



High Performance Copper Based Metal Organic Framework for Removal of Heavy Metals From Wastewater

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Specialty section:

This article was submitted to
Colloidal Materials and Interfaces,
a section of the journal
Frontiers in Materials

Received: 21 December 2021

Accepted: 24 January 2022

Published: 08 March 2022

Citation:

Haso HW, Dubale AA, Chimdesa MA
and Atlabachew M (2022) High
Performance Copper Based Metal
Organic Framework for Removal of
Heavy Metals From Wastewater.
Front. Mater. 9:840806.
doi: 10.3389/fmats.2022.840806

The biggest challenge of this century is the generation of wastewater which is released to the environment due to industrial expansion. Industrial development has caused the release of various pollutants including heavy metals such as Cd, Pb, and Cr into the environment. In this study, copper diphenylamine metal-organic framework (Cu-DPA MOF) has been synthesized via hydrothermal method and its adsorption capacity toward the removal of heavy metals from wastewater was examined. The removal efficiency of heavy metals by Cu-DPA MOF was tested at optimized adsorption parameters such as optimal adsorbent dosage, pH, initial metals concentration, and adsorption time. The heavy metals concentration in the wastewater before treated with the as-synthesized MOF was determined to be 0.3027, 0.0098, and 0.1021 mg/L for Cr, Cd, and Pb, respectively. The corresponding concentrations of heavy metals in wastewater were reduced to 0.0015, 0.00024, and 0.00016 mg/L when treated with the as-synthesized MOF. As a result, a maximum removal efficiency of 97.6%, 99.5%, and 99.5% was achieved for Cd, Cr, and Pb metals, respectively. This is possibly due to the high porous nature and huge surface area of the as-synthesized MOF. The adsorption data were best fitted with Freundlich isotherm throughout this study. The study sheds light on the design of adsorbents with high removal efficiency of pollutants found in the environment.

Keywords: wastewater, heavy metals, adsorption, removal efficiency, metal-organic framework

INTRODUCTION

Heavy metals contamination in water is a major environmental concern. Heavy metals from heavy industry, and agricultural and other human activities could enter the water body and cause danger to the environment and human health. The release of toxic chemicals from industrial wastewater degrades water quality and is hazardous for human beings and other living organisms. Heavy metals such as lead (Pb), cadmium (Cd), chromium (Cr), arsenic (As), copper (Cu), mercury (Hg), and nickel (Ni) are commonly found in the discharged wastewater from industries. The toxicity of heavy metals leads to obstructive lung disease, reduced growth and development, causes cancer, organ damage, nervous system damage, and death in extreme cases (Aksu, 2005; Ahluwalia and Goyal, 2007; WHO, 2011; Madarang et al., 2012; Tesfaye, 2016). Heavy metals are classified as hazardous

pollutants due to their severe toxicity. The presence of these harmful heavy metal elements, even at low concentrations, affects the health of humans and other living organisms (Bakhtiari and Azizian, 2015; Cui et al., 2015).

The development of the industrial sector in developing countries is the primary cause of heavy metals being released into water, air, and soil in all countries across the world (Majeed et al., 2014). Most industries, e.g., electroplating, chemical and petrochemical, metal and mining, leather, textile, ceramic, cement, fertilizer, tanneries, batteries, paper, and pesticides, release their wastewater containing various harmful heavy metals without treatment into the environment. Toxic heavy metals such as cadmium, lead, and chromium do not break down in the environment, contributing to their bioaccumulation in the kidneys and livers of vertebrates and invertebrates. These toxic heavy metals cause cancers of the brain, kidney, bladder, colon, and rectum. The maximum permitted value for cadmium, chromium, and lead in water is 0.003 mg/L, 0.05 mg/L, and 0.01 mg/L, respectively (WHO 2011).

Nowadays, the growth of industrial development for one country is a backbone for the economy, but side by side has an effect, mainly releasing wastewater that contains heavy metal ions (Sharma and Bhattacharya 2017) and other pollutants (Mahmoodi et al., 2014; Mahmoodi and Saffar-Dastgerdi 2019; Hoseinzadeh et al., 2021). Proper wastewater management should be applied by different wastewater management policies to prevent harm to the environment and to human health. The industrial sectors comply with environmental regulations to treat their wastewater.

Thus far, various treatment technologies including precipitation, ion exchange, membrane filtration, reversible osmosis, ultrafiltration, coagulation-flocculation, and flotation have been widely used to remove heavy metals from wastewater. However, these methods are time-consuming and expensive (Qasem et al., 2021). On the other hand, adsorption or sorbent-based treatment strategies have been found to be promising and effective for the treatment of heavy metals contamination (Rajasulochana and Preethy, 2016). It is reported that zeolites, commercial activated carbon and biomass derived adsorbent such as saw dust, orange peel, rice husk, tea and coffee waste, peanut shells, dry tree leaves and barks, papaya seed, egg shell, and coconut leaf powder, have been used as adsorbent for the removal of heavy metals from various wastewater sources (Nguyen et al., 2013; Hussain and sheriff, 2014; Jayaweera et al., 2018) However, most of the existing adsorbents are limited by some factors such as requirement of higher calcination temperature, longer time of reaction, relatively low surface area and porosity, low stability, reusability, and others. Therefore, it is critically important to develop low cost adsorbent with high surface area and porosity using simple and scalable synthesis strategies.

Recently, metal-organic frameworks (MOFs), a class of porous material with inherent large surface areas, uniform but tunable cavities, tailorable chemistry and useful physical and chemical properties, have obtained broad and comprehensive applications than activated carbon and zeolites (Dehghankar et al., 2021). Although MOFs have been explored for a wide range of

applications in catalysis, gas storage, chemical sensing, and drug delivery (Zhuang et al., 2014; Yang and Xu, 2017; Xie et al., 2018), there have been only a few reports on using MOFs for removal of heavy metals from wastewater (Efome et al., 2018; Asghar et al., 2021). Among all the reported MOFs, Cu-based MOFs are attractive because the high stability and earth-abundance of the Cu element makes them ideal sacrificial templates to prepare adsorbent with high surface area and porosity. Moreover, copper can preferably form many geometric complexes with a number of ligands (Burg and Meyerstein, 2012). To the best of our knowledge, no study has been conducted toward the removal of heavy metal from wastewater using the as-synthesized copper diphenylamine metal-organic framework.

