Isotherm Models of Heavy Metal Sorption onto Zinc-tricarboxylic

C. Kowsura, B. Pangkumhang, P. Jutaporn, and V. Tanboonchuy

***Abstract*—Zinc-tricarboxylic (Zn-BTC) consists of Zinc Acetate Dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and 1,3,5 Benzenetricarboxylic Acid (H_3BTC), a well-known metal-organic framework (MOFs). It was synthesized by hydrothermal process. This study was established to analyze the capability of Pb(II) and Cu(II) adsorption onto Zn-BTC synthesized. The adsorption isotherms of Pb(II) and Cu(II) were compared to Langmuir, Freundlich, and Dubinin-Radushkevitch models. The results show greater correlation coefficient between these two adsorption isotherms and Langmuir model. The maximum adsorption capacities of the synthesized Zn-BTC were 416.7 mg/g for Pb(II) and 85.5 mg/g for Cu.**

***Index Terms*—Zinc-tricarboxylic, MOFs, sorption, heavy metal, Pb(II), Cu(II).**

I. Introduction

Heavy metals contamination in water is one of the major environmental concerns. Heavy metals from heavy industry, agricultural, and other human activities could enter the water body and cause danger to the environment and human health. Heavy metals, such and lead (Pb) and copper (Cu), are commonly found in the discharged wastewater form industries. Industrial sector has to comply with environmental regulations to treat their wastewater. For example, Pollution Control Department of Thailand regulated maximum allowable concentrations of Pb and Cu in treated effluent to be 0.2 mg/L and 2 mg/L, respectively [1]. Heavy metal, even in low concentration, can bioaccumulate in a biological organism over time. This treated effluent, even though meets standard in term of concentration, but the presence of trace heavy metals in large volume of discharged effluent can still cause environmental impact in industrialized area.

Toxicity of heavy metal includes obstructive lung disease, reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Heavy metals, such as arsenic, cadmium, copper, lead, mercury, nickel, are regulated in drinking water by The World Health Organization (WHO) [2]. Electronic industry is one of the major parties in heavy metals discharge in wastewater stream. This study focuses on Pb and Cu because they can be found in abundance in wastewater from electronic industry.

Lead is considered a carcinogenic substance. It has adverse effect on human organs and can also cause disability in newborns. Copper is an essential trace element for living organism but excessive Cu acute exposure can cause vomiting and hypotension. Chronic effects of Cu exposure can damage the liver and kidneys and also Wilson's Diseases syndrome [2].

The current technologies used for heavy metals removal are precipitation, ion exchange, and adsorption process [1]-[4]. Removal by adsorption process is our major focus because the process was simple and effective [5]. Absorbents used in previous studies for heavy metal removal by adsorption process were activated carbon [4] and Zeolite [7]-[9]. A new type of absorbent material that has potential to be used for heavy metals adsorption is metal-organic frameworks.

Metal-organic frameworks (MOFs) consist of network framework of metal ions and organic molecules binding together with covalent bond, resulting in multiple dimensions structure [10]. MOFs are the highly crystalized and adjustable in porosity. The main advantage of MOFs is that their pore size and porosity can be designed to adsorb specific contaminants [11] and their structure can also be customized for the chemical specificity[12]. MOFs can be synthesized by variety of methods, such as microwave [13] and ultrasonic [14]. The commonly employed synthesis method is hydrothermal/solvothermal, which is a synthesis using heat [15]. Potential applications of MOFs adsorbents include gas storage and separation [12], ion exchange and chemical sensing [16]. It can also be used to control release of copper ions for antifungal propose [17]. Over all, application MOFs is a promising technology to be applied in full industrial scale. With these advantages of MOFs, they are attractive for new research. Previous study [18] reported that using MOF-808 as adsorbent is efficient at arsenic removal from water. $Cu_3(BTC)_2$–SO_3H also exhibited high Cd(II) uptake capacity, thus has a potential use for cadmium removal [19]. Other type of MOFs previously used in heavy metals absorption studies were Graphene Oxides (GO) [4], [6], EDTA-Graphene Oxide (EDTA-GO) [3], [20] for Pb(II) removal and MOF-5 [16] and Graphene Oxides-CdS [21] for Cu(II) removal. However, an optimum experimental conditions to maximize heavy metals absorption efficiency of MOFs were not well studied.

This study uses adsorption isotherm to evaluate the used of Zn-BTC as an adsorbent to remove Pb(II) and Cu(II). The Zn-BTC used in this study included Zinc Acetate Dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and 1,3,5 Benzenetricarboxylic Acid (H3BTC), which was synthesized by hydrothermal process The adsorption isotherms of Pb(II) and Cu(II) by Zn-BTC

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were compared to Langmuir, Freundlich, and Dubinin-Radushkevitch models and optimum experimental conditions were also determined.

