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METAL-ORGANIC FRAMEWORKS (MOFs) DERIVED FROM CARBOXYLATE LIGAND AS POTENTIAL MATERIALS FOR REMEDIATION OF Cd(II) AND Pb(II) FROM AQUEOUS SOLUTION

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Abstract: The remediation of cadmium and lead ions from their respective aqueous solutions was carried out with the use of metal-organic frameworks (MOFs) developed from copper and zinc with benzene-1,4-dicarboxylic acid (BDC). The experimental adsorption process was done in batches to determine the equilibrium characteristics, thermodynamics and kinetics of the sorption processes. The result was then tested using Langmuir, Freundlich, and Temkin isotherm equations with Langmuir being the best fitted isotherm, while the kinetics isotherm used were pseudo first order and pseudo second order. The result obtained shows that the MOFs are great potential adsorbent for the studied metals.

Keywords: Metal-Organic Frameworks, Lead, Cadmium, Remediation, Benzene-1,4-dicarboxylic acid (BDC)

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INTRODUCTION

The contamination of both terrestrial systems and water bodies by toxic materials like heavy metals is a well known problem due to their hazardous and dangerous potentials when ingested into the system of human body (1-3). It is an indisputable fact that this pollution is largely due to the high level of urbanization and technological advancement (4, 5) and others may include population density, industrialization, and mechanization that makes available the necessities and needs of the increasing population (6-9). They are generally carried into food web leaches from dump sites, contaminated soil to plants and water bodies. The toxicity level of the metals increases as they are moving higher on the scale of the food chain by a process called bio-magnification. (10-12). Metal-organic frameworks (MOFs) are presently undergoing an exponential number of researches and applications, as they are a unique type of porous materials (13-15). These are metal ions, which form covalent bonds with ligands to give crystal-like solids (16, 17). The presence of the ligands allows the structures to have spaces in

between them giving rise to a large surface area (18-20).

MATERIAL AND METHOD

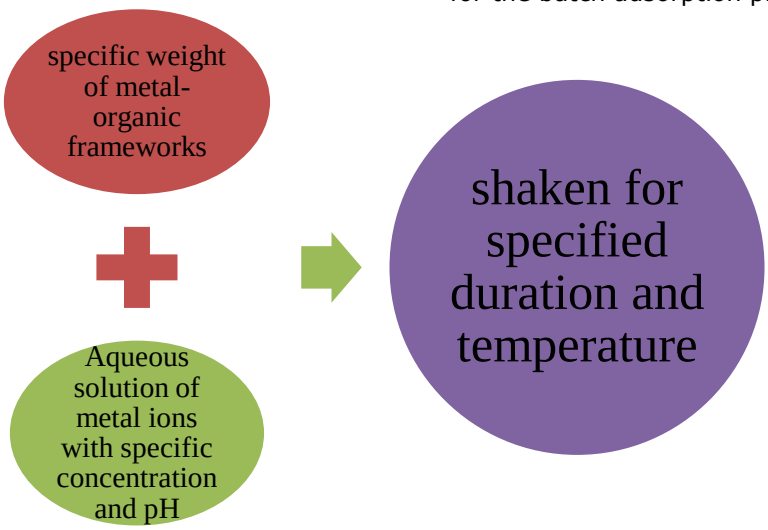
Synthesis of Metal Organic Frameworks

The copper- benzene 1, 4-dicarboxylic acid and zinc- benzene 1, 4-dicarboxylic acid metal-organic frameworks were synthesized using the method described by Tella *et al.* 2016 (21).

Experimental procedure

The MOFs were activated by heating at 120 °C for 20 mins; it was then introduced into the conical flask containing the heavy metal solution and into a shaker. The adsorptive power of the MOFs was evaluated under various condition such as pH, initial concentration of heavy metals, temperature, and adsorbent doses through various adsorption isotherm studies. The optimum removal condition for each metal was identified. The metal ions that were determined include cadmium and lead (22).

The scheme below shows the stepwise procedure for the batch adsorption process.



Scheme 1: The schematic representation of the adsorption process.

Effect of Contact Time

A weight of 0.025 g of the MOF was measured and added to 25 mL of the metal solution with a known initial concentration. The mixture was then placed into a shaker at a speed of 265 rpm for 10, 20, 40, 60, 80, 100, 150 minutes, respectively. The mixture was then filtered and the concentration of the metal ion in the filtrate was determined (23).

Effect of Adsorbent Dosage

Various weights ranging from 0.01, 0.03, 0.05, 0.07, 0.09 grams of the MOF was measured and added separately to 25 mL of a known concentration of the metal ion solution. The mixture was then placed into the shaker at a speed of 265 rpm for 60 minutes. The solution was then filtered and the concentration of the metal ion in the filtrate was determined (23).

Effect of Initial Concentration of Metal Ion

A weight of 0.025 g of the MOF was measured and added separately with 25 mL of the metal ion solution of varying concentration of the metal ion. The mixture was then placed into the shaker at a speed of 265 rpm for 60 min. The mixture was then filtered and the concentration of the metal ion was determined in the filtrate (22).

Effect of Temperature

A weight of 0.025 g of the MOF was weighed and introduced into a 25 mL solution of the metal ion. The mixture was then placed into a shaker at a speed of 265 rpm for 60 minutes at different temperature ranges of 20, 30, 40, 50, 60 °C. The mixture was then filtered and the concentration of the metal ion was determined in the filtrate (22).

