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Article

Cu (II) Ion Removal from Aqueous Solution Using Metal-Organic Framework Material

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Abstract: Copper is a heavy metal used in many industries and known for its negative impacts on the environment and human's health. A novel structured metal organic framework (MOF) was used for copper adsorption for this work. SEM, EDAX, XRD and FTIR were done to confirm the structure of MOF prepared. MOF of 0.05 gm was used to examine its ability in Cu+ 2 removals with different initial concentrations of Cu+2 and pH values (5, 7 and 9). The prepared MOF was able to achieve Cu removal with 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 average removal ranging from 93.9%-95% for pH 5 and 7 for the initial concentrations of 5, 10, and 15 respectively which indicate that the prepared MOF is of high ability in Cu+ 2 removal.

Keywords: Metal Organic Framework; Cu (II) ion- industrial waste water; pH; time; adsorption

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 environment 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 copper is an aspect of the environment, too much of it can cause liver and renal 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 natural 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 established 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 variety of various BDC derivatives. These derivatives are interchangeable in their crystal structure, and crystallography cannot pinpoint their

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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 distinguished; 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].

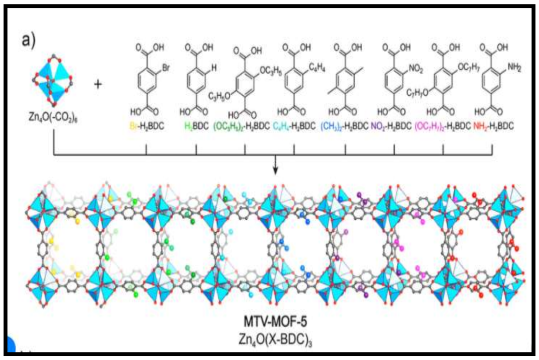

Figure (1): Framework with **multiple** linkers

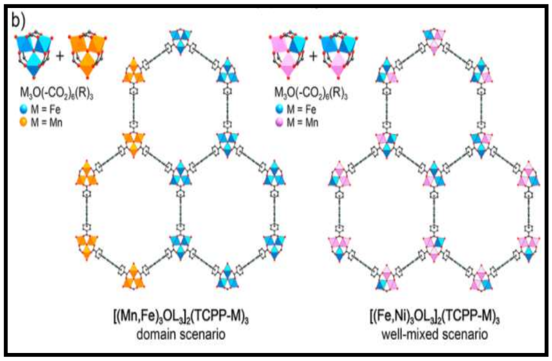

Figure (2): Secondary building units (SBU**)**

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.

2.1 Synthesis of the MOF (Zn-Ph-D CP)

As presented in Table (1) below, Phathelic acid (Ph) 98%, O-phenelyne diamine (D), Zinc acetate (Zn) 99 %, and deionized water (DW) are used without further purification in the synthesis of Zn-Ph-D CP. Typically, Ph (0.166 g), and D (0.1 g) were dissolved in DW (50 mL) at room temperature. The obtained mixture was transferred into the oven and maintained at 70 °C for 30 min the solution turns to dark brown color, being subsequently adding 0.2 g of zinc acetate the final solution was then transferred to the oven at 80 °C and allowed to react for 2 hr. The yellow crystals were then allowed to cool at the room temperature. The yellow solid crystal product was extracted by centrifugation and washed three times with DW and ethanol. This was then followed by drying in the vacuum oven at 100 °C for 4 h prior to being utilized for adsorption of Cu (II) ion.

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	$CuSO_4.5H_2O$

2.2 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 characterization, X-ray diffraction (PXRD, Shimadzu XD-l) was used. The instruments 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-1
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 25^{o}C.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, samples 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 alkalinity 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 important to determine the breakthrough curve).

Effect of initial Cu+ 2 concentrations (The experiment was conducted with synthetic copper solution of 100 ppm concentration separately. The various concentration of copper tested included in the previous experiment 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 determine 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.

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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: The characterization and the analysis of MOF

To study the characterization of the MOF prepared, SEM, EDAX, XRD and FTIR were done to confirm its structure. The results are presented as follows:

XRD Analysis

Figure (4) shows the XRD analysis for the prepared MOF; the X-ray diffraction powder patterns have been indexed and refined. The crystalline framework structure of the MOF (Zn-Ph-D CP) was constructed by exposing the amorphous phases to saturated water vapour at 30oC for 2 days; it was shown that recrystallization depends on the amorphous state. The recrystallized phases recovered over 90 % of their porous capacity. The X-ray absorption near edge structure spectra of the amorphous and crystallized state was identical to the pristine, amorphous and crystallized states of (Zn-Ph-D-CP). The coordination environment of (Zn-Ph-D-CP) in amorphous and crystallized states of the 1:1 mixture was retained to be octahedral. This pattern may be similar to the simulated pattern used by Carson and his colleagues [22].

