Nanomed Res J 6(3):287-295, Summer 2021

RESEARCH ARTICLE

The sorbent based on MOF-5 and its polyurethane nanocomposite for copper adsorption from aqueous solution

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ARTICLE INFO

Article History:
Received 18 May 2021
Accepted 25 Jul 2021
Published 01 Aug 2021

Keywords:
Metal–organic framework
MOF-5
Copper adsorption
Solution method

ABSTRACT

Objective(s): Copper (Cu) is a very strong toxic metal in environment. Therefore, copper sorbent can be of great help to the medical field. Metal organic framework (MOF) has attracted considerable attention as sorbent because of high porosity and surface area. In this work, MOF-5 was used for copper absorption from aqueous solution as a zinc-based metal organic framework. Then, polyurethane (PU) nanocomposite was modified with MOF-5 by press method as copper sorbent.

Methods: The samples were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) analysis, field emission scanning electron microscope (FESEM), BET surface area, and Ultraviolet–visible (UV–Vis) spectroscopy. The effect of amount and concentration were investigated on adsorption of copper in water solution. Based on the results, MOF-5 and its polyurethane nanocomposite were demonstrated the potential utility for copper removal from water solution.

Results: FESEM results confirmed that the samples are in nano scale. The copper absorption was approved by UV–Vis spectroscopy and BET surface area. The absorption value was increased by increase of amount and concentration.

Conclusions: This work focuses on the preparation of an efficient copper sorbent based on MOF-5 and its PU nanocomposite. MOF-5 is composed of zinc metal and benzene 1,4-dicarboxylic acid with the formula Zn4O(BDC)3 as a suitable candidate for adsorption of copper from aqueous solution. The results show that this nanocomposite can have a good potential for the development of environmental applications.

How to cite this article
Haftan F., Motakef Kazemi N. The sorbent based on MOF-5 and its polyurethane nanocomposite for copper adsorption from aqueous solution . Nanomed Res J, 2021; 6(3): 287-295. DOI: 10.22034/nmrj.2021.03.009

INTRODUCTION

Water pollution is one of the most important issues in the world today [1]. The toxicity of drinking water by heavy metals and the problems it has caused to organisms, especially humans, have led to extensive research into the removal of these pollutants from water. One of the most important heavy metals in drinking water is copper. Copper is a stable and biological element and is chemically toxic and is not easily broken and metabolized, and may be accumulated in the human or environmental food chain, and through consumption or absorption it may harm human health or environment. The safe level of copper in drinking water is different depending on the resources. Hence, the removal of copper from water and sewage is very important. Among the methods reported for the removal of heavy metals from water are methods such as oxidation, co-precipitation, ion exchange, adsorption, and membrane technology [2]. The adsorption method

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has been reported as a suitable method because no waste is added to the water and the adsorbents used can also be reused [3].

Today, metal organic frameworks have expanded as porous hybrid organic inorganic materials [4]. Omar M. Yaghi introduced MOF-5 in 1999 as the first metal organic framework. This MOF was synthesized by connection of Zn_4O units and 1,4-benzenedicarboxylate ligands to form a cubic network with the formula $Zn_4O(BDC)_3$ [5]. The metal organic frameworks have been typically synthesized by solution, solvothermal, hydrothermal, ionic liquids microwave, sonochemical, diffusion, electrochemical, mechanochemical, dry-gel conversion, and laser ablation methods [6]. MOFs have received a lot of attention in many areas due to their unique

properties such as drug delivery [7, 8], photoluminescence [9], optics [10], ion exchange [11], sensing [12], Raman spectroscopy [13], opto-electronic [14], sorbent [1, 15-17] and preparation of nanoparticles [18, 19] applications. Recently, MOF sorbent was applied for the removal of copper from aqueous solutions [20]. Newly, the polymer nanocomposite was used for easy separation of sorbent from the water is beneficial for reusing the materials and the removal of heavy metals during treatment [21]. Polyurethane is one of the most common polymers for the removal of heavy metals from aqueous solutions [22]. In this manuscript, MOF-5/polyurethane nanocomposites were prepared by a simple method and copper absorption was investigated by MOF-5 and its nanocomposites from aqueous solution.