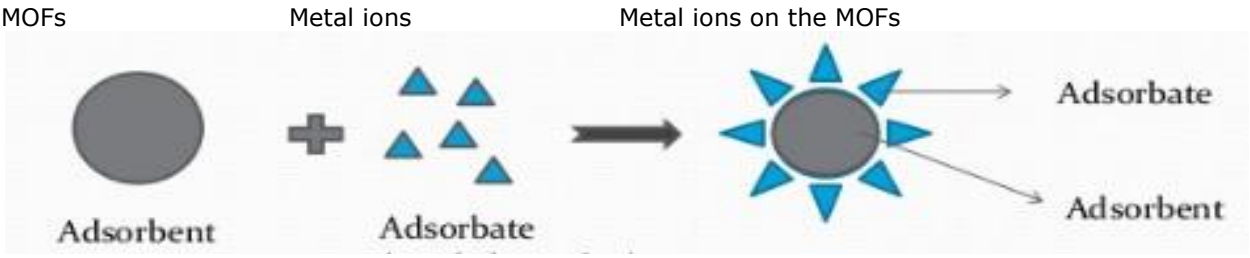
Effect of pH

A weight of 0.025 g of the MOF was weighed and added into 25 mL solution of the metal ion. The pH of the metal ion solution was varied using 0.01 M HCl and 0.01 M NaOH within the range of 3, 5, 7, 9, 11 and the mixture was then placed into the shaker at a speed of 265 rpm for 60 minutes. The mixture was then filtered and the concentration of the metal ion was determined in the filtrate (23).