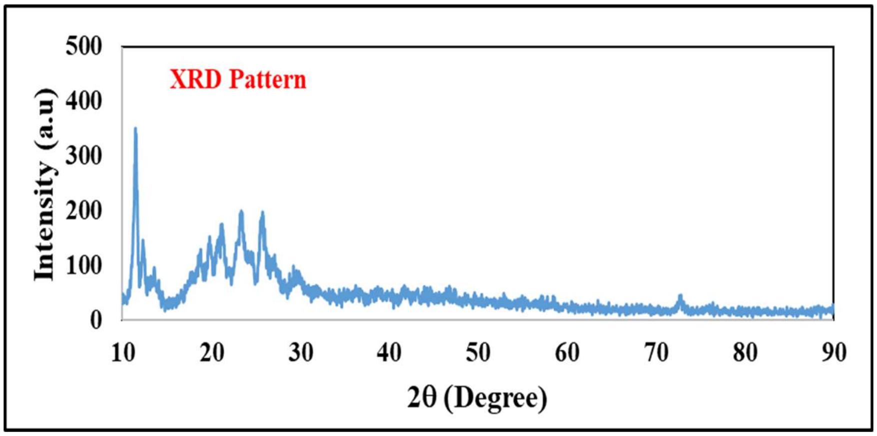

Figure (4) XRD for MOF (Zn-Ph-D-CP)

FTIR Analysis for prepared MOF

Figure (5) represent the FTIR analysis of the prepared MOF. Key products from Phthalic oxidation were visualized in the range of 1700–1100 cm-1 of the IR spectrum. Some of the products can be clearly identified the bands at about 1600 and 1200 cm-1 can be as-signed to the stretching modes of phthalic acid; the broad band centered at 1735 cm-1, with a potential shoulder at 1710 cm-1, might indicate contributions of the diamine stretching modes. The band at 1415 cm-1 is related to the C_H bending modes of various hydrocarbons. The formation of phthalic diamine cannot be clearly identified in thisr spectra. In the case of ZnO, as expected, adsorbed phthalic diamine is detected as the main selectively oxidized product.

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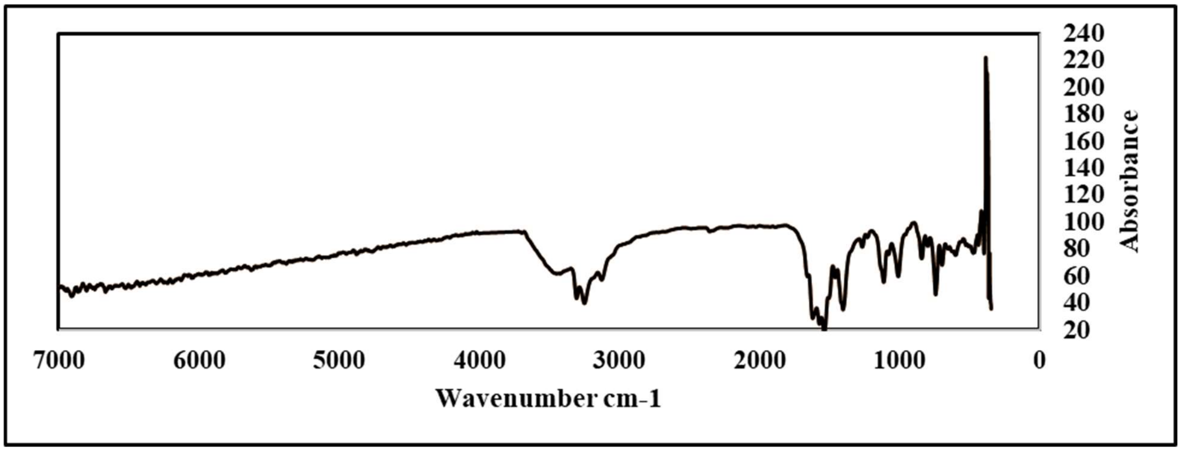

Figure (5) FTIR analysis for MOF(Zn-Ph-D-CP)

SEM and EDAX Result for prepared MOF

Figure (6) represents the SEM of the prepared MOF at 1.06 KX; it shows that the prepared MOF already contains voids capable of adsorbing Cu+2 within its inner tubes; it also shows that the prepared MOF is well organized and formed of many layers which agrees with the obtained results for the Cu+2 removal presented later. These photos show the morphology of MOF crystals that have been created, which is comparable to earlier researches [23, 24].