II. Materials and Methods

A. Chemical and Reagents

Zinc Acetate Dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), Benzenetricaboxylic acid (H_3BTC), were obtained from Sigma-Aldrich, Saint Louis, USA and Ethanol were obtained from RCL Labscan Ltd., Bangkok, Thailand. The 1000 mg/L-Pb(II) and 1000 mg/L- Cu(II) stock solutions were prepared from dissolving $Pb(NO_3)_2$ and $CuSO_4 \cdot 5H_2O$ in deionized water, respectively. HNO_3 and NaOH were used to adjust the pH of the stock solutions as required.

B. Zn-BTC Synthesis

Zn-BTC was synthesized by hydrothermal method using $ZnAc \cdot 2H_2O$ 0.99 g dissolved in 75 mL deionized water, then the solution was stirred for 30 minute. 0.64 g of H_3BTC was also dissolved in 75 mL ethanol and stirred for 30 minute. The $ZnAc \cdot 2H_2O$ and H_3BTC solutions were mixed together then stirred for another 30 minute. The mixture was then poured into Teflon-line stainless steel autoclave and heated to 103-105 °C for 24 hour. The Zn-BTC solution was dried at 200 °C in a electric muffle furnace for 24 hour and then the furnace temperature was increased to 350 °C for another 2 hour. This Zn-BTC was used as an adsorbent to remove Pb(II) and Cu(II) from aqueous solution. The Zn-BTC was characterized by X-ray diffraction analysis)XRD) (Model D8 Discover, Bruker AXS Germany) and point of zero charge (pH_{pzc}).

C. Batch Adsorption Experiment

Batch adsorption experiments were performed to determine the time of mixing needed to reach equilibrium of Pb(II) and Cu(II) adsorption by Zn-BTC. 20 mg/L Pb(II) and 20 mg/L Cu(II) working solutions were prepared from the 1000 mg/L stock solutions. HNO_3 and NaOH were used to adjust pH of Pb(II) and Cu(II) working solutions to 6 ±0.5 and 5 ±0.5, respectively [3, 22]. In the batch experiments, 0.5 g of Zn-BTC was added to Pb(II) and the Cu(II) working solutions separately. The water samples were collected over the time span of 0 - 120 minute. Treated water samples were analyzed by Atomic Absorption Spectroscopy (AAS) (Perkin-Elmer AAnalyst 800).

The adsorption capacities were calculated by the following equation [23]:

$$\% \text{ Removal} = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where C_0 and C are the initial concentration of heavy metal (mg/L), and the final concentration of heavy metal (mg/L), respectively.

D. Isotherm Models for the Adsorption of Heavy Metals

In isotherm models study, different initial concentrations of Pb(II) and Cu(II) were varied from 5–300 mg/L and the pH of each solutions was kept constant at 6 ±0.5 and 5 ±0.5, respectively. 0.025 g of Zn-BTC was added to 50 mL of heavy metal solutions and 60 min-mixing was provide by was a rotating mixer. Adsorption kinetics were compared to Pseudo-first and second orders [23], [24].

Pseudo-first order is described by the equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

Pseudo-second order is described by the equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where q_e (mg/g) and q_t (mg/g) are the amount of heavy metals uptake on the adsorbent at the equilibrium and at time t, respectively. k_1 and k_2 are the rate constant of pseudo-first and second orders, respectively.

Results of adsorption isotherms from the experiments were compared to Langmuir, Freundlich, and Dubinin-Radushkevitch isotherms [22]-[24] and isotherm models fitting was evaluated using R^2 values.

Langmuir isotherm assumes that adsorption process is a monolayer adsorption of adsorbate onto a homogeneous surface of adsorbent. Langmuir isotherm can be described by the following equation [24], [25]:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (4)$$

where q_e and q_{max} are the amount of heavy metals uptake on the adsorbent at the equilibrium (mg/g) and at maximum adsorption capacity (mg/g), respectively. K_L is the rate constant of Langmuir isotherm, and C_e is the concentration of adsorbate at the equilibrium (mg/L).The equation can be rearranged find the values of q_{max} and K_L by linear regression method with graphical approach. Experimental data $\frac{1}{q_e}$ can be plotted as a function of $\frac{1}{C_e}$ as described by the equation:

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L C_e} + \frac{1}{q_{max}} \quad (5)$$

Freundlich isotherm was based on assumptions of multilayer adsorption of adsorbate onto heterogeneous surface of adsorbent with non-uniform distribution of heat of adsorption. Freundlich isotherm is described by the following equation [24], [25]:

$$q_e = K_F C_e^{1/n} \quad (6)$$

where K_F is the rate constant of Freundlich isotherm and n is the adsorption intensity.