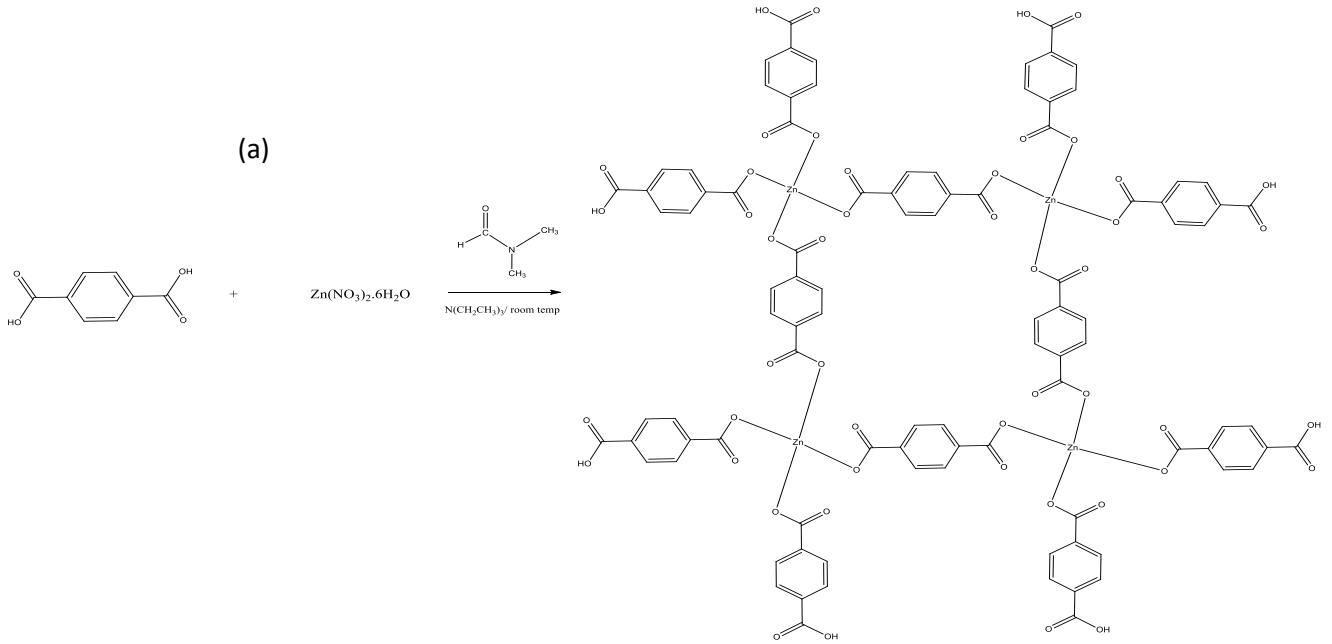
RESULT AND DISCUSSION

Mechanism of Adsorption

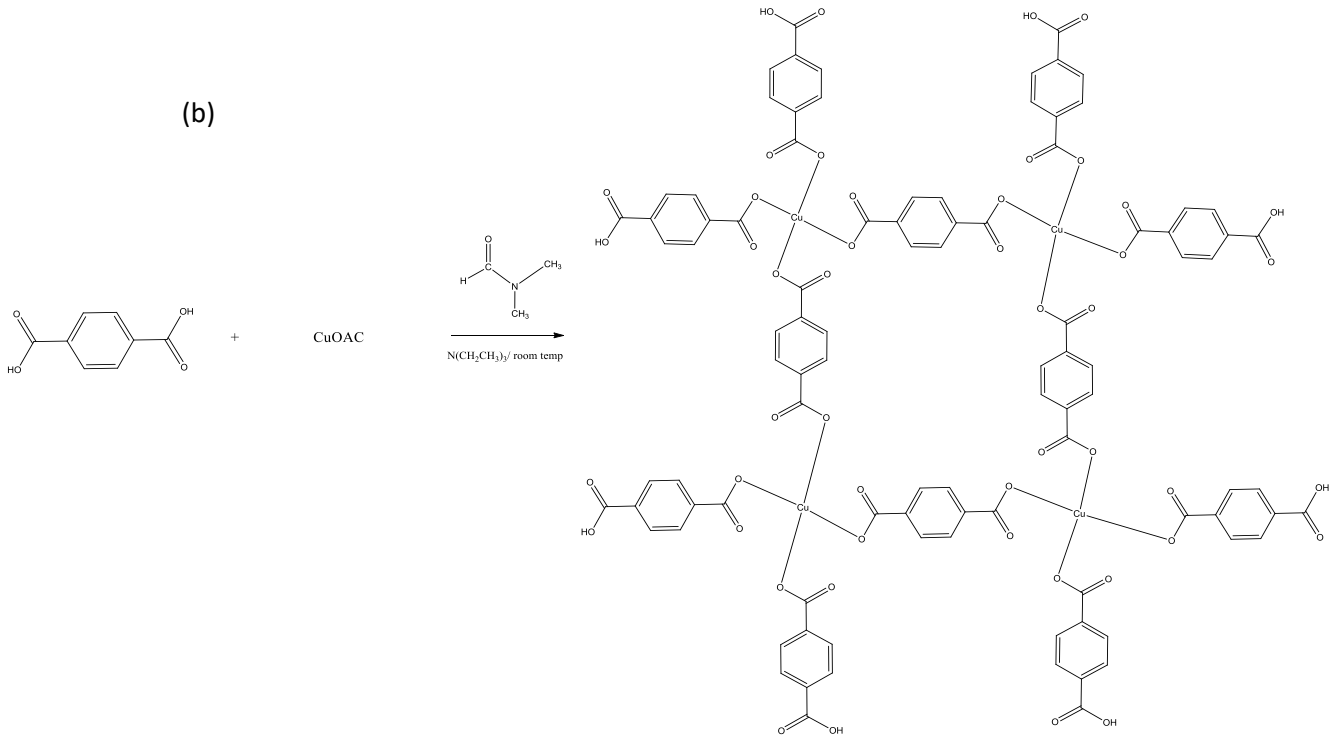
The mechanism of adsorption can be described as the relationship between the adsorbate and the adsorbent.



(a)



(b)



Scheme 2: Reaction scheme for the formation of (a) zinc and (b) copper metal organic frameworks.

Effect of Initial Metal Concentration

The adsorption performance of the Cu-BDC and Zn-BDC MOFs was determined as related to the concentration of the metal ions initially. These concentrations range from 40 ppm to 200 ppm for all the metals studied at a pH of 7, temperature of 30 °C, 0.025 g of adsorbent and 60 minutes of contact time. The adsorption of the metals increase with increase in the concentration of the metal was obtained initially then a gradual decrease in the adsorptivity of the metals with further increase in the concentration of the metals. Comparatively, the amount of metal adsorbed by the Cu-BDC MOFs is in the order Cd < Pb, while for the Zn-BDC MOFs its adsorptivity is in the order Cd < Pb. Comparing the two MOFs the adsorptive strength is in the order Cd-ZnBDC < Cd-CuBDC < Pb-ZnBDC < Pb-CuBDC.

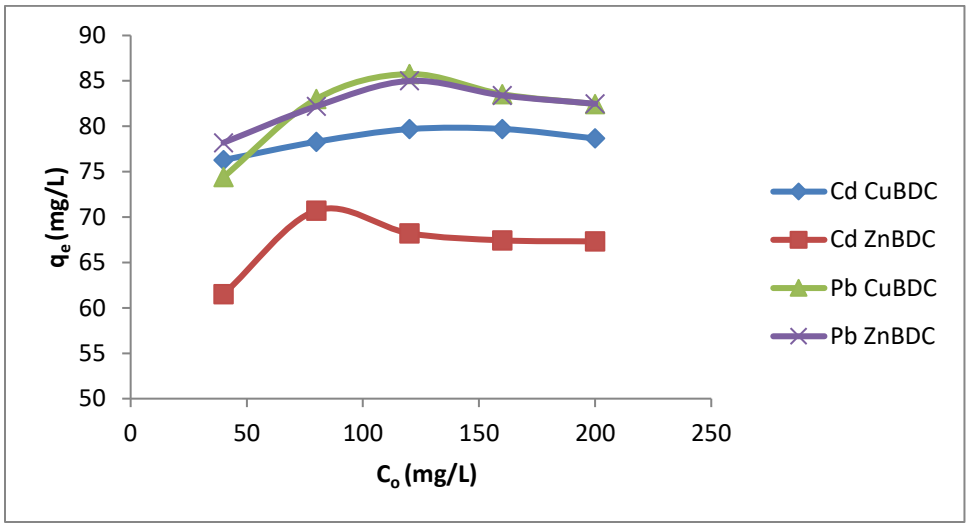


Figure 1: Effect of initial metal concentration for Cu and Pb metal with CuBDC and ZnBDC MOFs.

