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RESEARCH ARTICLE

Amide-functionalized metal-organic frameworks $Cu_3(BTC)_2$ as a new platform for efficient and selective removal of Cd (II) from aqueous solutions

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ABSTRACT

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This contribution indicated how to anchor amine-decorated pores of Cu-MOF, $Cu_3(BTC)_2$ (**1**), formulated **$Cu_3(BTC)_2$@AMT** (**1@AMT**) (where AMT=2-amino-5-mercapto-4,3,1-thiadiazole and BTC=1,3,5-benzenetricarboxlic acid or trimesic acid) as an efficient way to remove Cd (II) from an aqueous solution. Furthermore, the post-synthetic modification as exemplified in the context of functionalizing the MOF, **1** with AMT was performed, and the resultant structure was determined through Powder X-ray diffraction (P-XRD), FT-IR spectroscopy, and field emission scanning electron microscopy (FE-SEM). N_2 adsorption-desorption by Brunauer-Emmett-teller (BET) has been determined to evaluate the specific surface area (7.49 $m^2.g^{-1}$) and the pore volume (0.04 $cm^3.g^{-1}$) of the sample. Herein, we study the effect of various crucial factors, including pH, contact time, and other background metal ions, on **1@AMT** uptake capacity. Moreover, the reusability was studied and recycled without considerable loss of Cd (II) uptake capacity during five cycles. The resultant amine-functionalized MOF, **1@AMT,** showed a high Cd (II) uptake capacity of 692.3 $mg.g^{-1}$, surpassing that of the benchmark adsorbents. Our work thus paves the way for developing functionalized MOFs with significant affinity between the amide group and Cd (II) as a new type of platform with sufficient cadmium removal performance.

How to cite this article

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INTRODUCTION

Heavy metal ions as non-biodegradable pollution have become a worldwide issue, potentially posing risks for human health. It is mainly attributed to industrial and mining activities, which pose a crucial threat to the environment and public health. In the last few years, a rapid increase in industrial developments has led to the generation of enormous quantities of hazardous waste, which has a negative effect on drinking water and can change the chemical composition of water with heavy metal ions [1]. Hence, there is an immediate need to develop a sufficient method for the removal of heavy metal ions in order to preserve human health and the environment [2]. In particular, cadmium is a highly toxic heavy metal among the non-essential trace elements detected in potable water and is considered a major pollutant.

There is a diversity of strategies for cadmium removal, including ion exchanges, electrocoagulation, solvent extractions, chemical precipitation, and physical adsorptions, that have been investigated in the aquatic environment over the past [3, 4]. Among the recent innovations, adsorption is well-known candidate in water purification considering its cost-effectiveness, simple design, easy operation, and environmental friendliness [5]. There are different types of adsorbents, e.g., activated carbon, metallogels, layered double hydroxides, and polymers, in which metal-organic frameworks (MOF) modified the specific functional groups demonstrated an increase in the adsorption capacity of heavy metal ions according to their unique structures [6, 7].

Over the past decade, metal-organic frameworks (MOFs) constructed by metal-containing units as secondary building units (SBU) or metal ions/clusters and organic linkers are one of the most promising classes of organic-inorganic hybrid porous materials [8]. Their unique properties, such as tunable structure, significant flexibility, porosity, and high surface area, have attracted more attention in various fields. They have emerged as an unparalleled chance for widespread applications including gas storage, catalysis, liquid sorption, energy storage, adsorption, separation, and uptake of heavy metal ions, as well as sensing [9]. The synthesis and utilization of MOFs for removing heavy metal ions through the diffusion of contaminants into the framework has recently been applied, with a focus on introducing a variety of functional groups into MOFs. Hence, the investigation of MOFs for exclusively selective removal of Cd (II) from other metal ions remains a challenge to be addressed [6, 10].

This literature indicates how to anchor the amine-functionalized groups onto the pore surface of **1@AMT** *via* the technique of post-synthetic modification of **1** and surveys the affective parameters of the removal of Cd (II). The applied amine-functionalized MOF illustrated a high selectivity uptake capability for Cd (II) removal from an aqueous solution in the presence of other background metal ions.