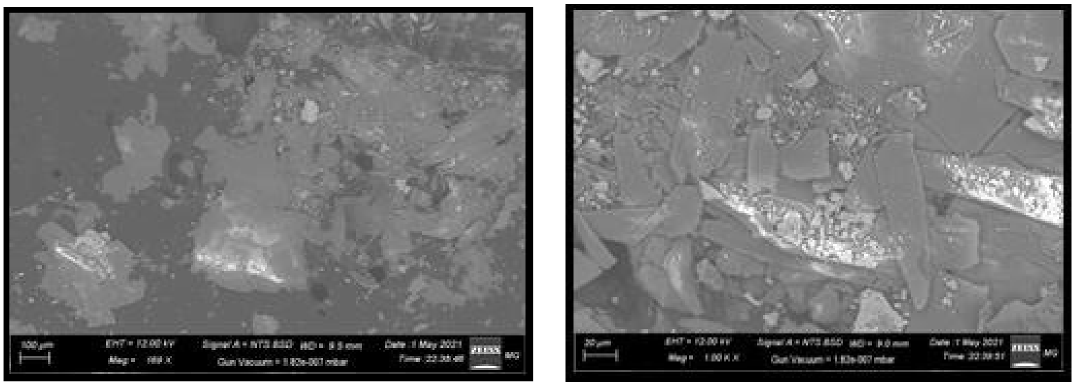

Figure (6) SEM for MOF (Zn-Ph-D-CP)

Figure (7) shows the elemental analysis of the prepared MOF. It confirms the presence of Zn, O, C and N which in combination with the presented SEM image confirm that the MOF is prepared with the correct composition required for Cu +2 adsorption.

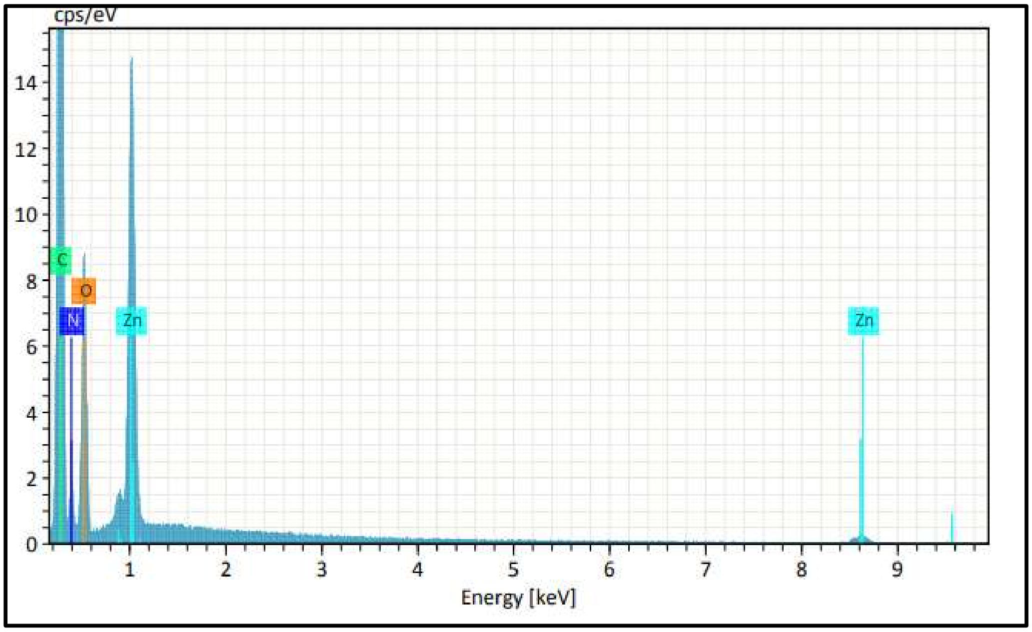

Figure (7) EDAX for MOF(Zn-Ph-D-CP)

3.2 Phase II 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 concentration 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 attained effluent levels of Cu+2, results show that for initial copper concentration 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 adsorption of $CuSO_4$ by the MOF prepared; the percentage removal ranged between 91.5% to 94.6.