MATERIALS AND METHODS

Materials

Materials containing zinc acetate dihydrate ($Zn(OAc)_2.2H_2O$), benzene-1, 4-dicarboxylate, dimethylformamide, chloroform ($CHCl_3$) and potassium nitrate were purchased from Merck KGaA, Darmstadt, Germany without any purification. Ultra-pure water was used to prepare all reagent solutions.

Methods

For preparation of MOF-5, each of zinc acetate dihydrate (2.111 g) and benzene 1, 4-benzenedicarboxylic acid (0.631 g) were dissolved in 62.5 mL of DMF. Then the two solutions were slowly added to each other and mixed for 2.5 hour at room temperature. Finally, the precipitates were washed by DMF and chloroform and then filtered. The result sample was placed in a vacuum furnace at 120 °C for 5 h to remove solvent from samples.

In this work, PU nanocomposites were prepared by press method. The casting method is not suitable for preparation of MOF-5/polyurethane nanocomposites because in this method the pore of MOF filled up with solvent and there is not any residual porosity for copper absorption. Different percentages of MOF-5 were evaluated for preparation of PU nanocomposites. First, PU polymer was placed in template and then placed at a temperature of 230 °C to form a homogeneous film. Then the MOF-5 sample uniformly put on the film and pressed at 130 ° C. Finally, the sample was placed in a cold press machine to stabilize MOF-5 samples on the polymer. Based on copper absorption, PU nanocomposites with 5 and 10 percentage of MOF-5 were shown better results and it was not possible to form a uniform nanocomposite with a higher percentage of MOF-5.

Characterization

FTIR was obtained by Shimadzuir 460 spectrometer in a KBr matrix in the range of 400–4000 cm^{-1} at room temperature for investigation of functional groups. XRD patterns were recorded by X'pert pro diffractometer (X' Pert Pro model, Panalytical, Peru) using Cu Kα X-ray radiation for determination of crystalline structure. FESEM was employed to see morphology and size (Sigma VP model, ZEISS, Germany). The surface area was evaluated using nitrogen gas sorption by MOF samples at 298 K and 0.88 atmosphere pressure (BElSORP Mini model, Microtrac Bel Corp, Japan). The UV–Vis spectroscopy (GENESYS 30 model, Thermo Scientific, America) was used to study absorption copper absorption. The UV-Vis spectroscopy was used to display the calibration curve of copper solution including 10, 30, 50, 70, 90 and 100 ppm. The parameters of sorbent amount and solution concentration were investigated on the adsorption rate at times of 0.5, 1, 2, 3, 4, 24 h.

RESULTS AND DISCUSSION

FTIR

Fourier transform infrared spectrum of MOF and its polyurethane nanocomposite were shown in Fig. 1. The O–H stretching vibration is appeared around 3500 cm^{-1}. The symmetric and asymmetric stretching of COO bonded to benzene ring in BDC ligand are shown the strong peaks at 1700 and 1500

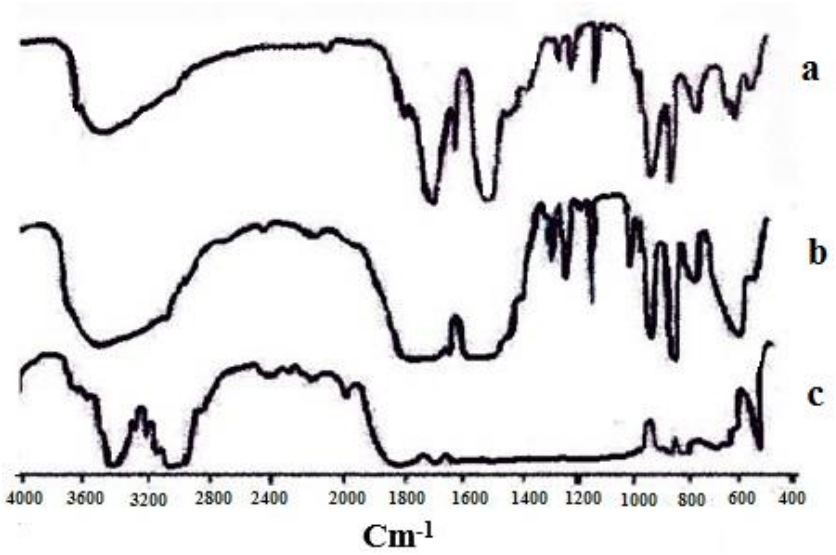

Fig. 1. FTIR spectra of MOF-5 a) before, b) after copper adsorption and its PU nanocomposite.

