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Bulletin of Chemical Reaction Engineering & Catalysis, 17 (3) 2022, 520-532

Research Article

High Selectivity and Stability Structure of Layered Double Hydroxide-Biochar for Removal Cd(II)

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Received: 22nd May 2022; Revised: 5th July 2022; Accepted: 6th July 2022
Available online: 7th July 2022; Published regularly: September 2022

Abstract

Composite M^{2+}/Al-BC (Ca/Al-BC, Cu/Al-BC, and Ni/Al-BC) have been successfully synthesized. Composite and pristine materials were used as adsorbents of cadmium(II) [Cd(II)] in an aqueous solution. Firstly the performance of composite and pristine materials was evaluated by reusability properties until five cycles adsorption process followed with a determination of isotherms and adsorption thermodynamic properties. The results show composite has ten-fold surface area properties than starting materials. The adsorption capacities of CaAl-BC, CuAl-BC, and NiAl-BC at a temperature of 333 K were 156.250 mg/g, 149.254 mg/g, and 208.333 mg/g, respectively.

Keywords: Layered Double Hydroxide; Biochar; Cadmium(II); Stability Structure; Adsorption

How to Cite: N.R. Palapa, P.M.S.B.N. Siregar, A. Wijaya, T. Taher, A. Lesbani (2022). High Selectivity and Stability Structure of Layered Double Hydroxide-Biochar for Removal Cd(II). *Bulletin of Chemical Reaction Engineering & Catalysis*, 17(3), 520-532 (doi: 10.9767/bcrec.17.3.14288.520-532)

Permalink/DOI: https://doi.org/10.9767/bcrec.17.3.14288.520-532

1. Introduction

The development of materials for various applications such as adsorption and catalysis have been conducted until this decade to solve environmental problems such as pollution and energy resources [1]. In the field of environmental area, the development of materials is especially to solve and use the materials as adsorbents for pollutants, such as heavy metals in the aquatic system and wastewater [2]. Heavy metals, such as cadmium, cause bioaccumulation in the food chain thus, the concentration of cadmium in the human body is higher than in fish and other animals [3]. Treatment to decrease and remove heavy metal ions in an aqueous solution is an excellent challenge for environmentalists, chemists, and other researchers. Various organic materials, such as algae, lignin, chitosan, chitin, cellulose, and inorganic materials, such as activated carbon, bentonite, layered double hydroxide, clay, montmorillonite, zeolite, have been used as adsorbents [4–10].

Layered double hydroxide (LDH) has the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}].nH_2O$, M is the divalent and trivalent metal, A^{n-} is the anion present in the interlayer with valence *n* [11]. Divalent and trivalent ions can be selected from

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various elements on the periodic table ranging from the main group to the transition group. The anions in the interlayer space can be exchanged depending on the LDH application [12−15]. In addition, LDH can be modified by impregnation and intercalation using supporting materials [13−15]. Adsorption process of Ag^+ ions at pH 5.9 using MoS_4-LDH has adsorption capacity of 8.2 mg/g [16]. Bin Ou *et al.* [17] confirmed that Cr(VI) can be removed using CoFe LDH with adsorption capacity of 33.5 mg/g. Pb(II), Cd(II), and Cu(II) can be removed using Mg/Al LDH with adsorption capacities of 6.128 mg/g, 5.255 mg/g, and 4.944 mg/g, respectively [18]. The adsorption process of Ar(II) and Hg(II) using MgFe LDH obtained an adsorption capacity of 56 mg/g and 24.8 mg/g [19].

The modification of LDH by intercalation using high anions, such as polyoxometalate or organic anions, has been conducted by many researchers. Carriaazo *et al.* [20] reported MgAl LDH was intercalated using $[H_2W_{12}O_{40}]^{6-}$ to form pillared compounds with polyoxometalate. ZnCr/$[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ in the process of removing metal ions from water had a higher adsorption capacity than ZnCr LDH, namely 76.9 mg/g and 45.4 mg/g [21]. CaAl LDH and CaAl LDH which are intercalated by the keggin ion $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ can be used as adsorbents such as the research conducted by Taher *et al.* [22]. Cd(II) and Fe(II) metals can be removed using the adsorption method with adsorption capacity of 11.93 mg/g for Fe(II) and 12.578 mg/g for Cd(II) when using Keggin ion intercalated CaAl adsorbent $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$. The adsorption capacity of Cd(II) was 1.78 mg/g and Fe(II) was 1.125 mg/g when using CaAl LDH as adsorbent. LDH/Hydroxyapatite was applied to remove U(VI) from aqueous solution with adsorption capacity reaching 845.16 mg/g at pH 6.0 and 298 K [23]. The other research was conducted NiCr LDH intercalated by diphenylamine-4-sulfonate (DS) and applied as an adsorbent of Pb(II). The results of adsorption capacity were obtained at 309 mg/g for NiCr-DS LDH, which is higher than NiCr LDH pristine (42 mg/g) at 293 K [24].

LDH is a material that is easily exfoliated, so it needs to be modified. In this study, BC was used as a support material in the modification process because the carbon content in BC can make the material more stable in the adsorption process and have a larger surface area than the base material. Ni/Al modified using H_3PO_4 (PAB) can be used as an adsorbent in the Cr(VI) removal process with an adsorption capacity of 275.1 mg/g [25]. Mg/Al-biochar was used in the Cr(VI) removal process with an adsorption capacity of 38 mg/g [26]. Li *et al.* [27] reported that invasive plant-derived biochar (IPB) has successfully loaded to CaAl LDH and was applied as an adsorbent of Eu(II).

The adsorption capacity of composites CaAl/IPB reached 120.482 mg/g at 338 K. Thus, the composite process can enhance the adsorption capacity for dye molecules, such as malachite green. A similar report was published by Palapa *et al.* [28]. CuAl/BC had a greater adsorption capacity than Cu/Al LDH in the malachite green removal process, namely 470.96 mg/g and and a potential candidate as a low-cost adsorbent with reusability properties. Research conducted by Li *et al.* [29] shows that metal Cd(II) can be removed using MgAl-rice husk biochar composite with adsorption capacity of 125.34 mg/g. Cd(II) metal could be removed using Mg/Fe-Kiwi branch biochar with adsorption capacity of 25.6 mg/g [30].

Based on these explanations thus, in this research, LDH was impregnated with biochar (BC). BC was obtained from local rice straw to form the composite. Ca/Al, Cu/Al, and Ni/Al were used in this research based on various M^{2+} ranging main to transition groups, while M^{3+} was aluminum. The formation of the composite was characterized by XRD, FTIR, BET surface area, and thermal analyses. Composites were applied as adsorbents of cadmium(II) [Cd(II)]. The reusability of adsorbents investigated the structural stability toward Cd(II) adsorption until five cycles adsorption process. The adsorption was studied by concentration and adsorption thermodynamic parameter.

2. Materials and Methods

2.1 Materials

Materials were used $Cu(NO_3)_2.3H_2O$ (EMSURE®, ≥98%), $Ca(NO_3)_2.4H_2O$ (EMSURE®, ≥98%), $Ni(NO_3)_2.6H_2O$ (EMSURE®, ≥98%), $Al(NO_3)_3.9H_2O$ (EMSURE®, ≥98%), NaOH (EMSURE®), $CdCl_2$ (Merck). Water was obtained by purification using Purite®.