EXPERIMENTAL

Materials and instruments

All reagents were purchased from Merck and Sigma-Aldrich commercial companies and used as received. Fourier-transform infrared spectra were recorded on an FT-IR spectrometer using KBr pellets. Powder X-ray diffractometer (P-XRD) measurements were recorded in the $2\theta = 5\text{-}50°$ range on a Philips PW1800 diffractometer using Cu-Kα radiation ($\lambda = 1.5406$ Å) at room temperature. Field emission scanning electron microscopy (FE-SEM) was performed on TESCAN MIRA III. The specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) method to evaluate a potential use of $Cu_3(BTC)_2$@AMT for Cd(II) ions at liquid nitrogen temperature (77k). Also, the samples were activated under vacuum at 423 K for 24 h before running the adsorption experiments. Thermo-gravimetric analyses

(TGA) were performed with a heating rate of 20 °C/min using a TA-Q600 TG-DSC instrument. The concentrations of Cd (II) ions were measured by using inductively coupled plasma-optical emission spectrometer (ICP-OES) (≤1 ppb).

Preparation of 1

The synthesis of **1** was carried out by the hydrothermal method. The aqueous solution (12 mL) containing $Cu(NO_3)_2.3H_2O$ (875 mg, 3.6 mmol) was added to a stirred solution of trimesic acid (420 mg, 2 mmol) in 12 mL of ethanol. After that, the mixed solution was sealed in a 15-mL Teflon reactor and kept under 120 ℃ for 12 hours. After cooling to room temperature, octahedral shaped crystals suitable for X-ray diffraction were obtained, washed with distilled water and ethanol, and dried at ambient temperature (yielding 76%). Anal. calc. for $C_{20}H_{14}Cu_3O_{15.75}$: C, 32.62; H, 2.27%. Found: C, 32.62; H, 2.27%.

Preparation of 1@ AMT

In order to achieve the conventional heating activation, **1** crystal was heated at 150 °C for 24 hours. 250 mg of activated **1** were suspended in 20 mL of toluene, followed by the addition of 2-amino-5-mercapto-4,3,1-thiadiazole (133 mg). The mixture was stirred at room temperature for 24 hours. After the reaction, the mixture was centrifuged to collect the solid product, which was subsequently washed with ethanol and then dried at 30 °C for 3 h to yield $Cu_3(BTC)_2$@ AMT. (yielding 63%). Anal. calc. for $C_{22}H_{16}Cu_3O_{15.75}S_2N_4$: C, 23.31; H, 2.11; N, 11.43%. Found: C, 23.31; H, 2.11; N, 11.43%

Cd (II) Adsorption studies

The impact of various parameters on the absorption proficiency of Cd (II) was examined using the batch method in aqueous solutions. In order to prepare 1000 ppm of Cd (II) stock solution, 137 mg of Cd $(NO_3)_2.4H_2O$ was dissolved in 50 mL of deionized water. Then, 10 mg of **1@AMT** adsorbent was subsequently added to 10 mL of Cd (II) solution and shaken for 60 min at ambient conditions. The mixture pH values were adjusted to 9 by using 0.1 M HNO_3 or NaOH solutions. After that, the final mixture was centrifuged for 6 minutes. The concentration of Cd (II) by sampling from the obtained solution was measured using an inductively coupled plasma-optical emission spectrometer (ICP-OES). The removal efficiency was measured according to the following formula:

Removal efficiency (%) = $(C_0 \times C_e)/C0 \times 100\%$

Where C_o and C_e (mg/L) refer to the initial and equilibrium concentrations of Cd (II) ions (mg L^{-1}), respectively.