Herein, we have successfully synthesized a highly porous nature Cu-DPA MOF via the hydrothermal method from copper nitrate trihydrate and diphenylamine linker. The use of as-synthesized MOF was investigated for the removal of heavy metals from wastewater. The adsorbents reported before for removal of heavy metals are time consuming, expensive, and are not stable. In this study, we reported highly porous copper-based MOF (Copper-diphenylamine combination) for the first time for removal of Pb, Cd, and Cr. The linker (i.e., diphenylamine) used in this study was not reported before and is by far much cheaper than other linkers. The percentage removal by the synthesized MOF is much higher (97.5%, 99.5%, and 99.5% toward Cr, Cd, and Pb metals, respectively, from wastewater sample) when compared with the literature. This indicates the adsorbent in this study reveals very good potential for simultaneous removal of toxic metals from high-volume contaminated wastewaters. Therefore, the technology reported in this study can also be used as an adsorbent instead of more expensive and ineffective materials.

EXPERIMENTAL SECTION

Chemicals and Reagents

All the reagents were commercially available and were used as received without further purification. Copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 98%), diphenylamine (99%), N, N-Dimethyl formamide (DMF, 99%), methanol (CH_3OH , 99.5%), and ethanol (EtOH) were purchased from Shanghai Chemical Reagent Co. Ltd.

Instruments and Apparatus

Wastewater samples were digested on a hot plate heating apparatus using round bottom flasks. Borosilicate volumetric flasks (25, 50, and 100 ml), pipettes (Pyrex, United States), measuring cylinders (Duran, Germany), and micropipettes (Dragonmed, 1–10 μl , 100–1,000 μl , Shanghai, China) were used for measuring different quantities of sample solution, acid reagents, and standard metal solutions. Graphite furnace atomic absorption spectroscopy (GFAAS) equipped with a deuterium background corrector was employed to quantify the heavy metals before and after absorption; iodine number analysis,

TABLE 1 | Method detection limits for wastewater samples.

Metal	Wavelength (nm)	r^2	MDL for wastewater sample
Pb	217.0	0.9999	0.0615
Cd	228.9	0.9995	0.0231
Cr	341.5	0.9998	0.0535

X-ray diffraction (XRD), and Fourier transform infrared radiation (FTIR) were used to characterize the adsorbent.

Wastewater Sampling and Study Area Description

A wastewater sample was collected from Gamo Gofa zone, Arba Minch town, from the car wash labajo area. The sampling area is defined geographically as 6°01'–7°12' N, and 37°32'–38° 02' E. Composite samples were collected in 2-a-week intervals during March–April 2017 and analyzed for Pb, Cd, and Cr levels. The concentrations of these heavy metals were determined using GFAAS before and after treatment.

Digestion of the Wastewater Sample

Wastewater samples were digested with HNO₃ and HClO₄ in the ratio of 5:3. Digestion was done on a hot plate at a temperature of 93 °C for 1 h following a method reported by Fanta et al. (2019).

Instrument Calibration and Method Detection Limit

To determine the concentrations of metals in the untreated and treated effluent sample solutions, calibration curves were created. The GFAAS instrument was calibrated using four series of working standards (0.1, 0.5, 1.0, 1.5 mg/L). A correlation coefficient of 0.999 and above was obtained for the three metals. The detection limits for the metals tested in this study were calculated by multiplying the weighted average of standard deviations of the reagent blank by three. The wavelengths at which analysis was done, the correlation coefficients of the calibration curve for each of the metals, and the method detection limits of each metal are given in **Table 1**. The results clearly show that the calibration curves with good correlation coefficients and lower method detection limits were obtained during the analysis.

Method Validation

The validity of the above-optimized digestion procedure toward analyzing the wastewater samples concerning each of the selected metals (Pb, Cr, and Cd) could be made possible via conducting spiking experiments. Accordingly, the efficiency of the optimized procedure was checked by adding fixed volumes of standard solutions containing 5 ml of 0.5 mg/L of each metal into 50 ml wastewater. The spiked samples were then digested in the same manner as the original sample. Then the digests were diluted to 25 ml with deionized water. Finally, the solutions were analyzed for metal concentration with GFAAS. As used for the original

samples, triplicate spiked samples were prepared, and the readings were recorded, and recovery was calculated using Eq. 1.

$$R = \frac{C_s - C_n}{S} \times 100\%, \quad (1)$$

where R is percent recovery, C_s is metal concentration of spiked sample, C_n is the metal concentration of the non-spiked sample and S is the concentration equivalent of analyte added.

Synthesis of Copper Based Metal Organic Framework

Copper metal-organic framework (Cu-DPA MOF) was prepared from Cu(NO₃)₂·3H₂O and diphenylamine ligand following a solution-based method. Briefly, 1 g of diphenylamine was dissolved in 5 ml of ethanol, and 1 g of copper nitrate trihydrate was dissolved in 5 ml of distilled water. The two solutions were mixed and stirred by a magnetic stirrer on a hot plate for 1 h until a homogeneous mixture was observed. The mixture was then kept for 3 days until a blue precipitate was formed. The resulting precipitates were isolated by centrifugation, washed four times with de-ionized water, DMF, and ethanol, respectively, and dried at 40°C for 24 h. The obtained precipitate, named Cu-DPA MOF afterward, was kept for further characterization and experimentation.

Optimization of Metal to Ligand Ratio

The metal to ligand ratio of the copper metal-organic framework was optimized by taking a different metal to ligand ratio (1:1, 2:1, 3:1, and 4:1). The synthesized MOFs were then subjected to an optical microscope, and the iodine number was determined following the American Society for Testing and Materials methods. The one with the smallest particle size and largest iodine number value was taken as the optimum ratio.