2.2 Methods

2.2.1 Synthesis of M^{2+} (Cu, Ca, and Ni)/Al

In this work, M^{2+} (Cu, Ca, and Ni)/Al was synthesized by the coprecipitation method as previously reported by Palapa *et al.* [15]. M^{2+} (Cu, Ca, and Ni) 0.75 M as much as 100 mL was added with 100 mL of Al. The mixture was added with 2 M NaOH to pH 10 and stirred for 17 h at 80 °C. After the stirring process, the precipitate is filtered and dried at 100 °C.

2.2.2 Impregnation of LDH with BC

Preparation of composite M^{2+}/Al-BC (M^{2+} = Cu, Ca, Ni) was conducted as previously reported [30,31]. The composite was prepared by mixing a divalent solution (0.75 M, 10 mL) with aluminum nitrate (0.25 M, 10 mL) and stirred for 2 h. The mixture was added with BC (2 g), adjusted the pH to 10 using NaOH, the mixture was stirred (72 h at 80 °C). The M^{2+}/Al-BC were washed and dried at 110 °C.

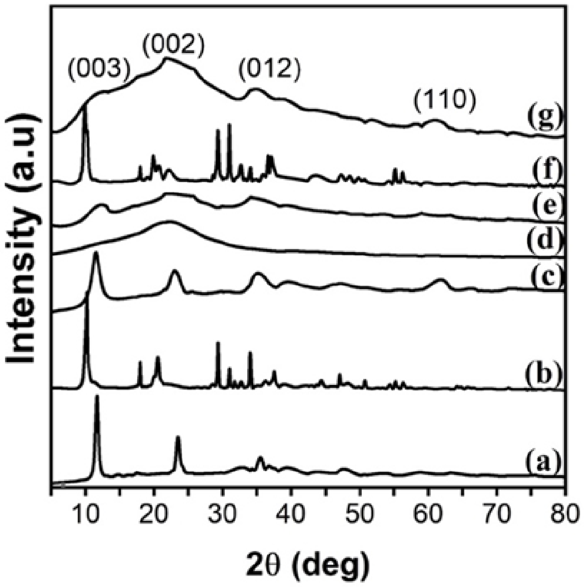

Figure 1. XRD of (a) Cu/Al, (b) Ca/Al, (c) Ni/Al, (d) BC, (e) Cu/Al-BC, (f) Ca/Al-BC, and (g) Ni/Al-BC.

2.2.3 Regeneration of Adsorbent

Adsorbents of composite and LDHs were reused for the readsorption process. The ultrasonic system desorbed Cd(II) on adsorbent at 40 °C for 30 min. The adsorbent was dried then used for Cd(II) adsorption. Readsorption using reuse adsorbent was performed five times during the adsorption process.

2.2.4 The Effect of Variations in Concentration and Temperature

The effect of concentration and adsorption thermodynamics was studied by varying the initial concentration (1; 1.5; 2; 2.5; 3 mg/L) and temperature. Cd(II) was added as much as 0.02 g of adsorbent and stirred for 2 h using various temperatures (30, 40, 50, and 60 °C).

3. Results and Discussion

Figure 1 shows the XRD of LDHs, BC, and LDH-BC composite with a similar synthetic condition composed of M^{2+}/Al (M^{2+} = Cu, Ca, Ni). Figure 1 showed that LDH has similar diffraction patterns at 9–11° (003), 22–24° (006), 35° (012), and 58–61° (110), which indicated the formation of layer structure [31,32]. Ca/Al LDH has a slightly different pattern at 29°. The diffraction at 29° showed the formation of M−O on the layer. The diffraction of BC has a broad pattern, and only one diffraction peak was detected at 22° (002). These diffractions were assigned as carbon diffraction [33]. BC is an organic compound and has carbon as the main content. A composite of LDH-BC was presented in Figure 1. A largely different diffractions were found in the composite of

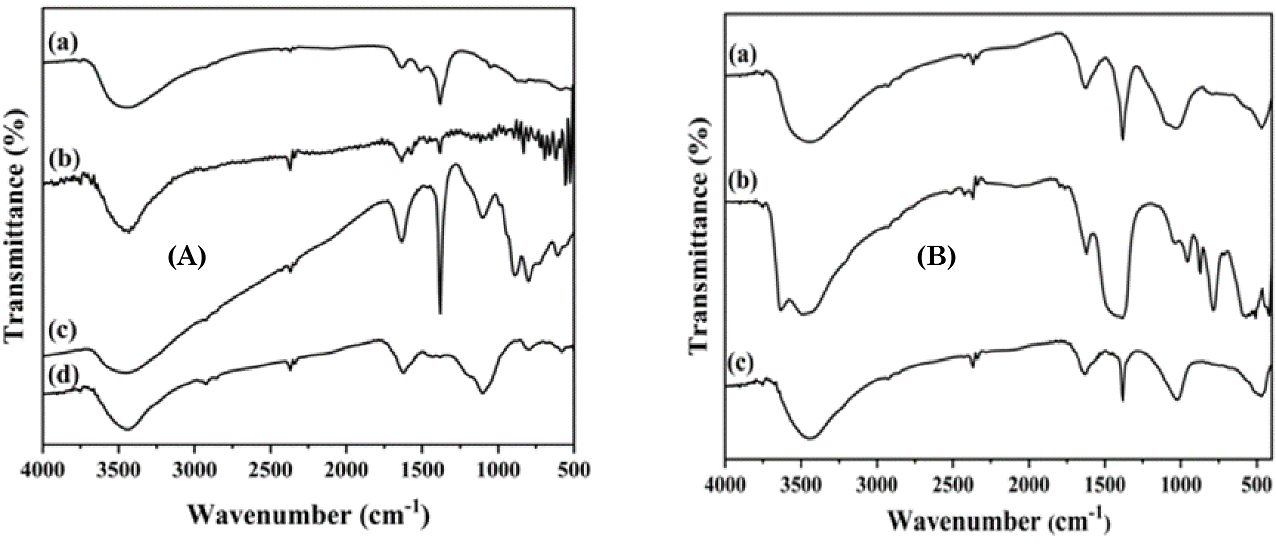

Figure 2. FTIR spectrum of (A) = (a) Cu/Al, (b) Ca/Al, (c) Ni/Al, (d) BC; (B) = (a) Cu/Al-BC, (b) Ca/Al-BC, (c) Ni/Al-BC).

LDH-BC, which was different from the diffraction of LDH. The diffraction peaks for Ca/Al-BC were 10.92° (003), 21.21° (002), 23.94° (006), 36.09° (012), 56.32° (110), 58.93° (116). The diffraction peaks of Cu/Al-BC and Ni/Al-BC also have similar Miller indices with Ca/Al-BC at (003), (002), (006), (012), (110), and (116). All these diffraction peaks show the diffractions of LDH and BC, thus, composites based on LDH-BC were facile formed. On the other hand, the crystallinity of Cu/Al-BC and Ni/Al-BC was lower than Ca/Al-BC. The decrease in the crystallinity of Cu/Al-BC and Ni/Al-BC is probably due to BC content to LDH. The crystallinity of Ca/Al-BC is high, probably due to the main element of M^{2+}, while Ni^{2+} and Cu^{2+} are transition elements. The size of Ca^{2+} is also larger than Ni^{2+} or Cu^{2+} [34,35], which also probably creates the crystallization stability of Ca/Al-BC.