RESULTS AND DISCUSSIONS

Characterization of 1@AMT

Fig. 1 demonstrates the FT-IR spectra of the synthesized **1** and **1@AMT**. For **1**, the peaks manifested at 1372, 1448, and 1657 cm^{-1} regions are attributed to the stretching carboxylate groups of trimesic acid. The modification of MOFs by reaction with AMT was confirmed by the observed bands at 1617, 3374, and 3460 cm^{-1} which are assigned to C=N in rings and asymmetric stretching N-H stretch, respectively. Also, the C-S, N=C-s, and N=C-C are appearing at 1010, 2100, and 2256 cm^{-1}, respectively, as observed in the FT-IR spectrum of **1@AMT**.

The P-XRD patterns of **1** and **1@AMT** are illustrated in Fig. 2. The P-XRD patterns of synthesized **1** indicated a set of narrow, well-defined reflections attributed to a highly crystalline phase (Fig.2a). Furthermore, the positions of all peaks in the synthesized **1** were in good agreement with the simulated **1** pattern, to indicating that the sample was successfully synthesized. The P-XRD pattern of **1@AMT** refers to very weak peaks and low crystallinity in these materials compared to **1,** as represented in Fig. 2b. Due to the amorphous nature of **1@AMT**, the behavior of the very weak characteristic peaks compared to **1** may be due to the possible decrease in regularity of the structure based on the contribution of AMT groups in this compound.

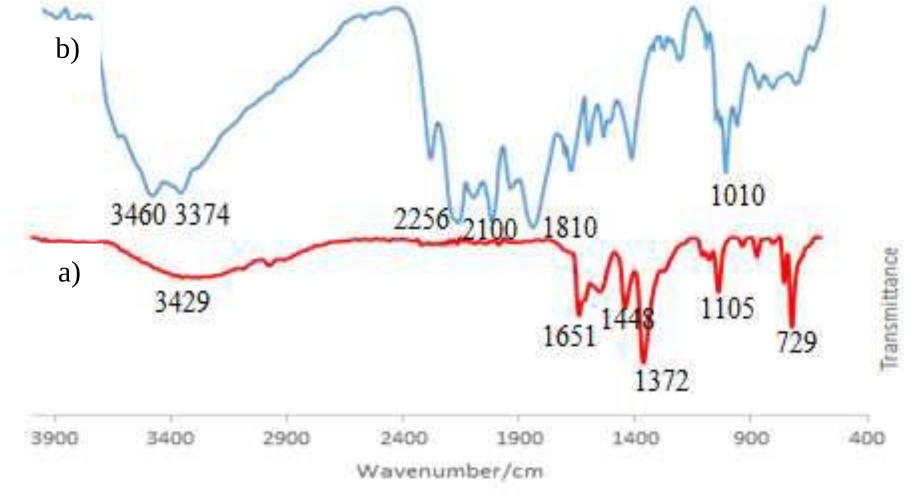

Fig.1. FT-IR spectra (a) **1** and (b) **1@AMT**.

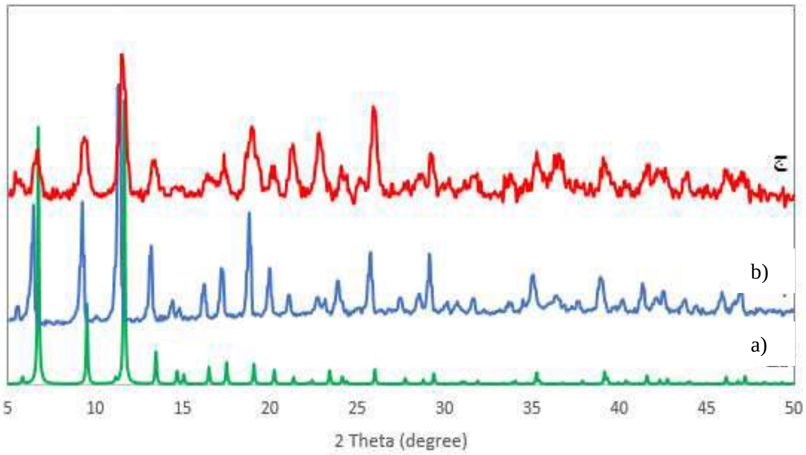

Fig.2. Powder X-ray diffraction patterns (a) **1** and (b) **1@AMT**.