As shown in Figure 1 above, the quantity of cadmium and lead metal ions adsorbed by both CuBDC and ZnBDC increased with increase in concentration but a gradual reduction in the quantity of metal ions removed was noted with further increase in the concentration of the metal. The optimum quantity of cadmium metal adsorbed was 157.316 mg/g and 134.643 mg/g likewise 79.7% and 70.7% for the CuBDC and ZnBDC MOFs respectively while the optimum quantity of lead metal ion adsorbed was 164.906 mg/g and 164.960 mg/g likewise 85.7% and 84.9% for the CuBDC and ZnBDC MOFs respectively. A similar result was observed by Shooto *et al*. (24).

Effect of Adsorbent Dose

The result of the effect of adsorbent dosage on the removal of Cd and Pb metal ions from aqueous solution. The results show the relationship between the quantity of the adsorbent and the amount of metal adsorbed.

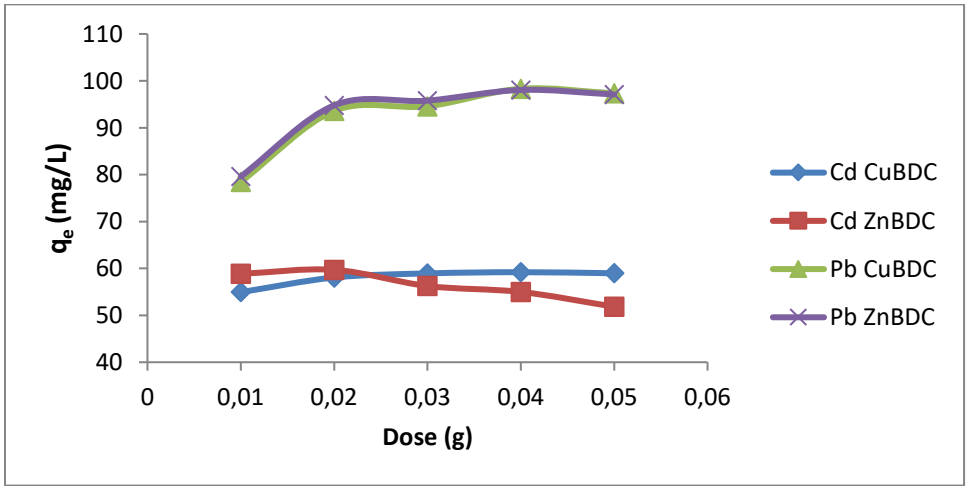


Figure 2: Effect of adsorbent dose for Cd and Pb metal ions with CuBDC and ZnBDC MOFs.

The Figure 2 above shows the behavior of the dose of the adsorbent on the quantity of the cadmium and lead metal adsorbed by the Cu-BDC and Zn-BDC. The Cu-BDC performed the best with 0.04 g of the adsorbent while the Zn-BDC was 0.02 g of the MOFs for cadmium metal, while the Cu-BDC performed the best with 0.04 g of the adsorbent while the Zn-BDC was 0.04 g of the MOFs for the lead metal ions.

Effect of Contact Time

The significance of contact duration arises from the fact that there is need for the identification of the rapidness at which the metal ions bind to and removed from the surface of the MOFs. Thus the optimal time for the adsorptive procedure of the heavy metals were obtained.

The effect of contact time for Cd and Pb ions was studied at pH 7, temperature of 30 °C, 0.025 g of the adsorbent and a concentration of 100 ppm. The contact time was varied in the range 10, 20, 40, 60, 80, 100, 120 and 150 minutes.

An initial increment in the amount of the ions adsorbed was noticed with increase in time until equilibrium was reached, a decrease was then obtained with further increase of the contact time. The Figure 3 below shows the effect of the contact time on each of the metals and the MOFs.

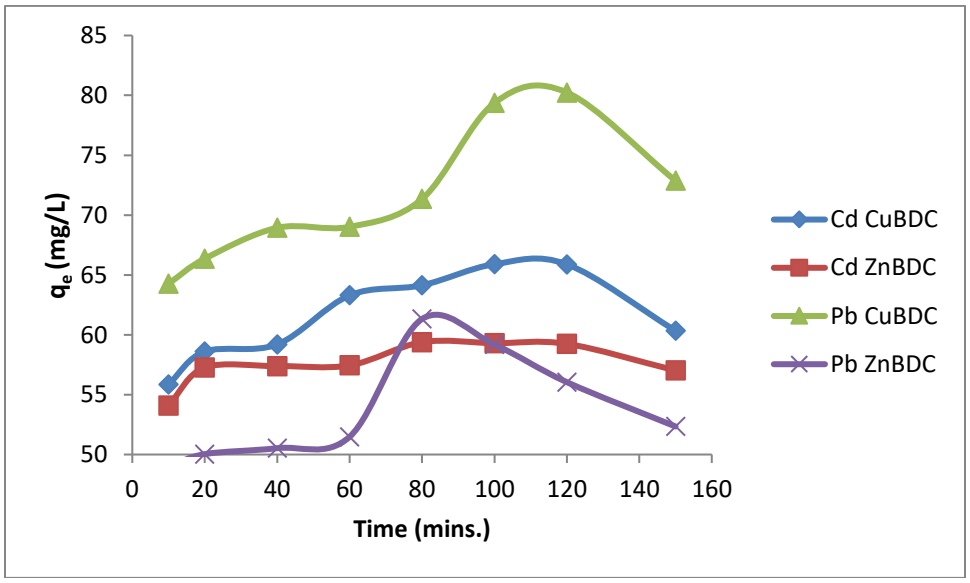


Figure 3: Effect of contact time for Cd and Pb metal ions with CuBDC and ZnBDC MOFs.