FTIR spectrum of LDH, BC, and composite was presented in Figure 2. Ca/Al, Cu/Al, and Ni/Al LDHs have main vibration peaks at 3400 cm^{-1} (υ O−H stretching), 1630 cm^{-1} (υ O−H bending), and 1381 cm^{-1} (υ N−O nitrate) [36]. Divalent M^{2+} and trivalent M^{3+} have vibrations in the range of 700-400 cm^{-1} depending on M^{2+} ions, as shown in Figure 2(A). Composite Ca/Al-BC, Cu/Al-BC, and Ni/Al-BC have similar vibrations with LDH, while broad vibration at 1380 cm^{-1} was found, especially on Ca/Al-BC. These vibrations occurred due to the insertion of BC on the interlayer space of LDH, and some nitrate ions were exchanged for BC. Although the size of BC is larger than nitrate ion, these possibilities can be found because some functional groups on BC have interacted with positive charges of LDH.

Vibrations of divalent and trivalent ions on composites were similar to pristine LDH in the range of 400–700 cm^{-1}. The diffraction of organic moiety on composite was found at around 2800 cm^{-1}, which was assigned as C−H vibration. The N$_2$ isotherms adsorption-desorption on LDHs and composites are shown in Figure 3.

The data in Table 1 showed that the surface area of Ca/Al-BC has ten-fold higher than pristine LDH. These increasing surface area properties are the highest for Cu/Al-BC and Ni/Al-BC, which are four-fold and seven-fold higher than original LDHs. On the other side, Ni/Al-BC was the highest surface area properties of other composites, up to 438 m^2/g. BC has a key role in this research's increased surface area properties of LDHs materials. This BC involvement causes decreasing the pore volume and pore diameter. BC has covered surface materials and thus can decrease volume and diameter

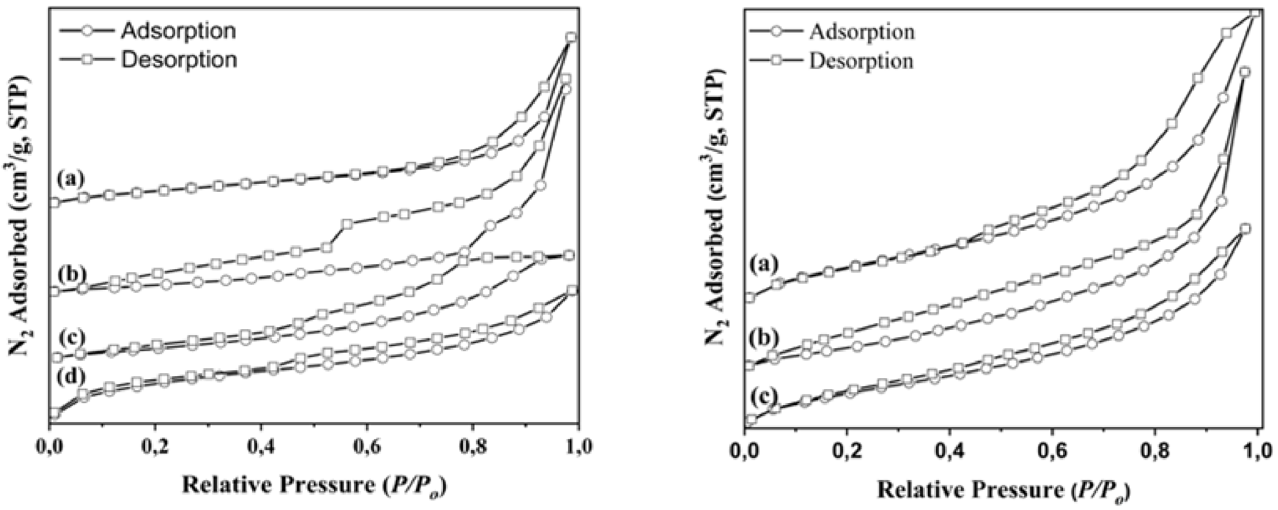

Figure 3. N$_2$ adsorption-desorption isotherm of M^{2+}/Al-BC (M^{2+} = Cu, Ca, Ni), LDHs, and BC.

Table 1. BET surface area analysis.

Materials	Surface Area (m^2/g)	Pore Volume (cm^3/g) BJH	Pore Diameter (nm)
BC	50.936	12.089	0.025
Ca/Al	15.106	0.043	2.897
Cu/Al	45.199	0.117	10.393
Ni/Al	56.930	0.117	5.027
Ca/Al-BC	158.291	0.017	2.474
Cu/Al-BC	200.909	0.324	7.032
Ni/Al-BC	438.942	0.002	12.301