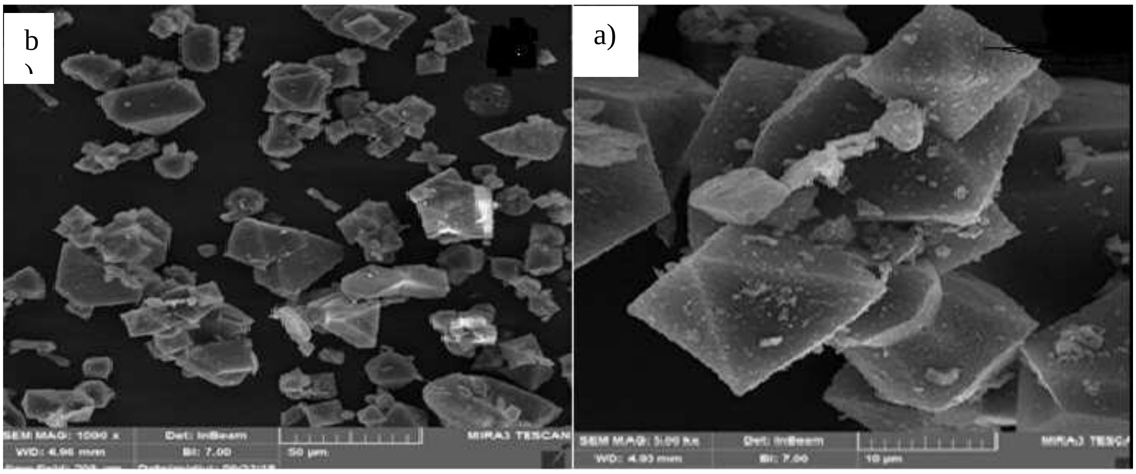

Fig.3. FE-SEM images (a) **1** and (b) **1@AMT**.

In addition, the morphologies of **1** and **1@AMT** were assayed via field emission scanning electron microscopy (FE-SEM) as shown in Fig. 3. The FE-SEM images displayed considerable differences between **1** and **1@AMT**, which are fundamentally emphasized by the prosperous AMT modification of **1@AMT**. The FE-SEM image of **1** shows octahedral particles in the range of 4–10 µm, while the images of **1@AMT** exhibit microscale aggregates in 6 µm.

The thermal gravimetric analysis (TGA) was deliberated to recognize the possible thermal stability characteristics of **1** and compare them with those of **1@AMT** (see Fig.4). The TGA thermogram of **1** is distinguished by two decomposition steps at 31.23–150 and 150–310 °C because of the loss of coordinated and uncoordinated water molecules adsorbed on the surface and trapped in cavities, respectively. Furthermore, the TGA thermogram of **1@AMT** manifested two degradation steps at 18.73–110.41 and 110.41–440.90 °C due to conceivable decomposed organic matter, finally collapsing metal-organic framework, which revealed that the stability of **1@AMT** is modified.