The Figure 3 above shows that the optimum contact time was obtained for cadmium and lead metal ions by the MOFs, the optimum time obtained for cadmium ion with the CuBDC is 100 minutes while that of the ZnBDC was found to be 80 minutes as well, on the other hand the optimum contact time obtained for lead ion by the MOFs, the optimum time obtained for the CuBDC is 120 minutes while that of the ZnBDC was found to be 80 minutes. Abbas *et al.* (23) reported a similar result.

Effect of Temperature

The exothermic or endothermic nature of the process was determined, the adsorption capabilities of the MOFs was studied over a range of temperature. The temperature range considered for this study is 20, 30, 40, 50 and 60 °C respectively at a pH of 7, 0.025 g of adsorbent, 100 ppm metal ion concentration and 60 minutes of contact time. A steady increase was observed until an optimum amount was obtained and further increase in the temperature leads to a decrease metal ions adsorbed. This can be attributed to the weakening effect that high temperature may have on the attractive forces between the adsorbent and adsorbate. At high temperature, there is an increased tendency of the metal ion escaping from the surface of the adsorbent to the solution due to the increase in kinetic energy that is supplied by the rise in temperature.

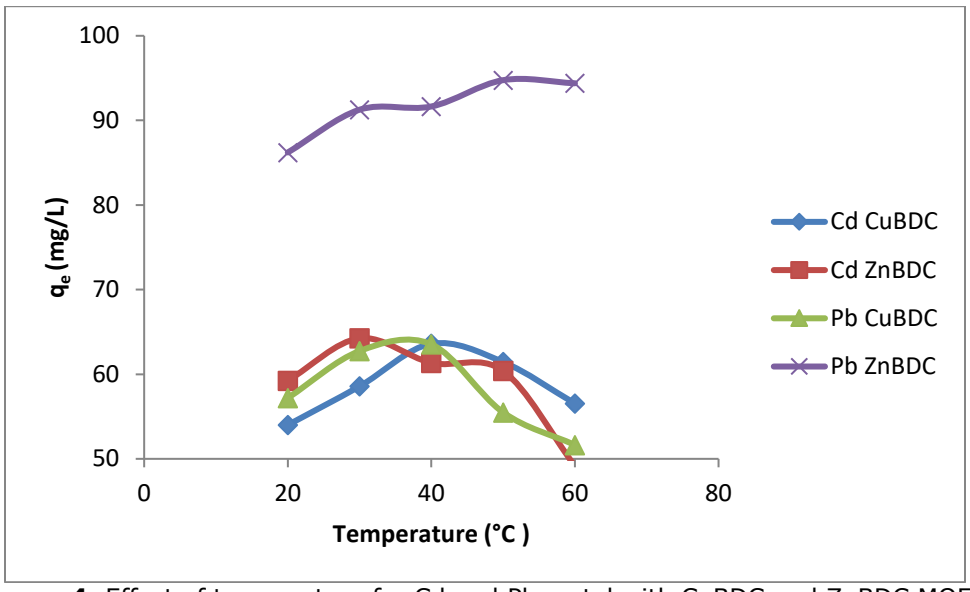


Figure 4: Effect of temperature for Cd and Pb metal with CuBDC and ZnBDC MOFs.

The Figure 4 above shows the optimum adsorption temperature obtained for cadmium and lead metal ions by the MOFs, the optimum temperature obtained for cadmium metal ion with the CuBDC is 40 °C while that of the ZnBDC was found to be 30 °C. The optimum temperature obtained for lead metal ion with the CuBDC is 40 °C while that of the ZnBDC was found to be 50 °C. Barka *et al*. (25) reported a similar result.

Effect of pH

pH is one of the major factors influencing the adsorptive capabilities of metal ions. The adsorption characteristics of the Cd and Pb ions were studied at various pH values ranging from 3, 5, 7, 9 and 11 at a temperature of 30° C, 0.025 g of adsorbent, 100 ppm of metal ion concentration, and 60 minutes of contact time. The result shows that the optimum pH for adsorption of Cd and Pb ions by the CuBDC MOFs is pH 9 while for the ZnBDC MOFs the values obtained shows that the optimum adsorption for Cd is pH of 5 and Pb is pH of 9.