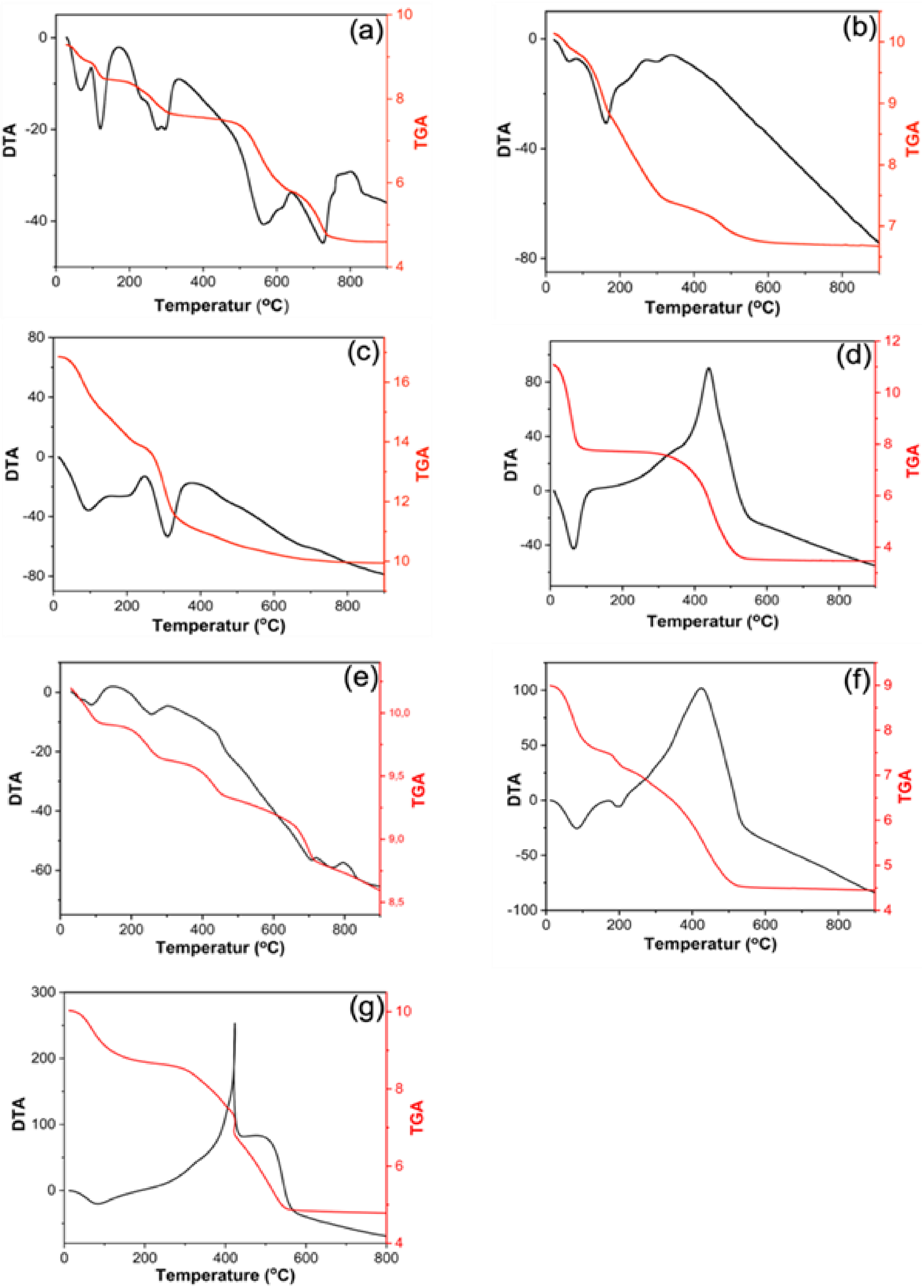

Figure 4. Thermogravimetric of (a) Ca/Al, (b) Cu/Al, (c) Ni/Al, (d) BC, (e) Ca/Al-BC, (f) Cu/Al-BC, and (g) Ni/Al-BC.

composites. The specific surface area of the composite is higher than that of LDH and BC, this is because the surface of LDH and biochar becomes heterogeneous so that the active site of the composite adsorbent increases [37]. The properties of LDH before and after the composite did not differ much before and after because LDH is a layered material, and biochar

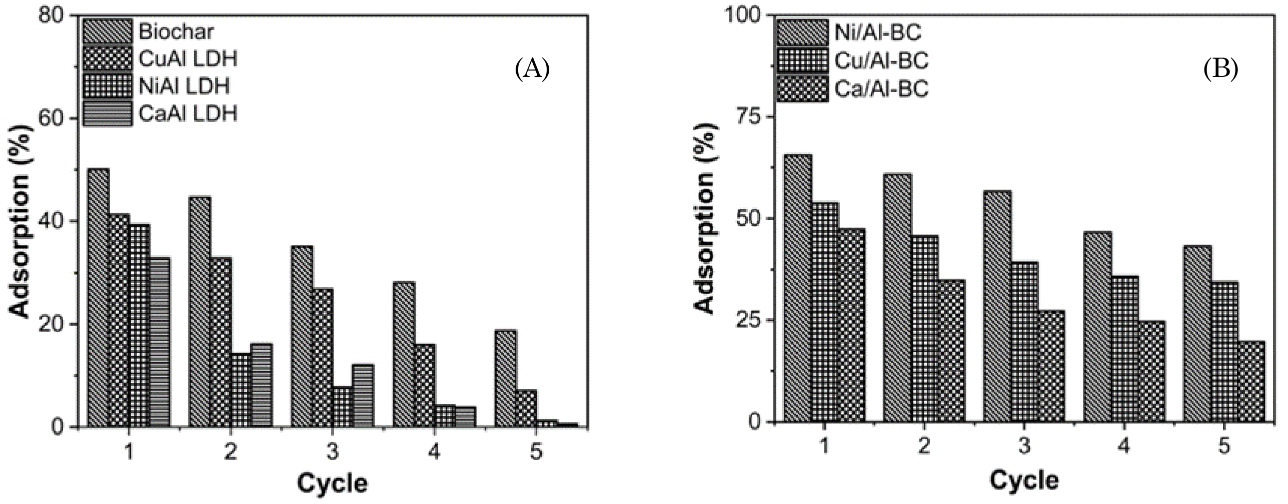

Figure 5. Reusability materials toward Cd(II) adsorption (1). Starting materials (Ca/Al, Cu/Al, Ni/Al, BC), and (2) composites (Ca/Al-BC, Cu/Al-BC, Ni/Al-BC).

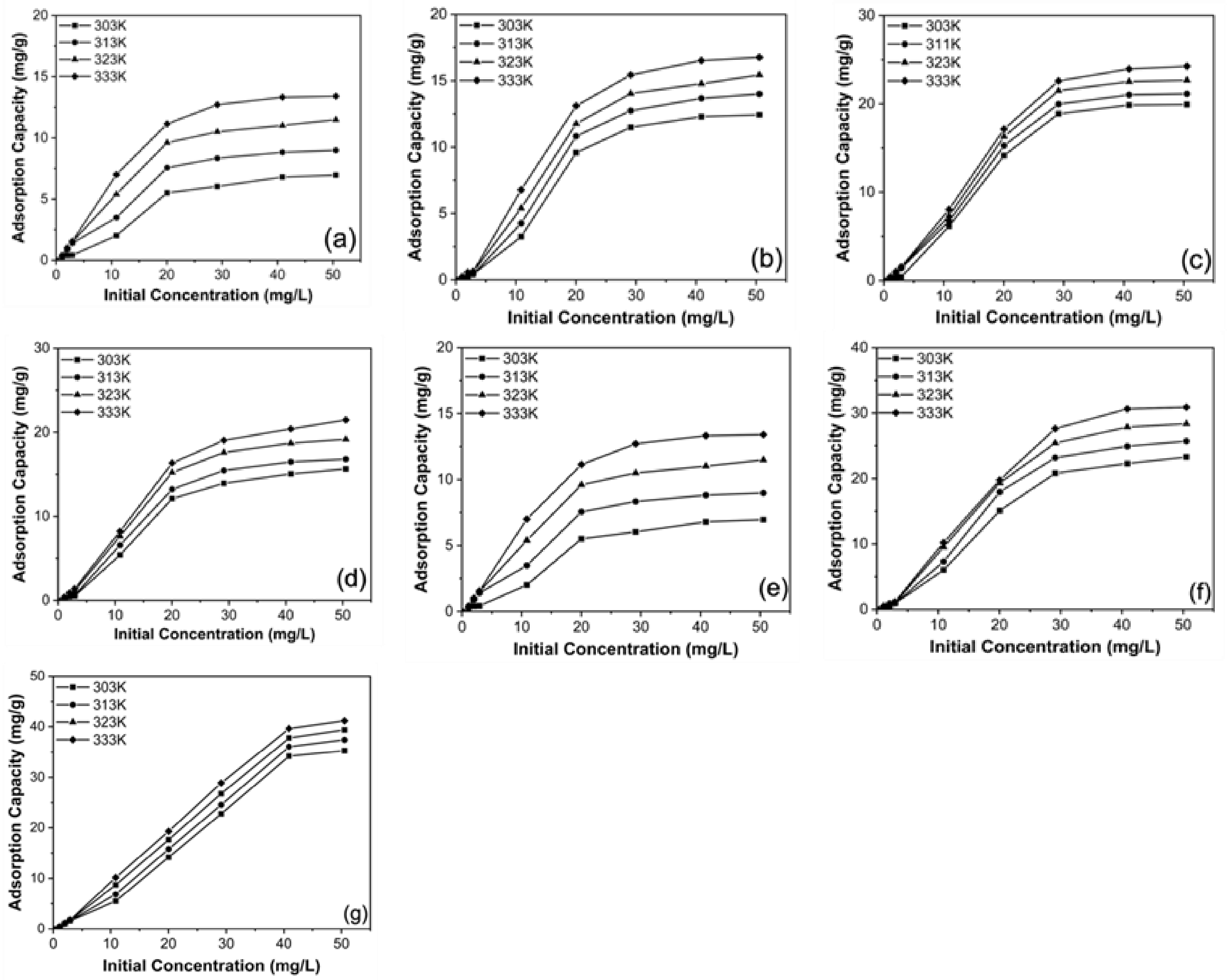

Figure 6. Effect of Cd(II) initial concentration and temperature on the adsorption using (a) Ca/Al, (b) Cu/Al, (c) Ni/Al, (d) BC, (e) Ca/Al-BC, (f) Cu/Al-BC, and (g) Ni/Al-BC.