cm^{-1}. The aliphatic C–H asymmetric stretching is poorly assigned at 2900 cm^{-1}. The stretching of the aromatic C-H groups of the benzene ring in BDC ligand is observed around 1200 cm^{-1} (Fig. 1a). The result confirms the formation of MOF-5 nanostructure [15, 9]. The flattening of the peaks after copper adsorption is due to the presence of water in MOF-5 nanostructure (Fig. 1b). The sharp peak at 2900 cm^{-1} is associated with $-CH_2$ stretching of PU polymer (Fig. 1c). The result is according to previous report studies [23].

XRD

The crystalline structure of MOF-5 was measured before and after copper adsorption by powder X-ray diffraction (Fig. 2). The XRD results provide evidence that MOF-5 samples were correctly synthesized and crystalline structure was similar to a previously reported pattern [15]. Based on the result, the copper adsorption has no effect on the crystalline structure. The high percentage of PU polymer in the nanocomposite was caused no observation of MOF-5 characteristic peaks. The result is according to the previous report [21].

FESEM

FESEM images were evaluated to examine morphology and size of the samples (Fig. 3). The size of MOF-5 nanostructures is measured about 800 nm with cubic shaped before and about 70 nm with rod shaped after copper adsorption respectively. Based on the result, the homogenization process for copper adsorption has caused the reduce of size and deformation of structure due to the sensitivity of MOF-5 in the aqueous medium. The FESEM of MOF-5/PU nanocomposite was shown in the form of image from the cross section. According to the result, MOF-5 is shown rod shaped with the size about 70 nm. Therefore, MOF-5 has the reduce of size and deformation of structure due to its proximity to the polymer and the press operations that confirmed the sensitivity of MOF-5 before copper adsorption. This result has presented for the first time.

BET

The surface area of sample was investigated by Brunauer–Emmett–Teller (BET) analysis by nitrogen adsorption before and after copper adsorption at room temperature (Fig. 4). Based on the results, the surface area of MOF-5 decreased with copper adsorption from 463.819 m^2/gr to 25.960 m^2/gr. The decrease of surface area indicate that copper molecules are almost in almost all MOF pores after absorption.

UV–vis spectroscopy

The copper absorption was investigated by UV-Vis spectroscopy. The calibration curve of copper was examined at λ_{max} = 214 nm with concentration of 10, 30, 50, 70, 90 and 100 ppm (Fig. 5).