Equation (6) can be rearranged in the form of linear equation to find the value n and K_F using graphical method. ln q_e is can be plotted as a function of C_e by the equation:

$$\ln q_e = lnK_F + \frac{1}{n} C_e \quad (7)$$

Dubinin-Radushkevitch isotherm describes the mechanism of adsorption of a physical adsorption or chemical adsorption. Dubinin-Radushkevitch isotherm is described by the equation [24].

$$q_e = q_{max} e^{-\delta \varepsilon^2} \quad (8)$$

Equation (8) can be rearrange as:

$$ln\, q_e = -\delta \varepsilon^2 + \ln q_{max} \quad (9)$$

where δ is the rate constant of the energy absorption per quantity of adsorbent (mol^2/J^2), and $\mathcal{E}$ is the Polanyi potential. $\mathcal{E}$ is determined by the following equation

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \quad (10)$$

where R is the gas constant (J/mol-K), and T is temperature (K).

The free energy (E, kJ/mol) of sorption per molecule of adsorbent occur when adsorbate moves to the surface of the solid in solution, and can be describe by the equation:

$$E = \frac{1}{\sqrt{2\delta}} \quad (11)$$

E can be used to categorize adsorption process. If the value of E is between 8 - 16 kJ/mol, the process is considered chemical absorption, while the value of E < 8 kJ/mol indicates physical absorption nature.

III. Results and Discussion

A. Characterization of the Adsorbent

The Zn-BTC was characterized by X-ray diffraction analysis (XRD) (Model D8 Discover, Bruker AXS Germany). The XRD pattern was collected using continuous scan mode in 2θ range between 5 - 50 ° with a scanned speed at a counting time of 1 s per step. The instrument was operated at 40 kV and 40 mA using as a source copper radiation [13], [15]. The phase structure of Zn-BTC sample by XRD pattern was shown in Fig. 1. The flat shape of XRD pattern after the main peak suggests that Zn-BTC has a crystallized structure with high purity.

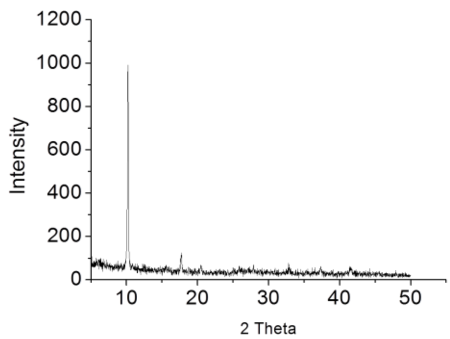

Fig. 1. Characterization pattern of the synthesized Zn-BTC by X-Ray Diffraction Analysis (XRD).

Fig. 2 illustrates the point of zero charge (pH_{pzc}) for Zn-BTC. 0.1 g Zn-BTC was added into 1M NaCl solution and the pH adjustment from 2 to 11 was done by addition of HCl and NaOH. Then the aqueous solution was shaken for 48 hour.

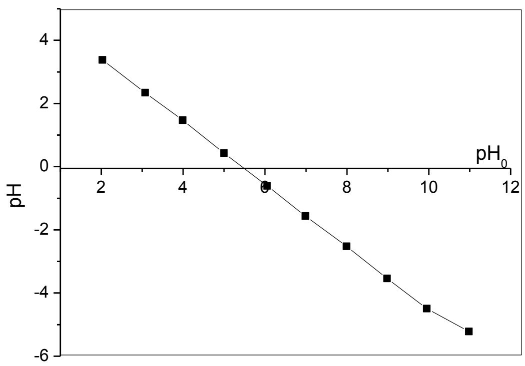

Fig. 2. Point of Zero Charge (pH_{pzc}) of Zn-BTC.

As shown in Fig. 2, pH_{pzc} of Zn-BTC is 5.4, which mean pH less than 5.4 resulting in negative charge at the surface of Zn-BTC. And when pH of Zn-BTC is more than 5.4, the surface of Zn-BTC is positive charged.

B. Heavy Metal Removal

Fig. 3 presents Pb(II) and Cu(II) removal efficiency of Zn-BTC as a function of time. The results indicate that adsorption of Pb(II) and Cu(II) by Zn-BTC reached equilibrium within 60 min contact time. Removal efficiencies at equilibrium were 90% and 70% for Pb(II) and Cu(II), respectively.