Table 2. Isotherm adsorption.

Adsorbent	Adsorption Isotherm	Adsorption Constant	T (K)			
			303	313	323	333
CaAl	Langmuir	Q_{max}	8.143	9.785	12.330	14.306
		k_{L}	0.137	0.276	0.317	0.437
		R^2	0.9978	0.9999	0.9993	0.9995
	Freundlich	n	0.4462	6.882	7.570	7.651
		k_{F}	3.019	5.291	7.073	8.543
		R^2	0.9808	0.9735	0.9929	0.9099
CuAl	Langmuir	Q_{max}	13.947	15.504	16.892	19.802
		k_{L}	0.048	0.265	0.290	0.190
		R^2	0.9981	0.9997	0.9992	0.9797
	Freundlich	n	0.519	0.649	5.525	6.398
		k_{F}	30.570	8.020	0.8221	9.906
		R^2	0.8857	0.9062	0.9365	0.9359
BC	Langmuir	Q_{max}	17.094	18.018	20.121	22.472
		k_{L}	0.296	0.422	0.626	0.609
		R^2	0.9999	0.9999	0.999	0.999
	Freundlich	n	9.757	0.769	8.130	7.704
		k_{F}	8.562	2.684	12.723	13.890
		R^2	0.9862	0.8525	0.9695	0.9921
NiAl	Langmuir	Q_{max}	21.692	22.573	23.886	25.381
		k_{L}	0.431	0.578	0.774	0.912
		R^2	0.9958	0.998	0.9987	0.9994
	Freundlich	n	19.120	19.646	22.936	19.084
		k_{F}	16.773	17.898	19.706	20.516
		R^2	0.9197	0.9435	0.9605	0.9785
CaAl-BC	Langmuir	Q_{max}	88.496	75.188	104.167	156.250
		k_{L}	0.137	0.174	0.163	0.143
		R^2	0.9999	0.9998	0.9998	0.9986
	Freundlich	n	0.001	5.157	4.953	4.627
		k_{F}	12.685	13.280	14.870	16.162
		R^2	0.9331	0.9312	0.9463	0.9189
CuAl-BC	Langmuir	Q_{max}	30.448	84.034	80.000	149.254
		k_{L}	0.300	0.067	0.683	0.143
		R^2	0.9961	0.9999	0.9963	0.9999
	Freundlich	n	0.492	7.077	9.940	8.889
		k_{F}	4.869	16.831	24.038	20.730
		R^2	0.9929	0.9113	0.9693	0.9426
NiAl-BC	Langmuir	Q_{max}	39.216	58.140	110.461	208.333
		k_{L}	0.021	0.015	0.007	0.004
		R^2	0.999	0.988	0.999	0.996
	Freundlich	n	1.067	0.648	0.258	0.377
		k_{F}	1.156	1.114	1.389	1.149
		R^2	0.988	0.910	0.951	0.983

is a porous material, thus increasing the effectiveness and active site of the adsorbent.

Figure 4 shows the thermogravimetric patterns of starting materials and composites. In general, the decomposition peaks of LDH have three parts *i.e.* dehydration of water on the lattice (100–110 °C), decomposition of nitrate on the interlayer (around 300–350 °C), and decomposition of layer (above 600 °C). All peak was assigned as endotherm peak. The thermogravimetric pattern of BC contains two main peaks endothermic and exothermic peaks. The endothermic peak at 105 °C is due to the removal of water from crystallization, and the exothermic peak at 490 °C is the oxidation of organic molecules on BC. Ca/Al-BC, Cu/Al-BC, and Ni/Al-BC have both endothermic and exothermic peaks due to LDH and BC. Thus the formation of a composite based on LDH and BC in this research was successfully synthesized.

The performance of composite was evaluated through reuse material in Cd(II) adsorption from an aqueous solution. Figure 5(A). The reusability adsorbent for cadmium(II) adsorption by LDH was largely decreased, although in the second re-adsorption process. This phenomenon is due to the exfoliation of the LDH structure. The structure of LDH is almost unstable toward reuse material. The reusability of BC was better than LDH. The carbon on the material creates the resistance of structure thus, BC is appropriate to support for LDH to form LDH-BC composite. Composite LDH-BC, as shown in Figure 5(B) has better stability toward reusability adsorbent on cadmium(II) adsorption. All composites Ca/Al-BC, Cu/Al-BC, and Ni/Al-BC show a larger adsorption capacity than the starting materials. Ni/Al-BC was more stable toward re-adsorption than Cu/Al-BC and Ca/Al-BC. The stability of composite for cadmium(II) readsorption is in the order Ni/Al-BC > Cu/Al-BC > Ca/Al-BC.

The adsorption of Cd(II) was relatively low at low temperatures. The increasing temperature will increase the adsorption amount of Cd(II) on all adsorbents (Figure 6). The adsorption of Cd(II) was also small at low Cd(II) concentrations and was increased at higher Cd(II) concentrations. The Cd(II) adsorbed on composite was also higher than LDH and BC. These quantitative data were used to obtain isotherm and thermodynamic data by equations are as follows:

$$\text{Langmuir}\ :\quad \frac{C}{m} = \frac{1}{bK_L} + \frac{C}{b} \qquad (1)$$

$$\text{Freundlich}\ :\quad \log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (2)$$

The isotherm adsorption was calculated using the Freundlich and Langmuir equation [38,39]. The adsorption isotherm of each adsorbent used followed the Langmuir isotherm model as evidenced by the R^2 = 1 shown in Ta-

Table 3. Adsorption of Cd(II) using various adsorbents.

Adsorbents	Experiment Operating Conditions	q_{max} (mg/g)	References
HAp@Fe_3O_4@bentonite	pH: 3.0; 60 min	309	[40]
Ca/Al-$SiW_{12}O_{40}$	pH: 9.0; 90 min	12.57	[41]
iron-trimesic MOF	pH: 5.0; 298 K	0.84	[42]
chitosan/Mg-Al LDH	pH: 3.0; 60 min	140.8	[2]
HA-MgAl LDH	90 min; 298 K	155.28	[31]
NiCoTi LDH	150 min, 302 K	37.87	[43]
Mg-Fe-Kiwi branch biochar	pH: 6.5; 303 K	25.6	[30]
MgAl-Cys-LDH	pH: 5.8; 298 K	93.11	[44]
Ni/Mo-LDH	318 K	68.4	[45]
magnetic rice husk biochar-$KMnO_4$	pH 3.5	42.49	[46]
Polyethyleneimine-AC	pH: 6.0; 298 K	45.5	[47]
maleylated modified hydrochar	303 K; 120 min	90.99	[48]
BC	333 K; 90 min	22.472	Present Work
Ca/Al		14.306	
Cu/Al		19.802	
Ni/Al		25.381	
Ca/Al-BC		156.250	
Cu/Al-BC		149.254	
Ni/Al-BC		208.333	

ble 2. The data in Table 3 also shows the adsorption capacity (Q_{max}) of Cd(II) on all adsorbents at various temperatures. The Q_{max} at 333 K was the highest value. The Q_{max} for LDH and BC was 14.306–25.381 mg/g and 22.472 mg/g, respectively. Q_{max} of the composite was almost ten-fold that of LDH. The Q_{max} of the composite was largely increased equally with increasing surface area properties of the composite. Thus the adsorption of Cd(II) on composite depended on the surface area of the materials.