The copper absorption was investigated at

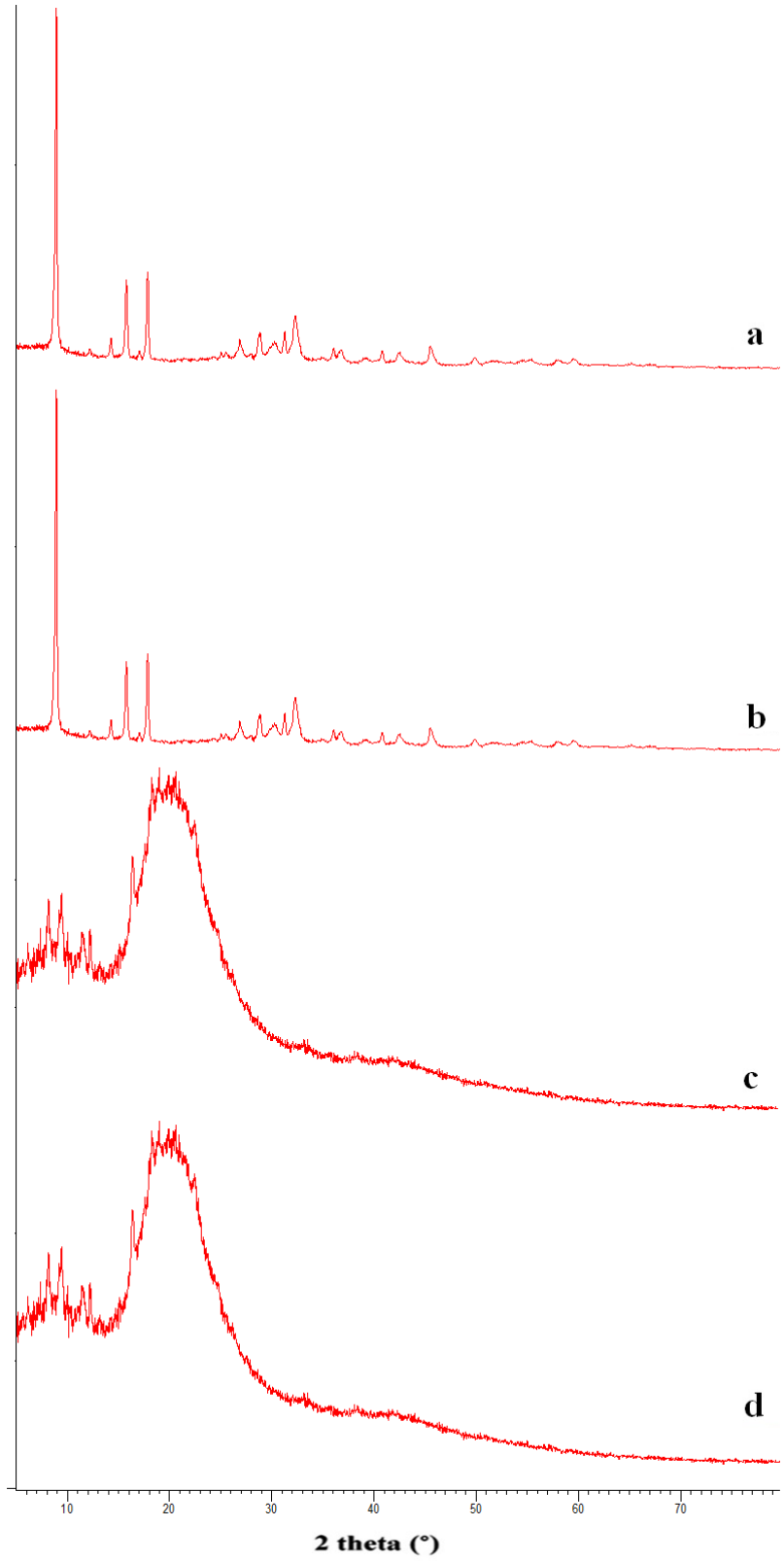

Fig. 2. XRD patterns of MOF-5 a) before and b) after copper adsorption

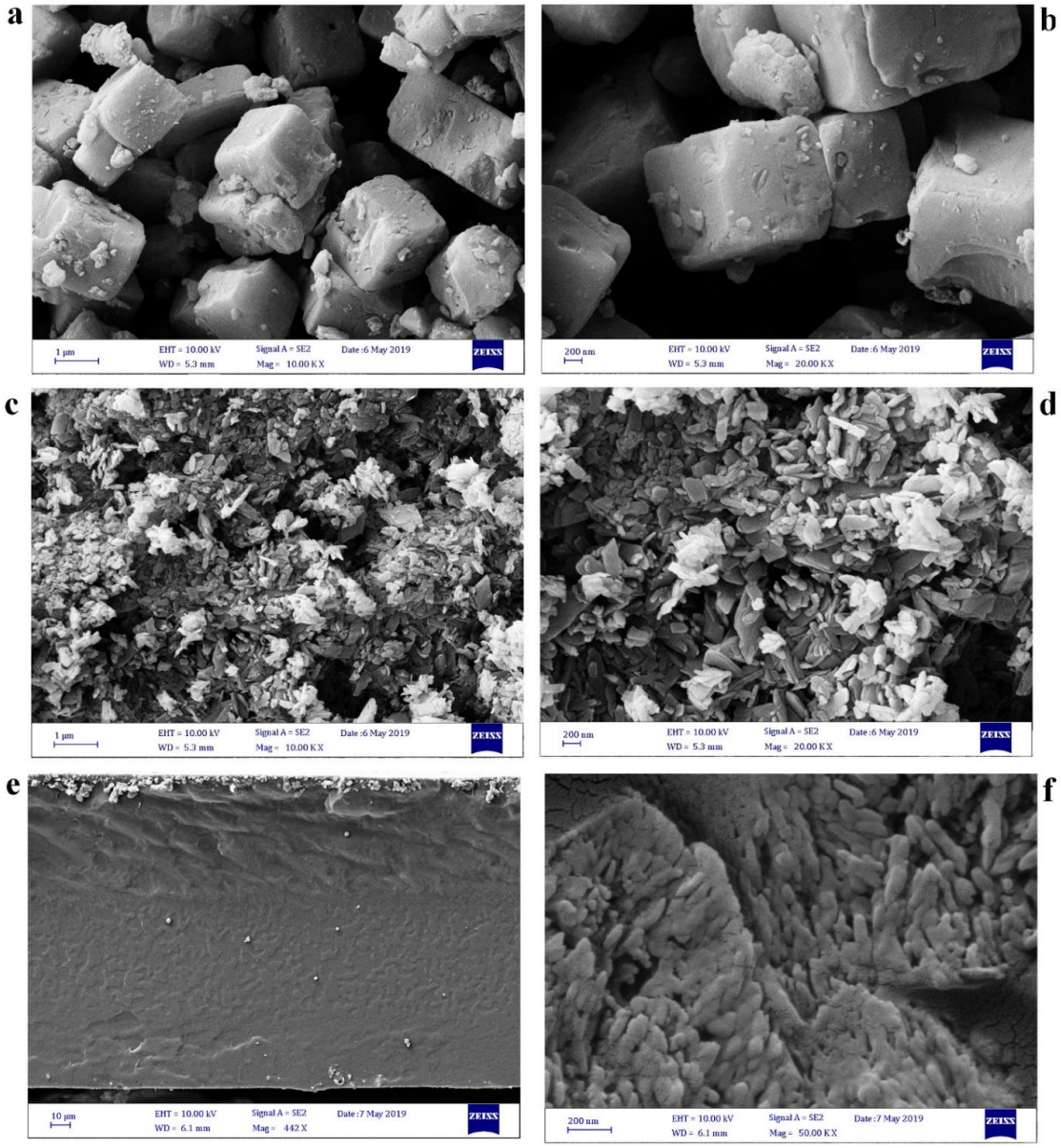

Fig. 3. FESEM images of MOF-5 before copper adsorption in a) 1 µm, b) 200 nm scale bare and MOF-5 after copper adsorption in c) 1 µm, d) 200 nm scale bare, and MOF-5/PU nanocomposite in cross section image in a) 10 µm, b) 200 nm scale bare.

