movals. The results showed that for pH5 and pH7 solutions, the removals rates reached 93% and 95% respectively for the initial concentrations of Cu+2 (15ppm) after 1 hour. This could be reasoned to the fact that Cu+2 was well dispersed and dissolved in the solution allowing the MOF to adsorb it. After 12 hours the removal was 98.8 % and it was fixed at that percentage which indicates that the MOF was completely saturated. However, at pH 9 the removal percentage was 57 % after 1 hour and it was fixed at 63 % indicating the poor performance of the MOF in an al-kaline media due to the fact that Cu+2 precipitated under this high pH banning the MOF from capturing it. The results also indicate that around 5 hours could be a suggested timing sufficient to remove enough copper ions to reach the allowable limits stated by WHO (1.3 mg/l) and would be sufficient for designing the required reactor for removal in case of treating industrial wastewater.

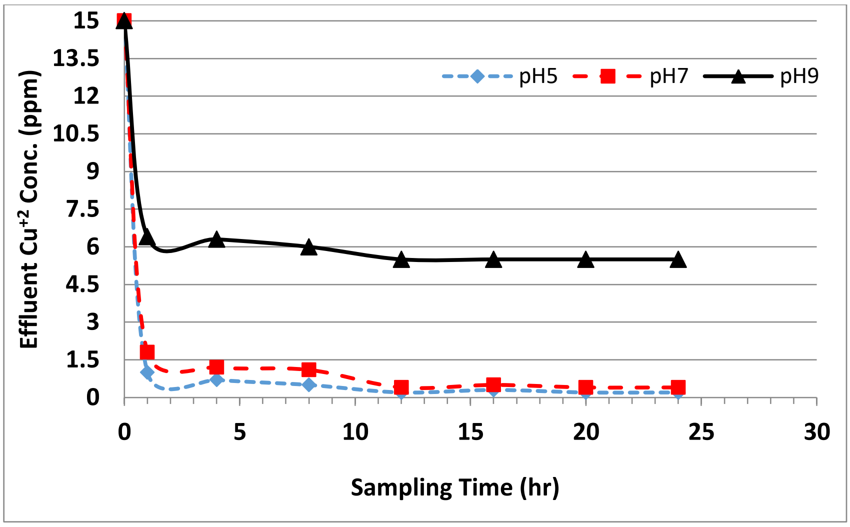
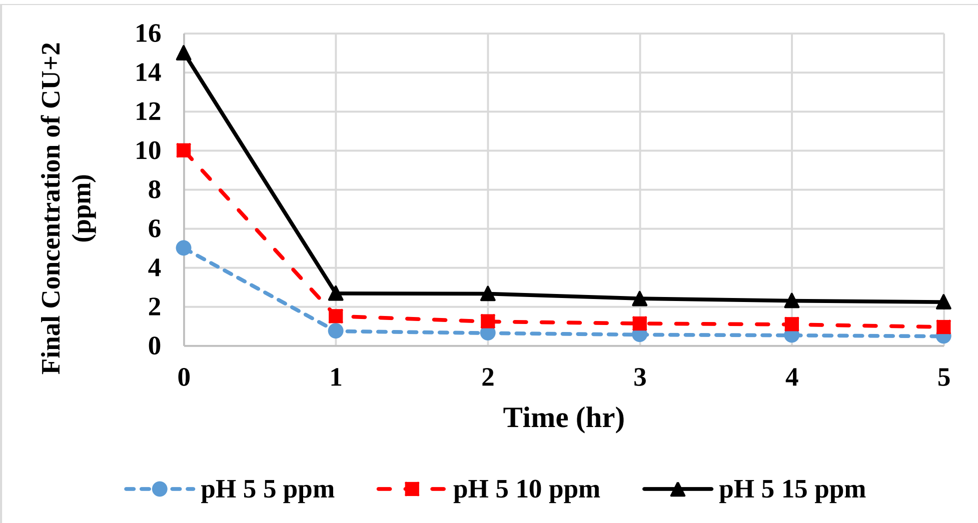