Characterization

The prepared Cu-DPA MOF was characterized by XRD, FTIR, GFAAS, and iodine number analysis. XRD measurements were taken on a D2 phaser XRD-300 W using Cu K α radiation at 40 kV and 100 mA. A linear silicon strip 'Lynx Eye' detector was used to record X-ray patterns from 10° to 80° at a scan rate of 0.1° min⁻¹. The FTIR spectra were obtained using a Nicolet NEXUS-670 FT-IR spectrometer in transmission mode. Each sample in the KBr blend was scanned 64 times with a resolution of 4 cm⁻¹ from 4,000 to 400 cm⁻¹. The morphology of the samples in this study was studied with field emission FEI Nova NanoSEM 450 scanning electron microscope (SEM). The wastewater samples' Pb, Cd, and Cr content were measured using GFAAS. The surface area associated to pore volume was characterized using iodine number analysis. The American Society for Testing and Materials (ASTM D4607-94) method is used to calculate the iodine number. In a nutshell, a typical iodine solution was treated with three different weights of adsorbent and 10.0 ml of 5% HCl under controlled conditions. This mixture was brought to boil for 30 s before being cooled. Following that, 100.0 ml of 0.1 N iodine solution was added and agitated for 30 s. The resulting solution

was filtered, and 50.0 ml of the filtrate was titrated with 0.1 N sodium thiosulfate, using starch as an indicator. Finally, the iodine number, X/M value was calculated by using Eq. 2:

$$\frac{X}{M} = \frac{(N_1 \times 126.93 \times V_1) - \left[\frac{V_1 + V_{HCl}}{V_F} \right] \times (N_2 \times 12693.0 \times V_2)}{M}, \quad (2)$$

Batch Adsorption Experiment

Batch adsorption experiments were carried out to determine the effect of the adsorbent dose, contact time, pH, initial metal ion concentration, and time of mixing to reach equilibrium for Pb, Cd, and Cr adsorbed by Cu-DPA MOF. About 0.5–3.5 g of adsorbent (as synthesized Cu-DPA MOF) was added into a synthetic solution of each metal and stirred for 4 h, and then kept for 24 h until equilibrium could be achieved and filtered. The experiment was conducted three times. The optimum mass of the adsorbent was obtained by plotting the percentage removal vs the mass of the adsorbent. The effect of contact time in the removal of Pb, Cd, and Cr from wastewater using Cu-DPA MOF is studied in a contact time range of 20–120 min. Removal of metal ions was also carried at a different initial concentration of metals (5–80 mg/L) and pH (2–10). Following the optimized procedure, 1.5 g of Cu-DPA MOF was added to 50 ml of the composite wastewater containing the Cd (0.0098 mg/L), Cr (0.3027 mg/L), and Pb (0.1021 mg/L) metals (at pH 2 for Cr and 6 for Pb and Cd). The solution was shaken for 80 min in the case of Cd and Cr (60 min for Pb), filtered using Whatman filter paper stored in refrigeration prior to GFAAS analysis. The adsorption capacity and removal efficiency were calculated using Eqs 3, 4, respectively:

$$q_e = \frac{(C_o - C_e)V}{m}, \quad (3)$$

where q_e is heavy metal ions concentration adsorbed on adsorbent at equilibrium (mg of metal ion/g of adsorbent), C_o and C_e are the initial and equilibrium concentration or final concentration of metal ions in the solution (mg/L), V is the initial volume of metal ions solution used (in L) and m is the mass of adsorbent (in g). The removal efficiency was calculated using Eq. (4):

$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} \times 100, \quad (4)$$

where C_o and C_e are the initial concentration of heavy metals (mg/L) and the equilibrium concentration of heavy metals (mg/L), respectively.

RESULTS AND DISCUSSION

Iodine Number Analysis for the Prepared Cu-DPA MOF

The synthetic process was conducted at five different (i.e., for 1, 2, 3, 4 and 5 days) times of reaction. The copper nitrate trihydrate and diphenylamine precursors were completely

TABLE 2 | Iodine number of Cu-PDA MOF for metal to ligand in different ratio.

Sample	Metal to ligand precursor ratio (g)	Iodine value (mg/g)	Yield (%)
1	1:1	635.4	92
2	2:1	581.7	81
3	3:1	472.1	68
4	4:1	368.4	43

dissolved in ethanol and distilled water, respectively prior to mixing and stirring. The two solutions with 1:1 M ration were then mixed, stirred for 1 h, and allowed to settle for 1, 2, 3, 4, and 5 days. The separated yield (based on metal precursor) increases from 38 to 92% as the reaction time increases from 1 d to 3 days. However, further increase in reaction time up to 5 days did not show significant improvement in yield, indicating the saturation level of the synthetic route. Analysis of iodine adsorption number is used to investigate the pore nature (e.g., microporous, mesoporous, and macroporous) of most adsorbents. The type of pores is an indication of adsorption capacity. Furthermore, the iodine adsorption number is used to evaluate the level of activation (a higher degree indicates stronger activation), and it is commonly provided in mg/g (with a typical range of 500–1,200 mg/g). The metal to ligand precursor ratio and their corresponding iodine number and isolated yield are shown in Table 2. The 1:1 metal to ligand ratio provided maximum iodine value (635 mg/g) and yield (92%), indicating good adsorption capacity with high porosity and high surface area. The adsorption capacity of Cu-DPA MOF decreases with increasing metal to ligand precursor ratio from 1:1 to 4:1. This is because the macropore structure of Cu-MOF deteriorated due to excessive copper metal that leads to the formation of a macropore in the MOF and basically due to the effect of pore widening that leads to the destruction of pore walls between neighboring pores, which decreases adsorption performance (Gupta et al., 2003). The iodine number value obtained for the 1:1 Cu-DPA MOF is comparable with zeolite-based adsorbents (641.7 mg/g) and twofold higher than activated carbon-based adsorbent from tamarind seeds (300 mg/g) reported before (Mopoung et al., 2015; Fanta et al., 2019). On the other hand, relatively higher iodine number (895 mg/g) was reported for activated carbon obtained from bean husk (Evwierhoma et al., 2018). Based on the determined iodine value and isolated yield, the 1:1 ratio is considered to be the optimal combination ratio. Fascinated by this observation, we fully characterized the prepared Cu-DPA MOF using a 1:1 ratio of metal to ligand combination.