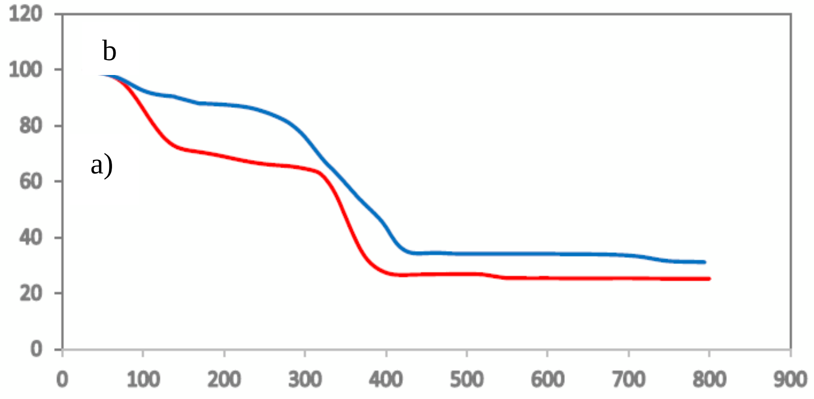

Fig.4. TG/DTG curves of samples

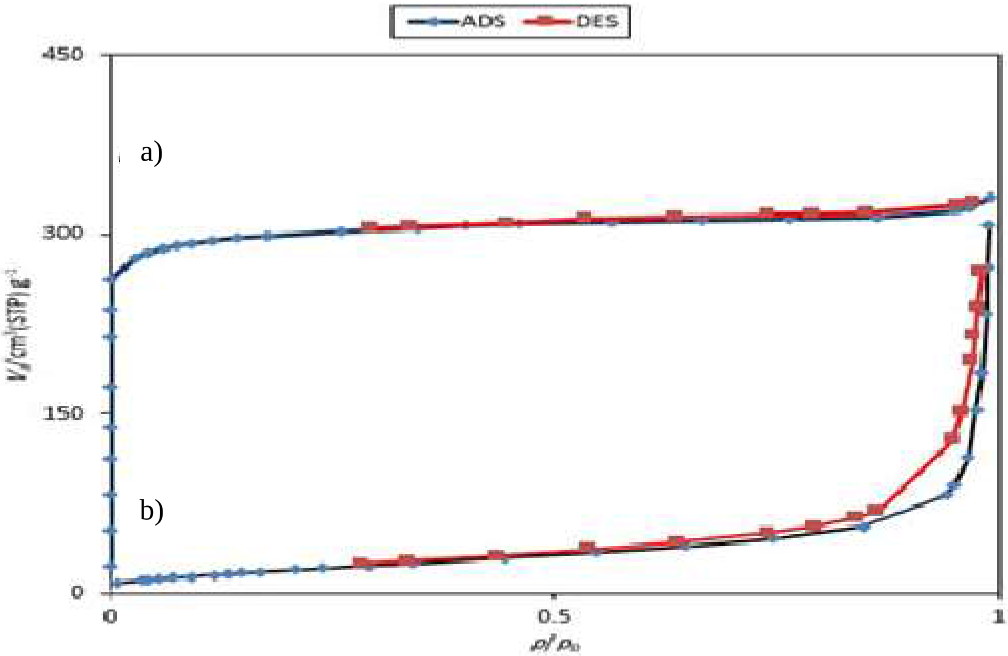

Fig.5. N_2 adsorption-desorption isotherms of **1** (a) before and (b) after amine-functionalization

The N_2 adsorption-desorption isotherms can be observed in Fig. 5 to determine surface area and pore volume of **1** and **1@AMT**. The isotherm curve of types I/IV is observed with a small hysteresis loop for **1,** which indicates the co-existence of microporous and mesoporous structure of **1**. However, the isotherm curve of type II appears for **1@AMT,** which implies a nonporous structure that might result from the crystal accumulation of **1@AMT**. In addition, the parameters of specific surface area and pore volume are 1167.63 m^2/g and 0.51 cm^3/g for **1**, respectively. In addition, the specific surface area pore volume of 7.49 m^2/g and 0.04 cm^3/g, respectively, were decreased for **1@AMT** because of the grafting of the amino group.

Adsorption of Cd (II) by 1@AMT

Influence of pH

The absorption efficiency of cadmium (II) onto the adsorbent strongly depends on the pH value because of the ionization state and surface charges of the adsorbent. The adsorption of 1000 ppm Cd (II) solution by around 10 mg of **1@AMT** was examined in a pH range of 1–9 in separate containers. As observed in Fig. 6, the adsorption rate for the removal of Cd (II) metal ions were improved noticeably with increasing pH values from 6.0 to 9.0. According to the presence of an NH_2 group within the structure of **1@AMT** that is recognized to play a significant role in raising and improving the binding characters with the target metal ion, coordination between Cd (II) and NH_2 groups is highly preferred, which results in a direct increase in the pH values. At lower pH values ($pH<4$), the adsorption rate of cadmium (II) would be unfavorable because it would occupy most of the adsorption sites on the adsorbent surface and cause anticipated repulsion between Cd (II) and protons in **1@AMT**.