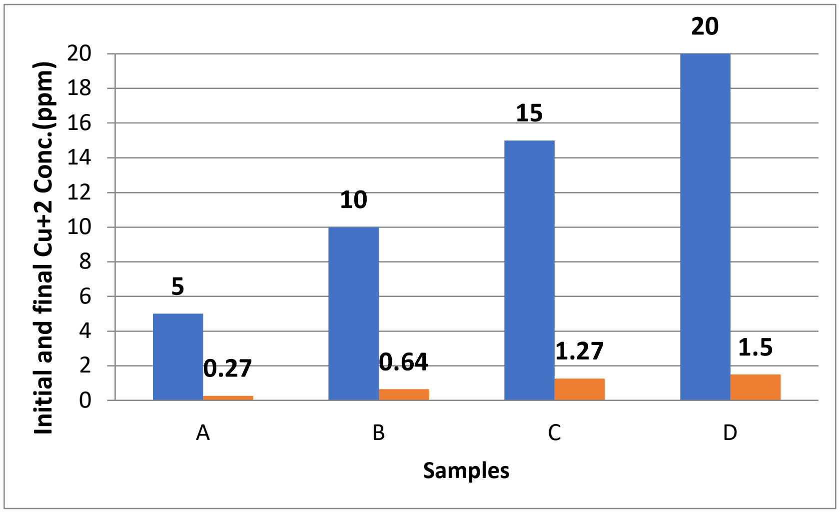

Figure 8: Effect of MOF(Zn-Ph-D-CP) on Cu II ion adsorption

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3.3 Phase III: Testing adsorption rate of MOF for Cu^{+2} with concentration 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 removals. 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 alkaline 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.

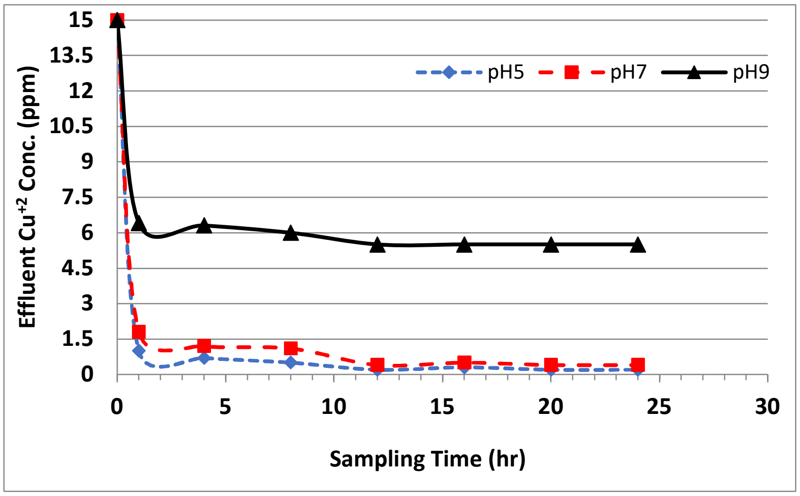

Figure 9: Effect of time on Cu+2 removal for different pH

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

In this phase, synthetic solutions of 5, 10, 15 ppm from Cu (II) ion solution were prepared to test its removal using MOF by adsorption. Samples were prepared as mentioned before and collected over a time range of 5 hours after the selected timing of 5 hour was determined from the breakthrough curve. Figure 10a, 10b, and 10c below illustrate the final concentration for the three-initial concentration for Cu+2 at pH5, pH7, and pH9 respectively. The obtained results demonstrated the promising performance of the prepared MOF for Cu+2 adsorption at pH5 for the initial copper concentrations of 5 and 10 ppm that would comply with WHO requirements. 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 [25]. However, the alkaline media (pH9) hindered the performance of the MOF in adsorbing the copper ions as previously mentioned.