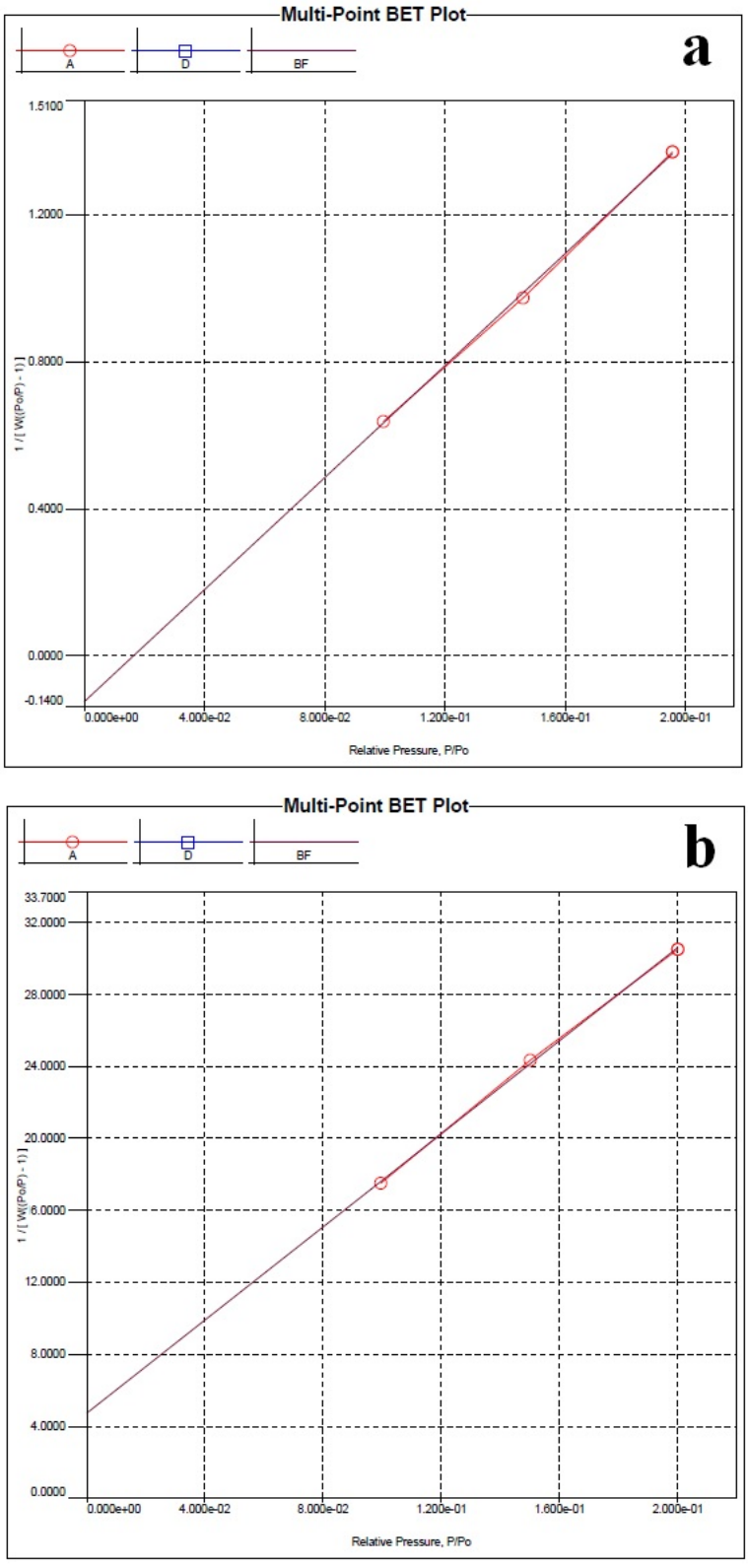

Fig. 4. BET of MOF-5 a) before and b) after copper adsorption.