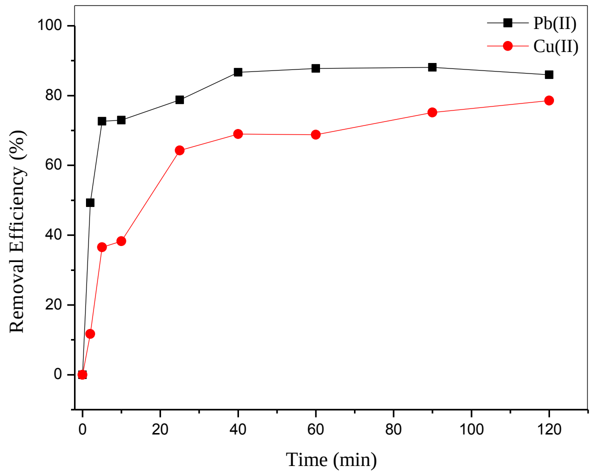

Fig. 3. Heavy metals removal by adsorption onto Zn-BTC (Zn-BTC= 0.5g/L (C_0 = 20 mg/L for both Pb(II) and Cu(II)).

C. Adsorption Kinetics

Table I presents pseudo-first order and pseudo-second order fitting with the experiment data. The greater R^2 value in the case of pseudo-second order suggests that the adsorption mechanism follow pseudo-second order in nature. The R^2 of fitting experimental data to the pseudo-second order were 0.999 for Pb(II) and 0.997 for Cu(II).

TABLE I: Kinetic of the Adsorption of Pb(II) and Cu(II) by Zn-BTC

	Pb(II)	Cu(II)
Pseudo-first order		
k_1 (1/min)	-0.025	-0.030
q_e (mg/g)	7.270	11.41
R^2	0.883	0.739
Pseudo-second order		
k_2	0.011	0.003
q_e (mg/g)	39.37	36.10
R^2	0.999	0.997

The kinetic for adsorption process, fitting of kinetic models, show in Table I. The kinetic of heavy metal by Zn-BTC were analyzed by used of kinetic models, which were pseudo-first order and pseudo-second order. The experiment data calculate value was by R^2. The good of fit was evaluated by R^2 value that obtained for kinetic models. The pseudo-second order better fitting than the pseudo-first order because it has the higher R^2. The linear Pb(II) and Cu (II) obtained was R^2= 0.999 and 0.997, respectively.

D. Adsorption Isotherm

Table II presents Langmuir, Freundlich, and

Dubinin-Radushkevitch isotherms fitting with the experiment adsorption data. Isotherm fitting was evaluated using R^2 value. Langmuir isotherm (R^2=0.985 for Pb(II) and 0.997 for Cu(II)) provides better fitting than Freundlich isotherm (R^2= 0.866 for Pb(II) and 0.877 for Cu(II)). Thus, suggests the monolayer adsorption of Pb(II) and Cu(II) by Zn-BTC. The maximum adsorption capacity of Pb(II) was 417 mg and Cu(II) was 85.5 mg per g of Zn-BTC.

TABLE II: ADSORPTION DATA TO ISOTHERM MODELS FOR THE REMOVAL OF HEAVY METAL BY ZN-BTC

	Pb(II)	Cu(II)
Langmuir		
R^2	0.985	0.997
q_{max} (mg/g)	417.0	85.5
K_L	0.021	0.104
Freundlich		
R^2	0.866	0.877
n	1.88	3.51
K_f (mg/g)	19.08	19.07
Dubinin-Radushkevich		
R^2	0.846	0.999
□	6.00×10^{-6}	4.00×10^{-6}
E (kJ/mol)	0.289	0.354

The values of the free energy (E) was calculated with Dubinin-Radushkevitch isotherm. Adsorption of Pb(II) and Cu(II) onto Zn-BTC resulted in E = 0.289 and 0.354 kJ/mol, respectively. These free energy values were less than 8 kJ/mol, suggests that the absorption was the physical in nature.

IV. CONCLUSIONS

In this study, Zn-BTC was successfully synthesized by hydrothermal method. Zn-BTC was able to remove Pb(II) and Cu(II) by adsorption mechanism and the removal efficiencies were 90% and 70%, respectively. The point of zero charge (pH_{pzc}) of Zn-BTC was 5.4. Adsorption mechanisms followed pseudo-second order (R^2= 0.999 for Pb and R^2= 0.997 for Cu(II)). The adsorption isotherm also fitted well with Langmuir model (R^2=0.985 for Pb(II) and 0.997 for Cu(II)). The maximum adsorption capacity of Pb(II) was 417 mg and Cu(II) was 85.5 mg per g of Zn-BTC. The free energy (E) suggests that the absorption was the physical in nature. In the future, would to increase efficiency and develop adsorbent for heavy metal removal.

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