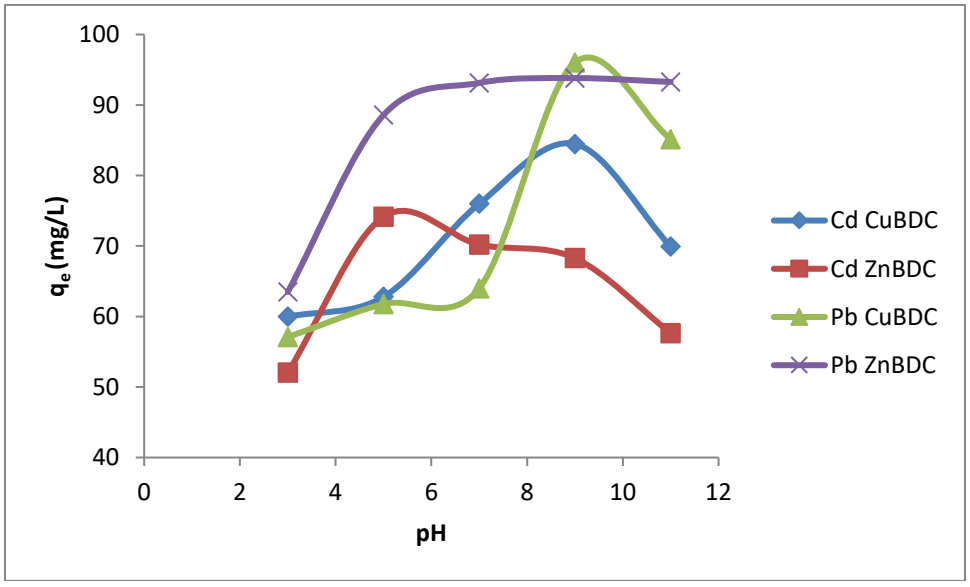


Figure 5: Effect of pH for Cd and Pb metal ions with CuBDC and ZnBDC MOFs.

The Figure 5 above shows the optimum pH obtained for copper and lead metal by the MOFs, the optimum pH values obtained for cadmium metal with the CuBDC is pH 9 while that of the ZnBDC was found to be pH 5, the optimum pH values obtained for lead metal by the MOFs, the optimum pH

obtained for the CuBDC is pH 9 while that of the ZnBDC was found to be pH 9 as well. Ajmal *et al.* (26) reported a similar result.

Adsorption Isotherm

Adsorption isotherm is an important description on how solutes interact with adsorbents. A number of models have been developed over the years for evaluating the equilibrium for adsorption of substances from their solution. The adsorption data obtained from this work were tested with Langmuir, Freundlich, and Temkin adsorption isotherms.

Langmuir Adsorption Isotherm

The data obtained from the adsorption process for cadmium and lead ions with Cu-BDC and Zn-BDC MOFs over the concentration range of 40 – 200 ppm at 30° C has been correlated with the Langmuir isotherm. A graph of Ce/qe versus Ce was plotted and a linear plot was obtained. The data obtained and parameters tested are reported in the Table 1 below.

Table 1: The Langmuir isotherm parameters and the value obtained for each metal and MOFs.

Parameter / Metal-MOFs	Cadmium Cu-BDC	Cadmium Zn-BDC	Lead Cu-BDC	Lead Zn-BDC
R^2	0.9996	0.9979	0.9961	0.9988
q_{max}	79.365	68.027	84.75	84.03
K_L	4.200	2.774	1.84	4.10
R_L	0.0059	0.0089	0.013	0.0061

Where: R^2 is the correlation coefficient, q_{max} is the maximum amount of adsorbate adsorbed per unit mass of adsorbent, K_L is Langmuir isotherm constant, R_L is the separation factor.

The regression coefficient values (R^2) show the applicability of the isotherm to the adsorption process. The values obtained shows that the Langmuir isotherm is suitable for the adsorbents studied. A similar result was obtained by Demirbas *et al.* (27).

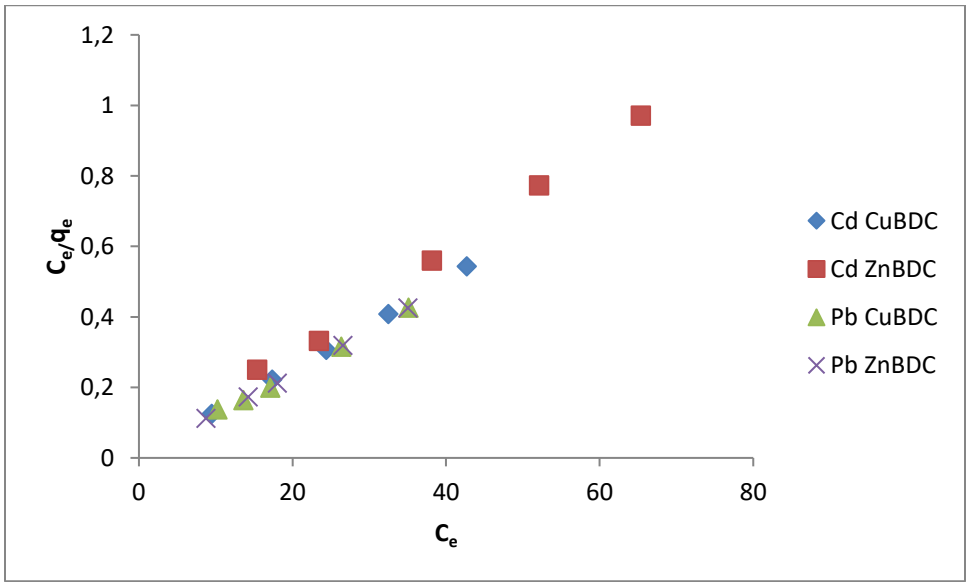


Figure 6: Langmuir adsorption isotherm plot for cadmium and lead metal ions with CuBDC and ZnBDC MOFs.