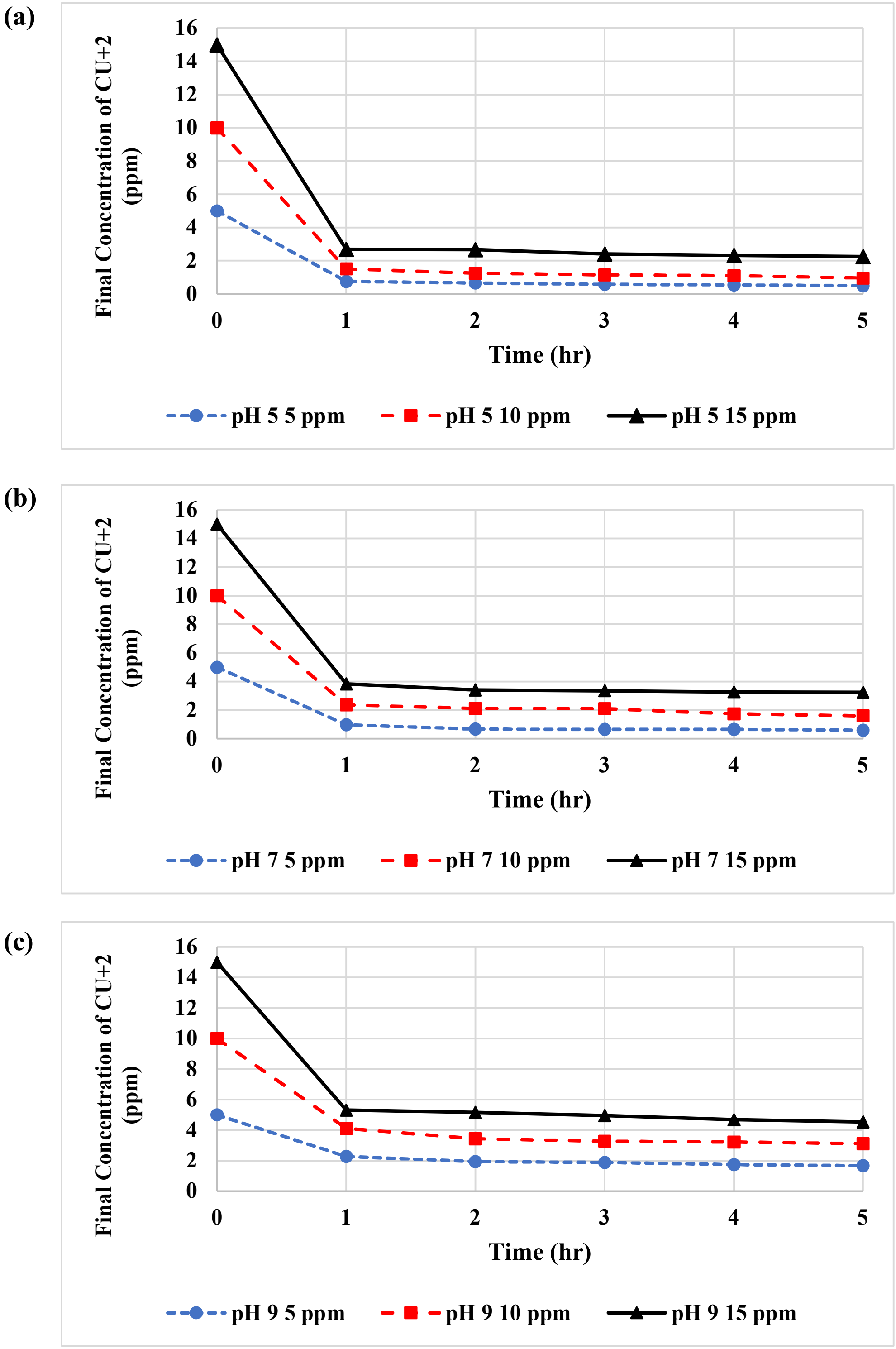

Figure 10: Effect of time and pH media on Cu+2 removal

4. Conclusions

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 [17]. The prepared MOF (Zn-Ph-D-CP) composition was characterized by SEM, EDAX, FTIR and XRD. It was examined in the removal 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 adsorbing 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 average 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 required or more amount of MOF would be needed to correspond to the high initial concentration. However the overall performance indicated that the prepared MOF (Zn-Ph-D-CP) is of high ability in adsorbing Cu II ion.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided.

Khaled Elewa: Preparation of MOF and experimental design and paper writing, supervision of work

Dr. Ahmed Farghal: Preparation of MOF and experimental design and paper writing

Dr. Ola El Monayeri: Experimental procedure follow up, paper writing and editing, supervision of work

Prof. Adel Belal: Overall revision of experimental procedure, paper editing, supervision of work

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Conflicts of Interest: The authors declare no conflict of interest

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