Crystallinity Studies of Adsorbent

The crystal structure of the as-synthesized Cu-DPA MOF was examined using XRD measurements of the samples. Figure 1 displays XRD patterns of as-prepared Cu-DPA MOF. As visibly evidenced in Figure 1A, a strong diffraction peak observed at 2 Theta values of 12.8°, 18.6°, and 20.2° are characteristics of Cu-DPA MOF and have good similarity with the diffraction patterns

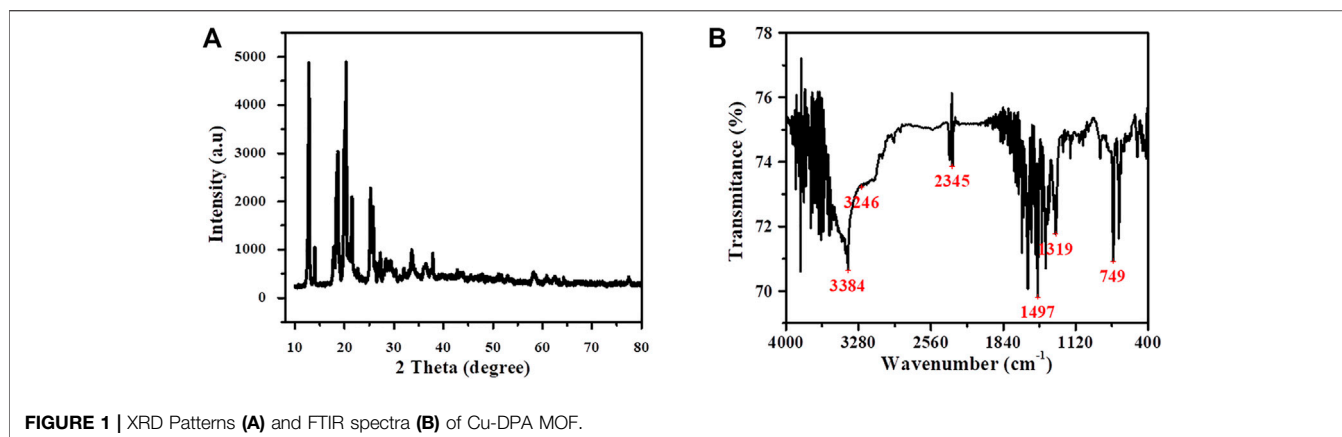


FIGURE 1 | XRD Patterns (A) and FTIR spectra (B) of Cu-DPA MOF.

TABLE 3 | Recovery test values for the optimized procedure for heavy metal analysis.

Metals	Conc. In sample (mg/L)	Amount added (mg/L)	Conc. In spiked sample (mg/L)	Recovery (%)
Cd	0.0098	0.5	0.50065	98.2
Pb	0.1021	0.5	0.587	96.98
Cr	0.3027	0.5	0.769	93.26

of other Cu-based MOF (Loera-Serna et al., 2012), indicating the profound crystalline nature of the prepared MOF. The calculated relative grain size (i.e., using the Scherer equation) was found to be 22.3 nm, indicating a mesoporous characteristic nature of the prepared MOF. This agrees well with the iodine adsorption number analysis. To examine the synthesized MOF's structural information, we also measured FT-IR spectra of the prepared Cu-DPA MOF in the region from 400 cm^{-1} to $4,000\text{ cm}^{-1}$ in KBr using an FTIR spectrometer. Figure 1B shows the FTIR spectra of Cu-DPA MOF. As clearly displayed in Figure 1B, the presence of a broad peak at $3,384\text{ cm}^{-1}$ in the as-prepared Cu-DPA MOF sample can be assigned to the N-H stretching. The diminished feature of this peak is a solid indicative for the linkage formed between copper and diphenylamine ligand. The peaks located at $1,497$ and $1,319\text{ cm}^{-1}$ are assigned to the N-H stretching vibrations of the aromatic ring. The Cu-diphenylamine ligand asymmetric stretching is observed at 749 cm^{-1} . The existence of NH functional group could act as a chemical binding agent via its dissociation into a negatively charged surface which could attract positively charged ions like metals. It can be seen that the IR-spectra indicated the presence of ionizable functional groups; their ionization leaves vacant sites which can be replaced by metal ions. This gives an indication that this material could be used as adsorbents for heavy metals removal (Aziz et al., 2005).

Method of Detection Limit and Method Validation

Before quantifying the metals in the wastewater samples, the MDL of the GFAAS was evaluated by analyzing six blank samples. It was found that the MDL of Pb, Cd, and Cr was

0.0615 mg/L , 0.0231 mg/L , and 0.0535 mg/L , respectively. By adding known concentrations of each element to the wastewater sample, the efficiency of the digestion technique and analytical method (GFAAS) was tested. In the same way, the spiked and non-spiked samples were digested and examined. By spiking 2.0 ml of 12.5 mg/L of each metal into a 50 ml wastewater sample, the efficiency of the optimized procedure was tested. As shown in Table 3, the calculated percent recoveries for studied metals in the wastewater sample (i.e., 93.26–98.2%) lie within the acceptable range (Mico et al., 2006).

Optimization Parameters for Removal of Heavy Metals (Using Synthetic Solution) Effect of pH

The initial pH of the metal ion solution is a significant factor in controlling the adsorption process. In this study, the effect of pH on removal efficiency of heavy metals was studied from a range of 2–10 at a contact time of 30 min, metal ion solution of 20 mg/L , Cu-DPA based adsorbents of 1.5 g , temperature of $25\text{ }^{\circ}\text{C}$, and at an agitation speed of 150 rpm (Figure 2). As shown in Figure 2, both the adsorption capacity (Figure 2A) and the percentage removal of Pb and Cd (Figure 2B) increase as the pH increases from 2 to 6. However, a decrease in adsorption capacity and removal percentages were observed when the pH values ranged from 6 to 10. The maximum percentage removal of Cd (92.4%) and Pb (94.05%) were obtained at pH 6. This is in good agreement with the findings obtained by Rashed et al. (2018) using modified physically activated sewage sludge adsorbents. The removal of Cd and Pb at lower pH ($\text{pH} < 3$ was low because protons could occupy most of the adsorption), however, at moderate pH, the