Freundlich Adsorption Isotherm

The data obtained from the adsorption process for cadmium and lead ions with Cu-BDC and Zn-BDC MOFs over the concentration range of 40 – 200 ppm at 30 °C has been correlated with the Freundlich isotherm. A graph of log qe versus log Ce was plotted and a linear plot was obtained. The data obtained and parameters tested are reported in the Table 2 below.

Table 2: The Freundlich isotherm parameters and the value obtained for each metal and MOFs.

Parameter/ Metal-MOFs	Cadmium Cu-BDC	Cadmium Zn-BDC	Lead Cu-BDC	Lead Zn-BDC
R^2	0.9941	0.9578	0.8824	0.9607
K_F	2.595	1.395	17.58	25.08
n	0.9003	0.903	0.779	0.837

Where: R^2 is the correlation coefficient, K_F is the Freundlich isotherm constant, n is the adsorption intensity. The regression coefficient values (R^2) show the applicability of the isotherm to the adsorption process. The values obtained shows that the Freundlich isotherm is suitable for the adsorption process studied.

Temkin Adsorption Isotherm

The data obtained from the adsorption process for cadmium and lead ions with Cu-BDC and Zn-BDC MOFs over the concentration range of 40 – 200 ppm at 30 ˚C have been correlated with the Temkin isotherm. A graph of qe versus ln Ce was plotted and a linear plot was obtained. The data obtained and parameters tested are reported in the Table 3 below.

Table 3: Temkin isotherm parameters and the value obtained for each metal and MOFs.

Parameters/ Metal-MOFs	Cadmium Cu-BDC	Cadmium Zn-BDC	Lead Cu-BDC	Lead Zn-BDC
R^2	0.9716	0.9839	0.9821	0.9886
B_T	85.021	72.311	76.612	71.303
K_T	0.136	0.0897	0.112	0.097

Where: R^2 is the correlation coefficient, B_T is the Temkin isotherm constant, K_T is the Temkin isotherm equilibrium. The regression coefficient values (R^2) show the applicability of the isotherm to the adsorption process. The values obtained show that the Temkin isotherm is suitable for the adsorption process studied.

The correlation of the adsorption data (R^2 values) obtained from the adsorption process of cadmium and lead by Cu-BDC and Zn-BDC MOFs with the Langmuir, Freundlich and Temkin adsorption isotherms is shown in the Table 4 below.

Table 4: Comparism of the R^2 values obtained for the adsorption process.

Isotherms/ Metal-MOFs	Cadmium Cu-BDC	Cadmium Zn-BDC	Lead Cu-BDC	Lead Zn-BDC
Langmuir	0.9996	0.9979	0.9961	0.9988
Freundlich	0.9941	0.9578	0.8824	0.9607
Temkin	0.9716	0.9839	0.9821	0.9886

From the Table 4 above, the adsorption data obtained from this study fitted best into the Langmuir adsorption isotherm suggesting that the adsorption process is more of monolayer sorption than heterogeneous energy distribution.

Adsorption Kinetic Models

To understand the adsorption kinetics, the adsorption process was performed at various durations of time and the amount of cadmium and lead ions adsorbed by the Cu-BDC and Zn-BDC MOFs respectively. The data obtained was subjected to the pseudo first order and pseudo second order kinetic models.

Pseudo First Order Kinetic Model

The adsorption data were tested with the pseudo first order kinetic model which is represented by the equation: $\log[qe-qt] = \log[qe] - [k_1/2.303]t$. A plot log (qe-qt) against time was done and the values of the first order kinetic constant (k_1) was determined by

$$K_1 = -\text{slope}/2.303.$$

Table 5: The pseudo first order kinetic model parameters and the value obtained for each metal and MOFs.

Parameter/ Metal-MOFs	Cadmium Cu-BDC	Cadmium Zn-BDC	Lead Cu-BDC	Lead Zn-BDC
R^2	0.2751	0.2860	0.4579	0.1430
q_e (exp)	65.898	59.386	80.238	61.321
$q_{e\ (cal)}$	10.141	3.236	17.758	9.894
K_1	0.00439	0.00295	0.00243	0.00134

Where: R^2 is the correlation coefficient, q_e(exp) is the experimentally measured adsorbate concentration at equilibrium, q_e(cal) is the calculated adsorbate concentration at equilibrium, K_1 is the rate constant of pseudo first order adsorption. The regression coefficient values (R^2) show that applicability of the kinetic model to the adsorption process. The values obtained shows that

the pseudo first order kinetic model is not suitable for the adsorption process studied.

Pseudo Second Order Kinetic Model

The adsorption data were tested with the pseudo second order kinetic model which is represented by the equation: $t/qt = 1/k_2q_e^2 + [1/qe]t$. A plot t/qt against time was carried out and the values of the second order kinetic constant (k_1) was determined by

$$K_2 = 1/q_e^2 * \text{intercept}$$

Table 6: The pseudo second order kinetic model parameters and the value obtained for each metal and MOFs.