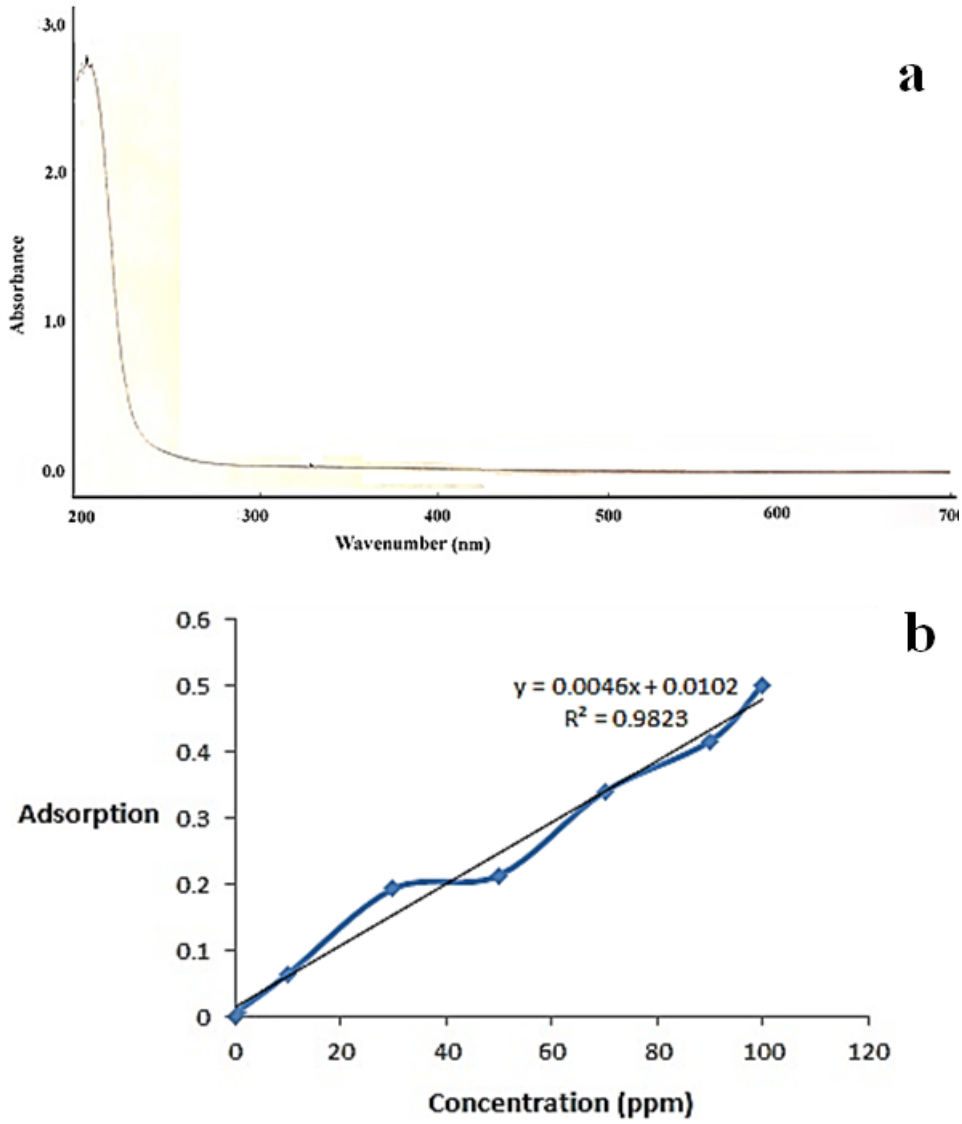

Fig. 5. UV–Vis absorption spectra of copper solution a) in 500 ppm and b) calibration curve at different concentrations in λ_{max}.

different concentrations including 10, 30, 50, 70, 90, and 100 ppm by MOF-5 at different times (Fig. 6a). According to the results, the increase of copper adsorption was resulted to the increase of concentration duo to the increase in available copper molecules. Appropriate adsorption at the desired time for a concentration of 70 ppm was the reason for its selection for other studies. The effect of amount of sorbent was shown on copper adsorption by MOF-5 (Fig. 6b). The adsorption diagram was evaluated at different MOF-5 amounts including 0.1, 0.25, and 0.5 g with a constant concentration of 70 ppm of copper at different times.

The copper adsorption was studied at different percentages of MOF-5 in nanocomposite including 5 and 10 % (Fig. 7a). The adsorption was investigated at different MOF-5/PU amounts of 10 % nanocomposite including 0.1, 0.25, and 0.5 g with a constant concentration of 70 ppm of copper at different times (Fig. 7b). Based on the results, the increase of copper adsorption was resulted to the increase of sorbent amount duo to increase of surface area.