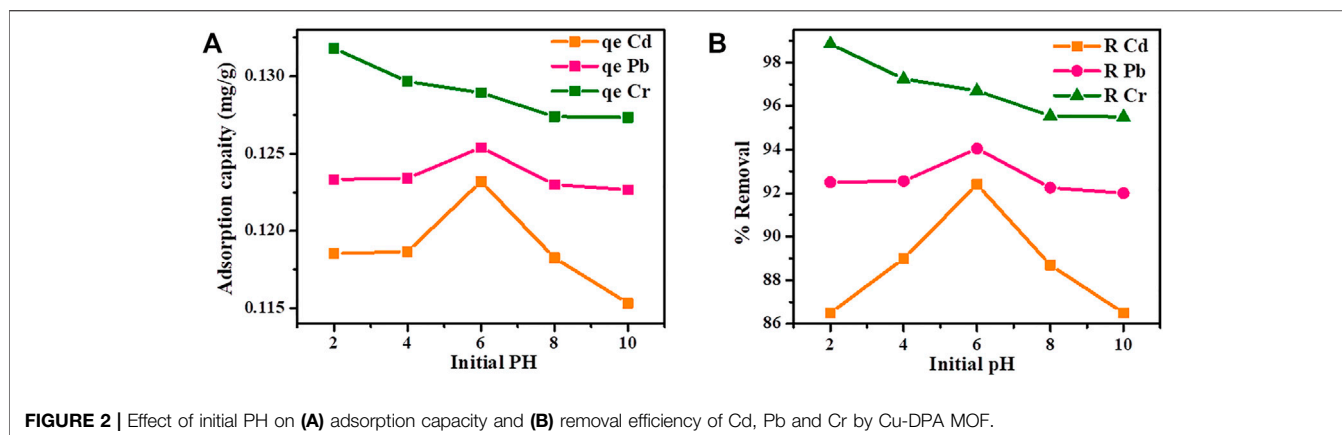


FIGURE 2 | Effect of initial pH on (A) adsorption capacity and (B) removal efficiency of Cd, Pb and Cr by Cu-DPA MOF.

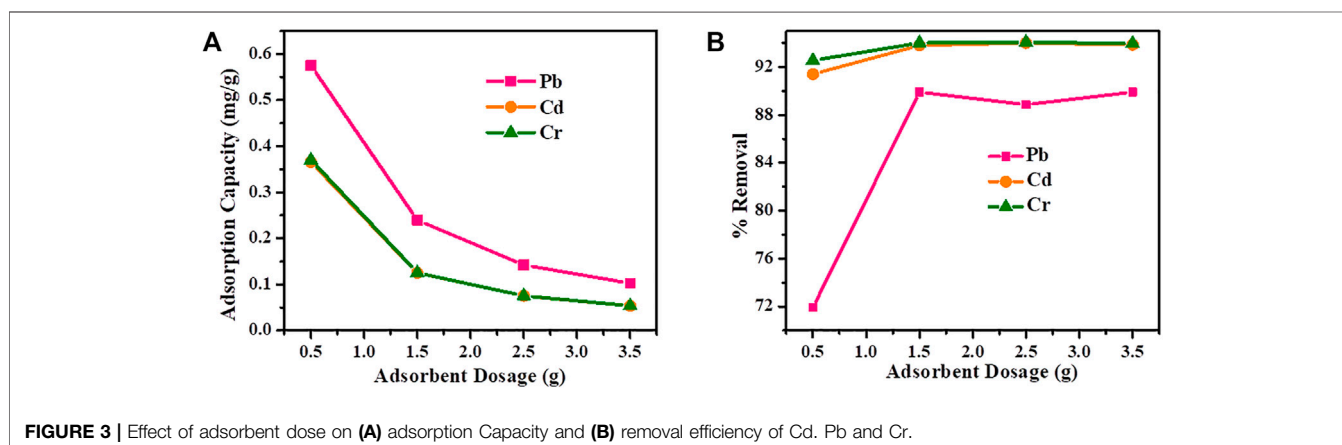


FIGURE 3 | Effect of adsorbent dose on (A) adsorption Capacity and (B) removal efficiency of Cd, Pb and Cr.

proton linked to the adsorbent surface gets released from the active sites of the adsorbent resulting in increased adsorbed metal ions. The low percentage removal efficiency of Cu-DPA at a higher pH value ($\text{pH} > 6$) might be due to the formation of metal precipitate that decreases adsorption. Increasing the adsorption capacity of metals with increasing pH is attributed to two possible mechanisms; cation exchange and surface complexation. The slow adsorption at high pH is probably due to electrostatic hindrance between adsorbed positively charged adsorbate into the surface of adsorbent and cationic adsorbate species in the solution, and slow pore diffusion into the bulk of the adsorbent.

On the other hand, as seen in **Figure 2B**, the percentage removal for Cr decreases as the pH increases from 2–10, and a maximum percentage removal (98%) was attained at pH 2. The finding in this study was in good agreement with the literature report. For instance, at pH 2, the study conducted by Liu et al. (2014) revealed a removal efficiency of 87% Cr from wastewater using *Zizania caduciflora* adsorbent. Mubarak et al. (2014) used manganese oxide as adsorbent to remove chromium from wastewater and obtained maximum removal efficiency of 85% at pH 2. The greater removal effectiveness of Cr at low pH is attributable to the neutralization of negative charges on the adsorption surface by abundant hydrogen ions, allowing hydrogen chromate ions to diffuse more easily (HCrO_4^-) and

their subsequent adsorption (Dula et al., 2014). At basic pH conditions Cr adsorption onto Cu-DPA MOF decreases due to the formation of hydrolysis and polymeric products such as CrOH^{2+} , $\text{Cr}_2(\text{OH})_2^{4+}$, and $\text{Cr}_3(\text{OH})_4^{5+}$. This can be best explained on the basis of the lower extent protonated hydroxyl groups with rising pH. In view of the aforementioned results, the optimum pH for Cd, Pb, and Cr adsorption is taken to be 6, 6, and 2, respectively, in the following experiments.