The adsorption of Cd(II) in this research was compared with several reported literatures using various adsorbents, as shown in Table 3. The adsorbent for Cd(II) adsorption was LDH, modified LDH, and other adsorbents by various adsorption conditions. Adsorbents of LDH, BC, Ca/Al-BC, Cu/Al-BC, and Ni/Al-BC in this research show a relatively high Q_{max} value than in previous research. The adsorption of Cd(II) on composite has Q_{max} up to 208.333 mg/g.

The thermodynamic parameter was also obtained by calculation using thermodynamic terms, such as ΔH, ΔS, and ΔG [49,50]. Table 4 shows the adsorption energy for LDH, BC, and composite in the range of 9.776–23.178 kJ/mol, 14.232 kJ/mol, and 23.726–35.183 kJ/mol, respectively. These energy values are very low to classify as chemical adsorption [21]. Although there is the possibility of the involvement of chemical interaction in the adsorption process, that is very low. Physical interaction is dominated for Cd(II) adsorption on LDH, BC, and composite. The ΔS value was also small and in the range of 0.037–0.129 J/mol.K. The trend of randomness increased from LDH to composite showed the increasing randomness of the adsorption process on composite [51]. That phenomena suggest the formation of composite will increase interaction between Cd(II) and materials due to the availability of various active sites on composite. The ΔG value of all adsorbents shows the negative value means the spontaneity process of Cd(II) adsorption on adsorbents. The increasing adsorption temperature gave the more negative value of ΔG. Thus, the spontaneity of adsorption was collated with the value of ΔS.

Table 4. Thermodynamic parameters.

Adsorbent	T (K)	Q_e (mg/g)	ΔH (kJ/mol)	ΔS (J/mol.K)	ΔG (kJ/mol)
CaAl	303	6.954	23.178	0.078	−0.440
	313	8.983			−1.220
	323	11.491			−1.999
	333	13.406			−2.779
CuAl	303	12.294	12.438	0.042	−0.378
	313	13.673			−0.801
	323	14.767			−1.224
	333	16.523			−1.647
NiAl	303	19.932	9.776	0.037	−1.411
	313	21.140			−1.781
	323	22.679			−2.150
	333	24.245			−2.519
BC	303	15.641	14.232	0.048	−0.419
	313	16.803			−0.903
	323	19.164			−1.387
	333	21.471			−1.870
CaAl-BC	303	21.117	23.726	0.079	−0.092
	313	23.545			−0.878
	323	26.318			−1.664
	333	29.202			−2.450
CuAl BC	303	22.291	25.634	0.086	−0.386
	313	24.921			−1.245
	323	27.871			−2.104
	333	30.650			−2.963
NiAl-BC	303	34.189	35.183	0.129	−1.705
	313	36.041			−3.904
	323	37.776			−6.104
	333	39.625			−8.304

4. Conclusion

Composite M^{2+}/Al-BC (Ca/Al-BC, Cu/Al-BC, and Ni/Al-BC) were successfully synthesized and had surface area properties almost ten-fold than pristine LDH. This composite has structural stability toward reusability adsorbent and can be used until five cycles. The maximum adsorption capacity in removing Cd(II) from aqueous solution using Ca/Al-BC, Cu/Al-BC, and Ni/Al-BC adsorbents was 156.250 mg/g, 149.254 mg/g, and 208.333 mg/g, respectively. This confirms that Ca/Al-BC, Cu/Al-BC, and Ni/Al-BC composites have potential for heavy metal wastewater treatment.

Acknowledgement

The authors thank to Research Center of Inorganic Materials and Complexes FMIPA Universitas Sriwijaya for equipment, analysis, funder, and instrumental supports.

References

[1] Sitko, R., Turek, E., Zawisza, B., Malicka, E., Talik, E., Heimann, J., Gagor, A., Feist, B., Wrzalik, R. (2013). Adsorption of divalent metal ions from aqueous solutions using graphene oxide. *Dalton Transactions*, 42(16), 5682–5689. DOI: 10.1039/c3dt33097d

[2] Lyu, F., Yu, H., Hou, T., Yan, L., Zhang, X., Du, B. (2019). Efficient and fast removal of Pb^{2+} and Cd^{2+} from an aqueous solution using a chitosan/Mg-Al-layered double hydroxide nanocomposite. *Journal of Colloid Interface Science*, 539, 184–193. DOI: 10.1016/j.jcis.2018.12.049

[3] Cherfi, A., Abdoun, S., Gaci, O. 2014. Food survey: Levels and potential health risks of chromium, lead, zinc and copper content in fruits and vegetables consumed in Algeria. *Food and Chemical Toxicology*, 70, 48–53. DOI: 10.1016/j.fct.2014.04.044

[4] Wang, F., Pan, Y., Cai, P., Guo, T., Xiao, H. (2017). Single and binary adsorption of heavy metal ions from aqueous solutions using sugarcane cellulose-based adsorbent. *Bioresource Technology*, 241, 482–490. DOI: 10.1016/j.biortech.2017.05.162

[5] Cheng, S.Y., Show, P.L., Lau, B.F., Chang, J.S., Ling, T.C. 2019. New Prospects for Modified Algae in Heavy Metal Adsorption. *Trends Biotechnology*, 37(11), 1255–1268. DOI: 10.1016/j.tibtech.2019.04.007

[6] Wang, T., Li, C., Wang, C., Wang, H. 2018. Biochar/MnAl-LDH composites for Cu (II) removal from aqueous solution. *Colloids Surface A Physicochemical Engineering Aspects*, 538, 443–450. DOI: 10.1016/j.colsurfa.2017.11.034

[7] Salman, N., Shaheen, H., Abbas, H., Khalouf, G. (2017). Use of Syrian natural zeolite for heavy metals removal from industrial wastewater: Factors and mechanism. *Journal of Entomology and Zoology Studies*, 5(4), 452–461. DOI: 10.22271/j.ento.2017.v5.i3b.04

[8] Ruan, X., Chen, Y., Chen, H., Qian, G., Frost, R.L. (2016). Sorption behavior of methyl orange from aqueous solution on organic matter and reduced graphene oxides modified Ni-Cr layered double hydroxides. *Chemical Engineering Journal*, 297, 295–303. DOI: 10.1016/j.cej.2016.01.041

[9] Boulaiche, W., Hamdi, B., Trari, M. (2019). Removal of heavy metals by chitin: equilibrium, kinetic and thermodynamic studies. *Applied Water Science*, 9, 39. DOI: 10.1007/s13201-019-0926-8

[10] Xiao, F., Cheng, J., Cao, W., Yang, C., Chen, J., Luo, Z. (2019). Removal of heavy metals from aqueous solution using chitosan-combined magnetic biochars. *Journal of Colloid and Interface Science*, 540, 579–584. DOI: 10.1016/j.jcis.2019.01.068