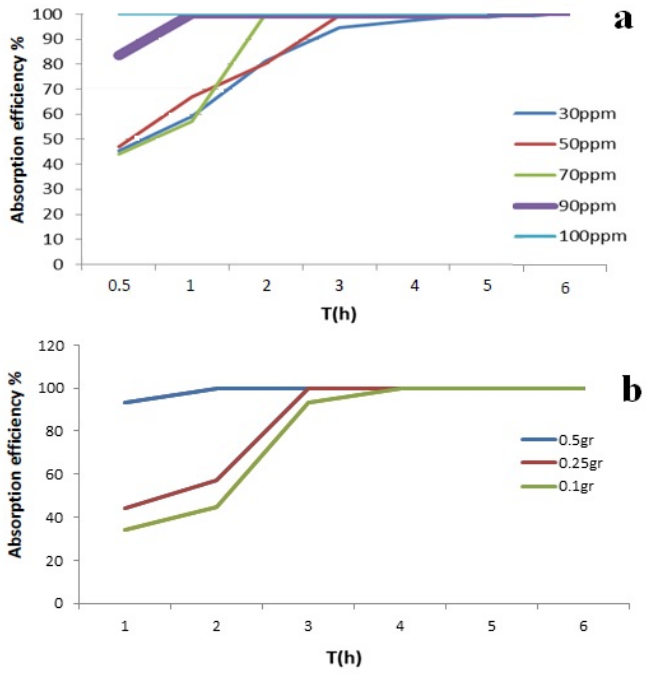

Fig. 6. The diagram of copper adsorption a) at different Cu concentrations by MOF-5, b) at different MOF-5 amounts.

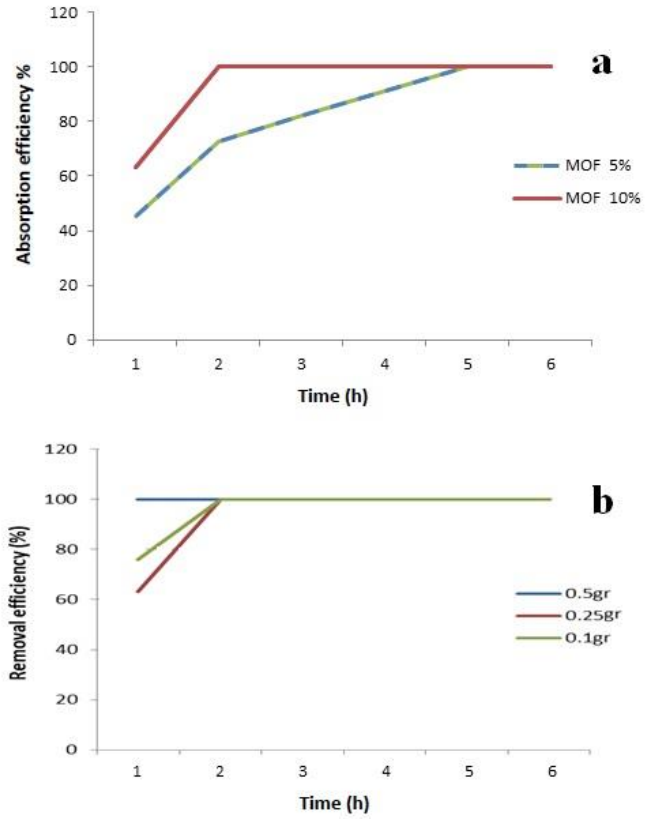

Fig. 7. The diagram of copper adsorption a) with different percentages of MOF-5 by MOF-5/PU nanocomposite and b) at different MOF-5/PU nanocomposite amounts.

CONCLUSIONS

MOF-5 was synthesized by simple solution method by self-assembly of zinc acetate dihydrate as a connector, benzene di-carboxylic acid linker as a ligand using DMF solvent. MOF-5/PU nanocomposite was prepared by press method with 5 and 10 percentage of MOF-5 for the first time. In this research, MOF-5 and MOF-5/PU nanocomposite were used for copper adsorption. Based on the result, the increase of copper adsorption was resulted to the increase of sorbent amount and solution concentration. FTIR results showed the formation of MOF-5, its nanocomposite, and copper adsorption by them. FESEM results confirmed the morphology, size of the nanoscale, and the coating of the polymer surface with MOF-5. BET and UV–vis spectroscopy results showed copper adsorption by MOF-5. Hence these compounds can a good and economical potential for copper sorbent from aqueous solution to develop environmental applications.

ACKNOWLEDGMENTS

We would like to thank Dr. Mohsen Shahrousvand for providing the polyurethane polymer.

CONFLICT OF INTEREST

The authors declare no conflicts of interest

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