Effect of Adsorbent Dosage

The effect of adsorbent dose was studied by varying the amount of Cu-DPA MOF from 0.5–3.5 g/20 ml (**Figure 3**). As seen in **Figure 3A**, the adsorption capacity of Cd, Pb, and Cr decreases with an increase in Cu-DPA MOF amount from 0.5–3.5 g. Here the response from Cd and Pb was observed to be the same. The percentage removal of Pb, Cd, and Cr were increased from 71.4 to 88.5%, 91–94% and 92.5–94.5%, respectively, when the Cu-DPA MOF dose increased from 0.5 to 1.5 g (**Figure 3B**) and remained nearly constant at adsorbent doses higher than 1.5 g. The constant removal efficiency with increasing dose of adsorbent is attributed to adsorption sites remaining unsaturated during the adsorption reaction which is a result of the larger number of available adsorption sites favoring the enhanced uptake of the metal ions (Liu et al., 2007; Zou et al., 2016).

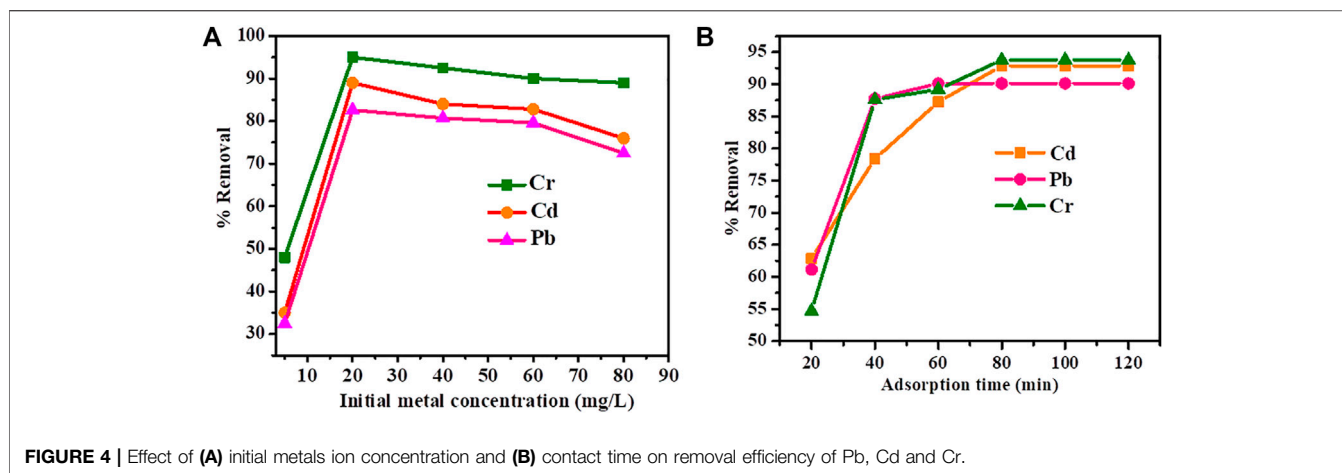


FIGURE 4 | Effect of (A) initial metals ion concentration and (B) contact time on removal efficiency of Pb, Cd and Cr.

Effect of Initial Metals Concentration and Contact Time

We also carried out intensive optimization experiments revealing the effect of initial metal concentration and contact time. To a different 50 ml size Erlenmeyer's flask, 25 ml sample of 10, 20, 40, 60, and 80 mg/L concentrations of Pb, Cd, and Cr were added. The optimum dose of Cu-DPA MOF (1.5 g for each metal ion) was added to each of the above metal concentrations, and the mixture was mechanically stirred for their optimum time. After filtration, the concentration of Pb, Cd, and Cr were analyzed using atomic absorption spectroscopy. **Figure 4** shows the effect of initial metal ion concentration of Cr, Pb, and Cd and contact time on Pb, Cd, and Cr removal efficiency by Cu-DPA MOF over Cu-DPA MOF under optimum pH and adsorbent dose. As shown in **Figure 4A**, the percentage removal efficiency increased from 48 to 95%, 35–85%, and 32–83% for Cr, Cd, and Pb, respectively, with increasing initial concentration from 5 to 20 mg/L. It is revealed that Cu-DPA MOF exhibited higher removal efficiency of metal ions in the order of Cr > Cd > Pb at all initial concentration value. The difference in percent removal of distinct heavy metal ions at the same initial metal ion concentration, adsorbent dose, and contact time could be related to differences in chemical affinity and ion exchange capacity with respect to the chemical functional group on the adsorbent's surface (Hermes et al., 2007). The maximum removal efficiency of the Cu-DPA MOF was found to be 83.3, 89.7, and 95.0% for Pb, Cd, and Cr, respectively, and the removal efficiency slightly decreased or reached the saturation point at higher initial concentrations. The increase in adsorption or removal capacities of adsorbents with rising metal ion concentration might be explained by an acceleration of metal ion diffusion into adsorbents due to an increase in concentration gradient with increasing initial metal ion concentration (Li et al., 2012). As a result, the extent of each metal ion uptake by the adsorbents increases significantly with the increase of contact time. The slight decrease in the removal capacity or remaining constant after the saturation point of the adsorbents at higher initial metal ion concentration could be due to a higher probability of collision between the adsorbent particle (Cu-DPA MOF) and the metal ions; and decrease in the available active sites for adsorption due to their saturation.