[11] Mubarak, M., Jeon, H., Islam, M.S., yoon, C., Bae, J.S., Hwang, S., Choi, W.S., Lee, H. 2018. One-pot synthesis of layered double hydroxide hollow nanospheres with ultrafast removal efficiency for heavy metal ions and organic contaminants. *Chemosphere*, 201, 676–686. DOI: 10.1016/j.chemosphere.2018.03.046

[12] Siregar, P.M.S.B.N., Palapa, N.R., Wijaya, A., Fitri, E.S., Lesbani, A. (2021). Structural Stability of Ni/Al Layered Double Hydroxide Supported on Graphite and Biochar Toward Adorption of Congo Red. *Science and Technology Indonesia*, 6(2), 85–95. DOI: 10.26554/sti.2021.6.2.85-95

[13] Belin, T., Mve-Mfoumou, C., Mignard, S., Pouilloux, Y. (2013). Study of physisorbed carbon dioxide on zeolites modified by addition of oxides or acetate impregnation. *Microporous Mesoporous Materials*, 182, 109–116. DOI: 10.1016/j.micromeso.2013.08.020

[14] Mohapatra, S., Sakthivel, R., Roy, G.S., Varma, S., Singh, S.K., Mishra, D.K. (2011). Synthesis of β-SiC powder from bamboo leaf in a DC extended thermal plasma reactor. *Materials and Manufucturing Process*, 26(11), 1362–1368. DOI: 10.1080/10426914.2011.557127

[15] Woo, M.A., Woo-Kim, T., Paek, M.J., Ha, H.W., Choy, J.H., Hwang, S.J. (2011). Phosphate-intercalated CaFe-layered double hydroxides: Crystal structure, bonding character, and release kinetics of phosphate. *Journal of Solid State Chemistry*, 184(1), 171–176. DOI: 10.1016/j.jssc.2010.11.003

[16] Ma, L., Wang, Q., Islam, S.M., Liu, Y., Ma, S., Kanatzidis, M.G. (2016). Highly selective and efficient removal of heavy metals by layered double hydroxide intercalated with the MoS_4^{2-} ion. *Journal of The American Chemical Society*, 138, 2858–2866. DOI: 10.1021/jacs.6b00110

[17] Ou, B., Wang, J., Wu, Y., Zhao, S., Wang, Z. (2020). Efficient removal of Cr(VI) by magnetic and recyclable calcined CoFe-LDH/g-C3N4 via the synergy of adsorption and photocatalysis under visible light. *Chemical Engineering Journal*, 380, 122600. DOI: 10.1016/j.cej.2019.122600

[18] Behbahani, E.S., Dashtian, K., Ghaedi, M. (2021). Fe3O4-FeMoS4: Promise magnetite LDH-based adsorbent for simultaneous removal of Pb (II), Cd (II), and Cu (II) heavy metal ions. *Journal of Hazardous Materials*, 410, 124560. DOI: 10.1016/j.jhazmat.2020.124560

[19] Li, S., Xu, H., Wang, L., Ji, L., Qu, Z., Yan, N. (2021). Dual-functional Sites for Selective Adsorption of Mercury and Arsenic ions in [SnS4]4-/MgFe-LDH from Wastewater. *Journal Hazardous Materials*, 403, 123940. DOI: 10.1016/j.jhazmat.2020.123940

[20] Carriazo, D., Lima, S., Martín, C., Pillinger, M., Valente, A.A., Rives, V. (2007). Metatungstate and tungstoniobate-containing LDHs: Preparation, characterisation and activity in epoxidation of cyclooctene. *Journal of Physics and Chemistry of Solids*, 68(10), 1872–1880. DOI: 10.1016/j.jpcs.2007.05.012

[21] Oktriyanti, M., Palapa, N.R., Mohadi, R., Lesbani, A. (2020). Effective removal of iron (II) from aqueous solution by adsorption using Zn/Cr layered double hydroxides intercalated with Keggin ion. *Journal of Ecological Engineering*, 21(5), 63–71. DOI: 10.12911/22998993/122190

[22] Taher, T., Christina, M.M., Said, M., Hidayati, N., Ferlinahayati, F., Lesbani, A. (2019). Removal of iron(II) using intercalated Ca/Al layered double hydroxides with [-$SiW_{12}O_{40}]^{4-}$. *Bulletin of Chemical Reaction Engineering & Catalysis*, 14(2), 260–267. DOI: 10.9767/bcrec.14.2.2880.260-267

[23] Guo Y., Gong, Z., Li, C., Gao, B., Li, P., Wang, X., Zhang, B., Li, X. (2019). Efficient removal of uranium (VI) by 3D hierarchical Mg/Fe-LDH supported nanoscale hydroxyapatite: A synthetic experimental and mechanism studies. *Chemical Engineering Journal*, 392 (6),123682. DOI: 10.1016/j.cej.2019.123682

[24] Asiabi, H., Yamini, Y., Shamsayei, M., Tahmasebi, E. (2017). Highly selective and efficient removal and extraction of heavy metals by layered double hydroxides intercalated with the diphenylamine-4-sulfonate: A comparative study. *Chemical Engineering Journal*, 323, 212–223. DOI: 10.1016/j.cej.2017.04.096

[25] Shixia, C., Huang, Y., Han, X., Wu, Z., Lai, C., Wang, J., Deng, Q., Zeng, Z., Deng, S. 2019. Simultaneous and efficient removal of Cr(VI) and methyl orange on LDHs decorated porous carbons. *Chemical Engineering Journal*, 352(6), 810–812. DOI: 10.1016/j.cej.2018.11.103

[26] Huang, D., Liu, C., Zhang, C., Deng, R., Wang, R., Xue, W., Luo, H., Zeng, G., Zhang, Q., Guo, X. (2018). Cr(VI) removal from aqueous solution using biochar modified with Mg/Al-layered double hydroxide intercalated with ethylenediaminetetraacetic acid. *Bioresource Technology*, 276, 127–132. DOI: 10.1016/j.biortech.2018.12.114

[27] Li, S., Dong, L., Wei, Z., Sheng, G., Du, K., Hu, B. (2020). Adsorption and mechanistic study of the invasive plant-derived biochar functionalized with CaAl-LDH for Eu(III) in water. *Journal of Environmental Sciences*, 96(1), 127–137. DOI: 10.1016/j.jes.2020.05.001

[28] Palapa, N.R., Taher, T., Rahayu, B.R., Mohadi, R., Rachmat, A., Lesbani, A. (2020). CuAl LDH/Rice husk biochar composite for enhanced adsorptive removal of cationic dye from aqueous solution. *Bulletin of Chemical Reaction Engineering & Catalysis*, 15(2), 525–537. DOI: 10.9767/bcrec.15.2.7828.525-537

[29] Li, A., Zhang, Y., Ge, W., Zhang, Y., Liu, L., Qiu, G. (2021). Removal of heavy metals from wastewaters with biochar pyrolyzed from MgAl-LDH-coated rice husk: mechanism and application. *SSRN Electron Journal*, 2, 1–36. DOI: 10.2139/ssrn.3929867

[30] Tan, Y., Yin, X., Wang, C., Sun, H., Ma, A., Zhang, G., Wang, N. (2019). Sorption of cadmium onto Mg-Fe Layered Double Hydroxide (LDH)-Kiwi branch biochar. *Environmental Pollutants Bioavailability*, 31(1), 189–197. DOI: 10.1080/26395940.2019.1604165