Figure 9: Effect of time on Cu+2 removal for different pH

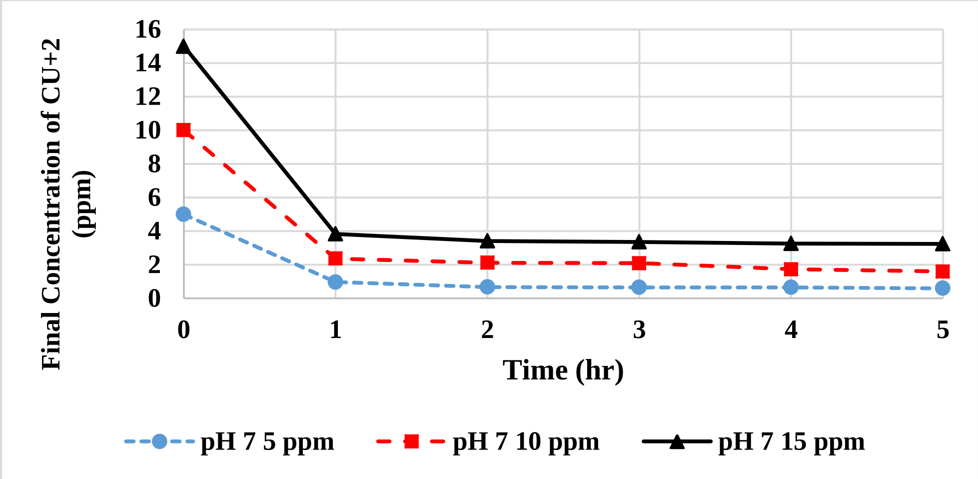
3.4 Phase III: Results achieved for concentrations of 5, 10 and 15 mg/l of Cu

Synthetic solutions of 5, 10, and 15 ppm of Cu (II) ion solution were produced in this phase to evaluate MOF adsorption removal. Samples were prepared as previously stated and collected across a time range of 5 hours following the breakthrough curve established the chosen timing of 5 hours. The end concentrations for the three-initial concentrations for Cu+2 at pH5, pH7, and pH9 are shown in Figures 10a, 10b, and 10c, respectively. The obtained findings showed that the produced MOF had a good performance for Cu+2 adsorption at pH5 for starting copper concentrations of 5 and 10 ppm, which met WHO criteria. For pH7, the MOF prepared performed well with initial copper concentration of 5 ppm, but for the 10ppm initial level, more time would be advised to reach WHO limits. The findings achieved comply with those attained by Bakhtiari and Azizian [22]. However, the alkaline media (pH9) hindered the performance of the MOF in adsorbing the copper ions as previously mentioned.

(a)



(b)



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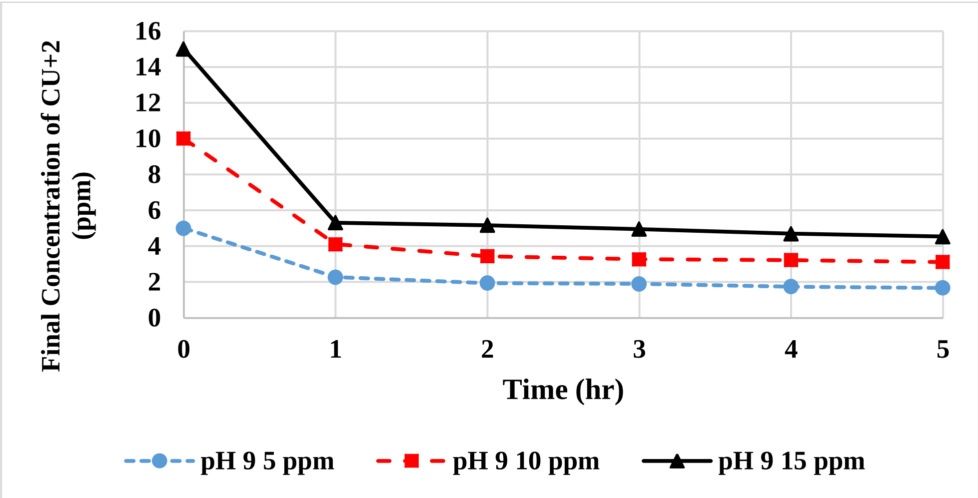

Figure 10: Effect of time and pH media on Cu+2 removal

4. Conclusion

Since few researches have examined the use of metallic organic framework in removal of heavy metals, the research herein has focused on preparing a structure that would help in removal of copper (II) ion which is one of the hostile heavy metals found in the effluent water for many industries [22]. The prepared MOF composition was char-acterized by SEM, EDAX, FTIR and XRD. It was examined in the re-moval of Cu+2 for different pH media (5,7 and 9). The results showed that the amount of 5 mg MOF prepared has the highest performance in ad-sorbing Cu+2 at pH5 and pH7 compared to pH9 which agreed with the fact that Cu+2 precipitates in alkaline media and was not adsorbed. The prepared MOF was able to achieve Cu+2 removal with rates of 94.6%, 93%, 91.5%, and 92.5 % for the initial concentrations of 5, 10, 15, and 20 ppm respectively. It also performed very well for pH 5 and 7 with av-erage removal ranging from 93.9%-95% for pH 5 and 7 for the initial concentrations of 5, 10, but not the 15 ppm as more time would be re-quired or more amount of MOF would be needed to correspond to the high initial concentration. However the overall performance indicated that the prepared MOF is of high ability in adsorbing Cu II ion.

5. Recommendation

Investigating the applicability of the research outcomes on real industrial wastewater

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