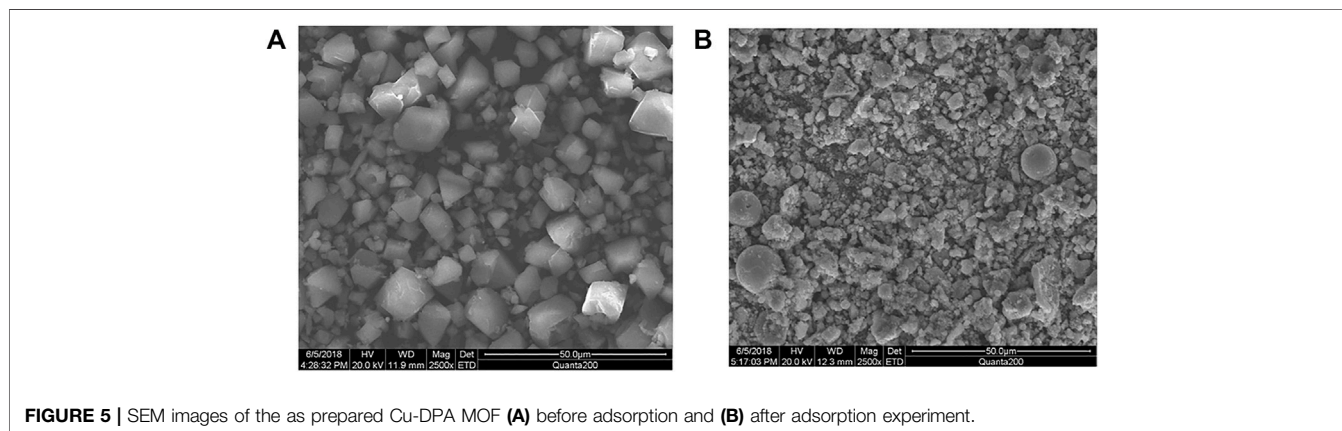
The effect of contact time on percentage removal of each metal ion by Cu-DPA MOF was also studied at various intervals (20–120 min) using optimum pH, adsorbent dosage, and initial metal concentration. As shown in **Figure 4B**, increasing the contact time increases the percentage removal of each metal until the system reaches the adsorption equilibrium. The adsorption was very fast from the beginning and with further increase of adsorption time. In this study, it is found that the optimum contact time revealing maximum percentage removal of Cd (92.9%) and Cr (93.8%) was 80 min. While in the case of Pb, high removal efficiency of 90.13% was attained within 60 min. This finding is in good agreement with the result obtained by Kowsura et al. (2017) on Pb removal from water using Zn₃(BTC)₂. Liu et al. (2007) reported chromium removal with zero-valent iron decorant on a graphene nanosheet by using 1 g adsorbent dosage within 90 min has a removal efficiency of 70%. It is best known that the rate of metal ion uptake was higher at the initial stage of adsorption; however, a slower adsorption would follow as the available adsorption site is gradually decreased. This can be best explained by the fact that initially, the rate of ion uptake was higher because all sites on the adsorbent were vacant and ion concentration was high, but remain constant since all sites occupied hence as it does not take up the additional adsorbate.

Adsorption Experiment for Real Sample

Fascinated by the above findings, we also carried out investigation of removal efficiency of the as prepared Cu-DPA MOF toward Cd, Pb, and Cr in real wastewater samples collected from the car wash Labajo area located at Gamo Gofa zone, Arba Minch town, Ethiopia. The experiments were conducted under optimized conditions shown in the previous section. As clearly demonstrated in **Table 4**, the concentration of Pb (0.1021 mg/L), Cd (0.0098 mg/L), and Cr (0.3027 mg/L) in the wastewater before treatment was much higher than the permissible limit set by the World Health Organization. However, the corresponding concentration of Pb, Cd, and Cr was reduced to 0.0056, 0.0024, and 0.0015 mg/L after the treatment with the Cu-DPA MOF adsorbent. As a result, the removal efficiency of Cu-DPA MOF adsorbent for heavy metals in a real sample was calculated to be 97.6%, 99.5%, and 99.5% for Cd, Pb, and Cr, respectively. This indicates the as-prepared metal organic

TABLE 4 | Removal of Pb, Cd, and Cr from real water samples collected from the car wash Labajo area using Cu-DPA MOF at optimized conditions.

Metal	Concentration before treatment (mg/L)	Concentration after treatment with Cu-DPA MOF (mg/L)	Removal efficiency (%)
Pb	0.1021	0.0056	99.5
Cd	0.0098	0.0024	97.6
Cr	0.3027	0.0015	99.5

**FIGURE 5** | SEM images of the as prepared Cu-DPA MOF (A) before adsorption and (B) after adsorption experiment.

framework is very powerful and promising toward treatment of wastewater. Motivated by these findings, we also studied the regeneration of the Cu-DPA MOF after adsorption experiment. Herein a methanol solution followed by irradiation of the sample with low power UV was used to regenerate the used Cu-DPA MOF (Gupta et al., 2021). We first submerged and stirred the used MOF in 10 ml of methanol for 24 h at 500 rpm, followed by centrifugation and drying at ambient temperature for 24 h. Then, the dried MOF was illuminated with a low power UV lamp using a Pyrex tube fitted in an acryl reactor. About 91%, 94%, and 93.5% of the Cd, Cr, and Pb, respectively, could be removed from the used Cu-DPA MOF based on GFAAS analysis from the supernatant solution. Next, we reuse the regenerated Cu-DPA MOF under the same condition, the corresponding Cd, Cr, and Pb removal efficiency was reduced to 81%, 86%, and 87%, respectively, indicating that the MOF still exhibits efficient removal efficiency after regeneration. We further conducted scanning electron microscopy measurements to examine the morphology and microstructure of the 1:1 Cu-DPA MOF. As clearly displayed in **Figure 5A**, the as-prepared MOF before adsorption experiment exhibited a bright surface with octahedral and triangular particle features. However, when the MOF was taken to the adsorption experiment (**Figure 5B**), the small particles are observed over the octahedral and triangular structures of the MOF, indicating the adsorption of the metals over the MOF surface. Regardless of the coverage of the MOF surface with a small particle, there was no significant change in morphology after adsorption experiment.