[31] Shi, M., Zhao, Z., Song, Y., Xu, M., Li, J., Yao, L. (2020). A novel heat-treated humic acid/MgAl-layered double hydroxide composite for efficient removal of cadmium: Fabrication, performance and mechanisms. *Applied Clay Science*, 187, 105482. DOI: 10.1016/j.clay.2020.105482

[32] Zheng, Y., Cheng, B., You, W., Yu, J., Ho, W. (2018). 3D hierarchical graphene oxide-NiFe LDH composite with enhanced adsorption affinity to Congo red, methyl orange and Cr(VI) ions. *Journal of Hazardous Materials*, 369, 214–225. DOI: 10.1016/j.jhazmat.2019.02.013

[33] Bhowmick, G.D., Sarmah, A.K., Sen, R. (2018). Production and characterization of a value added biochar mix using seaweed, rice husk and pine sawdust: A parametric study. *Journal of Cleaner Production*, 200, 641–656. DOI: 10.1016/j.jclepro.2018.08.002

[34] Rives, V., Carriazo, D., Martín, C. (2010). Heterogeneous Catalysis by Polyoxometalate-Intercalated Layered Double Hydroxides. In: Gil, A., Korili, S., Trujillano, R., Vicente, M. (eds) *Pillared Clays and Related Catalysts*. New York: Springer. DOI: 10.1007/978-1-4419-6670-4_12

[35] Benito, P., Herrero, M., Labajos, F.M., Rives, V. (2010). Effect of post-synthesis microwave – hydrothermal treatment on the properties of layered double hydroxides and related materials. *Applied Clay Science*, 48(2), 218–227. DOI: 10.1016/j.clay.2009.11.051

[36] Ravuru, S.S., Jana, A., De, S. (2019). Synthesis of NiAl-layered double hydroxide with nitrate intercalation: Application in cyanide removal from steel industry effluent. *Journal Hazardous Materials*, 373, 791–800. DOI: 10.1016/j.jhazmat.2019.03.122

[37] Zubair, M., Aziz, H.A., Ihsanullah, I., Ahmad, M.A. Al-Harthi, M.A. (2021). Biochar supported CuFe layered double hydroxide composite as a sustainable adsorbent for efficient removal of anionic azo dye from water. *Environmental Technology & Innovation*, 23, 101614. DOI: 10.1016/j.eti.2021.101614

[38] Lee, Y.C., Amini, M.H.M., Sulaiman, N.S., Mazlan, M., Boon, J.G. (2018). Batch adsorption and isothermic studies of malachite green dye adsorption using leucaena leucocephala biomass as potential adsorbent in water treatment. Songklanakarin *Journal of Science and Technology*, 40(3), 563–569. DOI: 10.14456/sjst-psu.2018.67

[39] Malkoc E., Nuhoglu, Y. (2007). Determination of kinetic and equilibrium parameters of the batch adsorption of Cr (VI) onto waste acorn of Quercus ithaburensis. *Chemical Engineering and Processing-Process Intesdification*, 46, 1020–1029. DOI: 10.1016/j.cep.2007.05.007

[40] Ain, Q.U., Zhang, H., Yaseen, M., Rasheed, U., Lui, K., Subhan, S., Tong, Z. (2020). Facile fabrication of hydroxyapatite-magnetite-bentonite composite for efficient adsorption of Pb(II), Cd(II), and crystal violet from aqueous solution. *Journal of Cleaner Production*, 247, 119088. DOI: 10.1016/j.jclepro.2019.119088

[41] Taher, T., Irianty, Y., Mohadi, R., Said, M., Andreas, R., Lesbani, A. (2019). Adsorption of cadmium(II) using ca/al layered double hydroxides intercalated with keggin ion. *Indonesian Journal of Chemistry*, 19(4), 873–881. DOI: 10.22146/ijc.36447

[42] Zhang, B.L., Qiu, W., Wang, P., Liu, Y., Zou, J., Wang, L., Ma, J. (2020). Mechanism study about the adsorption of Pb(II) and Cd(II) with iron-trimesic metal-organic frameworks. *Chemical Engineering Journal*, 385, 123507. DOI: 10.1016/j.cej.2019.123507

[43] Abasi, C.Y., Diagboya, P.N.E., Dikio, E.D. (2019). Layered double hydroxide of cobalt-zinc-aluminium intercalated with carbonate ion: preparation and Pb(II) ion removal capacity. *International Journal of Environmental Studies*, 76(2), 251–265. DOI: 10.1080/00207233.2018.1517935

[44] Zhang, X., Yan, L., Li, J., Yu, H. (2020). Adsorption of heavy metals by L-cysteine intercalated layered double hydroxide: Kinetic, isothermal and mechanistic studies. *Journal of Colloid Interface Science*, 562, 149–158. DOI: 10.1016/j.jcis.2019.12.028

[45] Bakr, A.S.A., Mostafa, M.S. (2020). Adsorption of Cd(II) from aqueous solutions via meso structured adsorbent based on Ni/Mo-LDH: kinetics, thermodynamics, and adsorption mechanism. Energy Sources, Part A Recover. *Utilizayion, and Environmental Effects*, 42(18), 2240–2248. DOI: 10.1080/15567036.2019.1607936

[46] Sun, C., Chen, T., Huang, Q., Wang, J., Lu, S., Yan, J. (2019). Enhanced adsorption for Pb(II) and Cd(II) of magnetic rice husk biochar by KMnO4 modification. *Environmental Science and Pollution Research*, 26(9), 8902–8913. DOI: 10.1007/s11356-019-04321-z

[47] Xie, X., Gao, H., Luo, X., Su, T., Zhang, Y., Qin, Z. (2019). Polyethyleneimine modified activated carbon for adsorption of Cd(II) in aqueous solution. *Journal Environmental Chemical Engineering*, 7(3), 103183. DOI: 10.1016/j.jece.2019.103183

[48] Li, B., Lv, J.Q., Guo, J.Z., Fu, S.Y., Guo, M., Yang, P. (2019). The polyaminocarboxylated modified hydrochar for efficient capturing methylene blue and Cu(II) from water. *Bioresource Technology*, 275, 360–367. DOI: 10.1016/j.biortech.2018.12.083

[49] Errais, E., Duplay, J., Darragi, F., Rabet, I.M., Aubert, A., Huber, F., Morvan, G. (2011). Efficient anionic dye adsorption on natural untreated clay: Kinetic study and thermodynamic parameters. *Desalination*, 275(3), 74–81. DOI: 10.1016/j.desal.2011.02.031

[50] Gao, M., Wang, Z., Yang, C., Ning, J., Zhou, Z., Li, G. (2019). Novel magnetic graphene oxide decorated with persimmon tannins for efficient adsorption of malachite green from aqueous solutions. *Colloids and Surfaces A Physicochemical Engineering Aspects*, 566, 48–57. DOI: 10.1016/j.colsurfa.2019.01.016

[51] Juleanti, N., Palapa, N.R., Taher, T., Hidayati, N., Putri, B.I., Lesbani, A. (2021). The Capability of Biochar-Based CaAl and MgAl Composite Materials as Adsorbent for Removal Cr(VI) in Aqueous Solution. *Science and Technology Indonesia*, 6(3), 196–203. DOI: 10.26554/sti.2021.6.3.196-203