Parameter/ Metal-MOFs	Cadmium Cu-BDC	Cadmium Zn-BDC	Lead Cu-BDC	Lead Zn-BDC
R^2	0.9939	0.9987	0.9921	0.9873
q_e (exp)	65.898	59.386	80.238	61.321
$q_{e\ (cal)}$	63.291	58.140	77.519	55.249
K_2	0.0294	0.269	0.00358	0.0287

Where: R^2 is the correlation coefficient, q_e(exp) is the experimentally measured adsorbate concentration at equilibrium, q_e(cal) is the calculated adsorbate concentration at equilibrium, K_2 is the rate constant of pseudo second order adsorption. The regression coefficient values (R^2) show that applicability of the kinetic model to the adsorption process. The values obtained shows that the pseudo second order kinetic model is suitable for the adsorption process studied.

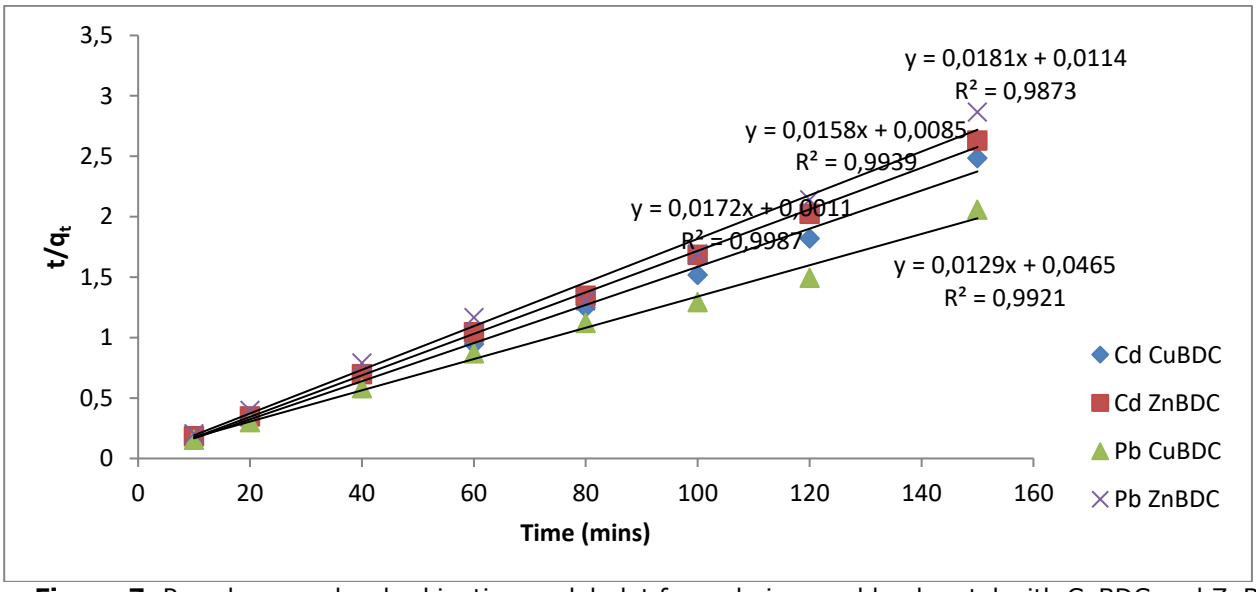


Figure 7: Pseudo second order kinetics model plot for cadmium and lead metal with CuBDC and ZnBDC MOFs.

The linearity of the second order kinetics is better when compared with the first order judging by the R^2 values. The R^2 of the plots of this study as shown on Table 6 above proves that the pseudo second order kinetics model is more effective in representing the kinetics data obtained from the study. This suggests that the kinetics of the adsorption of cadmium and lead onto CuBDC and ZnBDC MOFs can be described using pseudo second order kinetics model and hence suggests that the adsorption process is more of physical process. The pseudo second order also gave a better correlation of the calculated values of the adsorption capacities qe (cal) with those obtained from the experimental process. A similar result was reported by Okoli and Ezuma 2014 (28) and Ezekiel and Abdullahi (29).

Re-Usability Test

Table 7: Re-usability capacity of the MOFs for each metal ion studied.

Parameter/ Metal-MOFs	Cadmium Cu-BDC (%)	Cadmium Zn-BDC (%)	Lead Cu-BDC (%)	Lead Zn-BDC (%)
1	60.242	59.995	58.865	49.341
2	60.152	59.665	58.463	49.443
3	59.987	58.352	57.382	48.388
4	59.675	56.364	57.887	49.182
5	58.142	55.876	57.284	48.382

The table above shows the result of the re-usability test of the MOFs. This suggests that the MOFs have excellent recovery and re-usability capacity. A similar result was reported by Wu *et al.,* 2012 (30).

CONCLUSION

Two known MOFs were successfully synthesized by means of solvent based reflux procedure. They were prepared from Cu(II), Zn(II) and benzene-1,4-dicarboxylic acid. The adsorptive capabilities of the MOFs were carried out by using them for the adsorption of Cd and Pb metal ions from their respective solutions. The MOFs performed well when compared with others in the literature. The various adsorption physicochemical parameters were used to determine the optimal condition for the use of these MOFs in the removal of the metals in their solutions. The data were investigated by the Langmuir, Freundlich and Temkin adsorption isotherm which they fitted into well with regards to the correlation values (R^2) obtained, with the best being the Langmuir isotherm in comparison with others. The adsorption kinetics follows the pseudo second order kinetics model with reference to the correlation data obtained. The MOFs show a great strength in the recovery and re-usability study. Conclusively, the synthesized MOFs have proven to be potentially great heavy metal adsorbents from their aqueous solutions.

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