Influence of contact time

The uptake capacity of cadmium (II) by **1@AMT** at different contact times (in the range of 0-90 min) was measured by applying a 1000 ppm concentration of the Cd (II) ion. Fig. 7 showed a rapid increase in the adsorption capacity value in 60 min of contact time to reach equilibrium conditions, while no expected significant changes could be observed after 10 min. It is possible that more binding NH_2 sites were accessible at first, which were occupied by passing time. Hence, the maximum adsorption capacity of 1000 ppm Cd (II) solution is approximately 69.23% in 60 min, and the equilibrium was fulfilled in 90 min.

Investigation of Comparative Adsorption

In order to investigate the effect of other background ions on **1@AMT** performance, common heavy metal cations, including Cd (II), Co (II), Hg (II), Mn (II), Ni (II), Cu (II), and Pb (II) were selected. As shown in Fig. 8, **1@AMT** adsorbs Cd (II) more impressively compared to others. After the Cd (II) ion, nickel (II), cobalt (II), and magnesium (II) were adsorbed with high capacity. But other cations reveal a low considerable affinity toward **1@AMT**.

Reusability Study

One of the most significant issues that should be noticed in the removal of Cd (II), is protecting the uptake capacity during the multiple adsorption and desorption cycles. To check the recyclability of **1@AMT**, five adsorption–desorption cycles were performed. The obtained results are collected in Fig. 9. The desorption process was carried out by adding 10 mL of the EtOH/H_2O mixture (v/v: 1:1) to the material that was stirred for 90 minutes at ambient conditions. ICP-OES was used for investigating the amount of remained Cd (II). The percentage of five adsorption cycles confirmed the reusability of the adsorbent during adsorption-desorption cycles. The remarkable results indicated that **1@AMT** adsorbent could be revived and reused for more cycles with a regeneration efficiency of approximately 70%. It is notable that the cadmium uptake capacity of **1@AMT** outperforms some series of benchmark sorbent materials (Table 1), highlighting its potential for application in wastewater treatment.

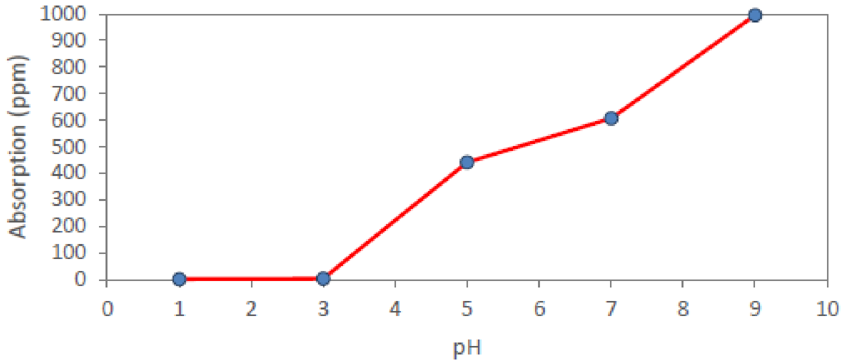

Fig. 6. Effect of solution pH on Cd (II) adsorption in **1@AMT**.

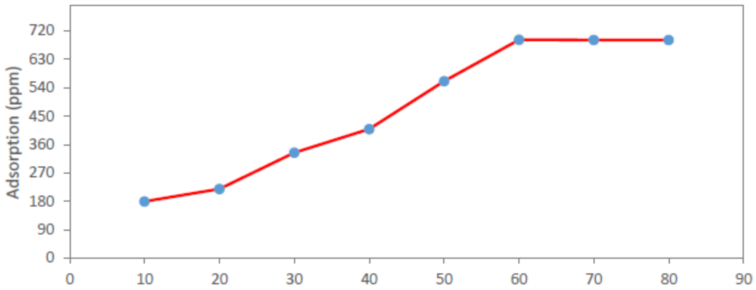

Fig. 7. Effect of contact time on Cd (II) adsorption in **1@AMT**.