Adsorption Isotherms

To further investigate the relationship between adsorbent and adsorbate, we also underwent analysis of the adsorption

process via the most commonly used models such as Langmuir and Freundlich isotherms. Adsorption happens at homogeneous locations, forming a monolayer, according to the Langmuir isotherm. In other words, once an adsorbate has been linked to a site, no additional adsorption can occur. Mathematically, the Langmuir isotherm is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{b_L q_m} + \frac{C_e}{q_m}, \quad (5)$$

where q_m is to the adsorption capacity (mg/g), q_e is the equilibrium concentration of metals in the adsorbed phase (mg/g), C_e is the equilibrium concentration in the liquid phase (mg/L), and Langmuir constants, which are related to the adsorption capacity (q_m) and energy of adsorption (b_L), can be calculated from the slope of the linear plot of C_e/q_e vs C_e ; a straight line with slope $1/q_{max}$ and intercept of $1/q_{max} b_L$ is obtained. The dimensionless factor, R_L , which is given by **Eq. (6)**, is an essential feature of the Langmuir isotherm used to predict whether the Langmuir isotherm is favorable or unfavorable.

$$R_L = \frac{1}{1 + b_L C_o}, \quad (6)$$

where C_o is initial concentration of adsorbate (mg/L), b_L is Langmuir constant (L/mg). If $R_L > 1.0$, the sorption isotherm is unfavorable, $R_L = 1.0$ (linear), $0 < R_L < 1.0$ (favorable), and $R_L = 0$ (irreversible). In determining the nature of the adsorption process, whether favorable or unfavorable, the dimensionless constant separation term R_L was investigated from **Eq. 6**. The obtained result ($R_L = 0.357, 0.436, 0.271$ for Cd, Pb, and Cr,

TABLE 5 | Calculated isotherm parameters for the adsorption of Pb, Cd, and Cr on Cu-DPA MOF at 300 K.

Adsorption isotherms constants	Corresponding values for each adsorbents		
	Cd	Pb	Cr
Langmuir isotherm			
q_m (mg/g)	1.334	2.19	3.21
k_L (L/mg)	0.04	0.0147	0.0847
R_L	0.357	0.436	0.271
R^2	0.89624	0.84438	0.959
Freundlich isotherm			
n	1.266	1.14	1.35
K_F (L/g)	0.144	0.26	0.575
R^2	0.995	0.997	0.996

respectively) shows that the sorption of Cd, Pb, and Cr onto the Cu-DPA MOF was favorable. On the other hand, the Freundlich isotherm is used to characterize heterogeneous surface and for description of multilayer adsorption properties of adsorbed molecules. The linear form of Freundlich isotherm is given by Eq. (7):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e, \quad (7)$$

where q_e is the amount adsorbed at equilibrium (mg/g), K_f and n are the Freundlich constant, $1/n$ is the heterogeneity factor which is related to the capacity and intensity of the adsorption, and C_e is the equilibrium concentration (mg/L). The values of K_f and $1/n$ can be obtained from the slope and intercept of the plot of $\log q_e$ vs $\log C_e$. The magnitude of the exponent, n , gives an indication of the favorability and capacity of the adsorbent/adsorbate system. **Table 5**, summarizes isotherm parameters of Langmuir and Freundlich models for adsorption Pb, Cd, and Cr over Cu-DPA MOF. The findings clearly reveal that the adsorption of Pb, Cd, and Cr metals on Cu-DPA MOF fits well with the Freundlich model. The fact that the Freundlich model is a good fit to the experimental adsorption data suggests physical adsorption as well as a heterogeneous distribution of active sites on the Cu-DPA MOF surface. The observed correlation coefficients for Freundlich isotherms were 0.995, 0.997, and 0.996 for Cd, Pb, and Cr, respectively. If the value of n is equal to unity, the adsorption is linear. If the value of the constant n is less than unity, the adsorption process is unfavorable; if the value of n is greater than unity, the adsorption process is favorable (Thamilarasu and Karunakaran, 2013). In the present study, the value of n at equilibrium was above unity, suggesting favorable adsorption. Furthermore, the values of the dimensionless factor, R_L , were between 0 and 1 which suggest a favorable adsorption between Cu-DPA MOF and each metal. The Freundlich adsorption capacity (K_f) shows easy separation of heavy metal ions from wastewater. The higher K_f value the greater the adsorption intensity (Esrafil et al., 2018).

The adsorption capacity of the Cu-DPA MOF after optimizing all the parameters was estimated to be 2.19, 1.33, and 3.21 mg/g for Pb, Cd, and Cr, respectively. More interestingly, the obtained adsorption capacity is much higher than the reported values Cr

(0.5–0.6 mg/g). Pb (1.9 mg/g) and Cd (0.63 mg/g) used activated carbon made from bamboo materials and carbon nanotube (Atieh et al., 2010; Lo et al., 2012). Furthermore, these adsorption capacity values are also comparable with activated carbon made from maize cob, 1.89 and 1.98 mg/g for Pb^{2+} and Cd^{2+} , respectively (Igwe and Abia, 2007). On the other hand, the adsorption capacity obtained in the present study is relatively lower than the reported values for adsorbents such as natural zeolite (>9.0 mg/g). Synthetic zeolite (500 mg/g) and activated carbon made from the coffee husk and rice husk (3.0–38 mg/g) (Oliveira et al., 2008; Srivastava et al., 2008; Hamidpour et al., 2010; Agarwal and Singh, 2017).

CONCLUSION

We have successfully synthesized a highly porous nature Cu-DPA MOF via hydrothermal method from copper nitrate trihydrate and diphenylamine linker. The use of as-synthesized MOF was investigated for the removal of heavy metals from wastewater. The Cu-DPA MOF was characterized by XRD, FTIR, and iodine number analysis that shows the material is capable of adsorbing the adsorbate. Our material revealed a maximum removal efficiency of 97.5%, 99.5%, and 99.5% toward Cr, Cd, and Pb metals, respectively, from wastewater sample. The adsorption parameters are found to be important factors for heavy metals removal, i.e., as initial metals concentration, pH value, contact time, and Cu-MOF dosage exhibited significant effect on the adsorption process. The adsorption process fit well with Freundlich isotherm with R^2 (0.995, 0.997, 0.996) for Cd, Pb, and Cr, respectively. This indicates the formation of a multilayer on the surface of the adsorbent. The adsorbent in this study reveals very good potentials for simultaneous removal of toxic metals from high-volume contaminated wastewaters. It can also be used as an adsorbent instead of more expensive and ineffective materials.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

HWH performed the experiment; HWH and MAC collected the data and drafted the manuscript; MA validated the data; AAD designed the study and supervision; AAD and MA edited the manuscript. All authors read and approved the final manuscript.

ACKNOWLEDGMENTS

The authors would like to gratefully acknowledged Dilla University for financial support and provision of laboratory facilities.

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