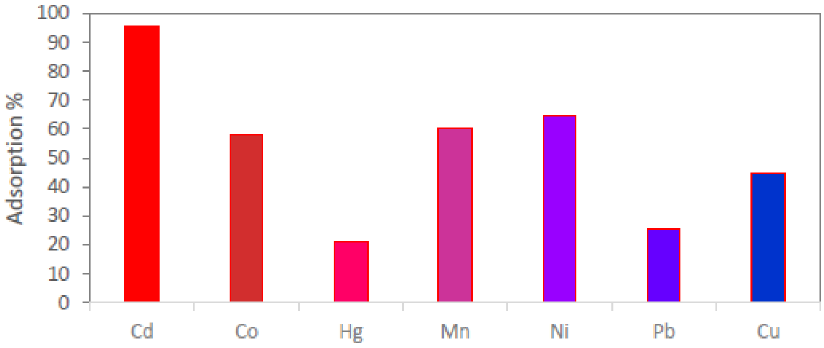

Fig. 8. Effect of co-existing ions on the removal of Cd (II) by **1@AMT**.

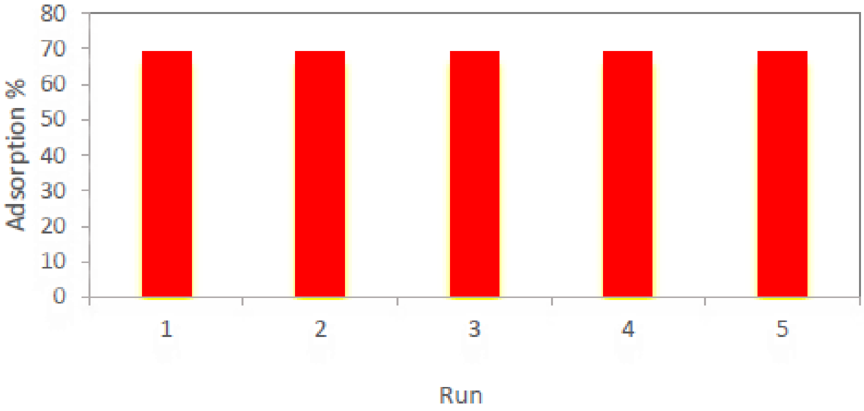

Fig. 9. Reusability of the **1@AMT** for Cd (II) adsorption.

Table 1. Comparison of Cd (II) adsorption performances by various adsorbents

Sorbent	Adsorption capacity (mg/g)	Adsorption time (min)	Ref.
Fe3O4@APS@AA-co- CA	29.6	48	[11]
Sulfonic-functionalized poly (dimethylsiloxane) networks	78.7	1440	[12]
Salicylic acid chelate	45	120	[13]
Magnetic yeast treated with EDTA dianhydride	48.7	30	[14]
PPBM	43.5	100	[15]
Si-TDC	40.5	60	[16]
MPGI	87.7	1	[17]
ZrO_2/B_2O_3	109.9	30	[18]
$Cu_3(BTC)_2$-SO_3H	88.7	10	[19]
CuBTC@AMT	**197.9**	**10**	**This work**

CONCLUSION

In the present study, an amine-decorated MOF, **1@AMT**, was successfully prepared *by* utilizing organic ligands to investigate the adsorption performance of a Cd (II) aqueous solution. The collected data indicated that resultant **1@AMT** uptake Cd (II) more efficiently, in which the effects of various experimental parameters, including pH, contact time, and other background ions, can influence **1@AMT** performance. The characterization results reveal that the amino group is successfully grafted into the framework structure of $Cu_3(BTC)_2$. The capacity of the Cd (II) absorption increases from 0.96 mmol/g to 692.3 mg.g^{-1} for **1@AMT** at ambient conditions due to the introduction of the amino group. Furthermore, the tested **1@AMT** adsorbent could be regenerated and reused for several cycles.

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