Adsorptive Performance of Congo Red using Copper-Aluminum LDHS Load to Rice Husk Biochar.pdf

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Adsorptive Performance of Congo Red using Copper-Aluminum LDHS Load to Rice Husk Biochar

(Prestasi Penjerapan Kongo Merah menggunakan Beban Tembaga-Aluminium LDHS kepada Bioarang daripada Sekam Padi)

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ABSTRACT

This work aimed that CuAl layered double hydroxide (LDH) is loaded to biochar to form CuAlLDH@BC composites by co-precipitation methods. CuAlLDH@BC composite was prepared and characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, surface area specific analysis BET method, thermalgravimetric, and scanning electron microscopy (SEM) for morphological analysis. CuAlLDH@BC composite used as adsorbent for the removal of Congo red. The adsorption ability of CuAlLDH@BC composite evaluated by pseudo-second-order kinetic model, with $Qe_{calculated}$ and $Qe_{experimental}$ of the composite were closed (47.619 and 46.143 mg/g, respectively). Furthermore, the adsorption conducts were more consistent with the Langmuir isotherm model, than the Freundlich isotherm model. The isotherm adsorption data obtained the maximum adsorption capacity was 61.350 mg/g. Thermodynamic studies illustrated the endothermic nature of CuAlLDH@BC, as well as the fact that the adsorption process is spontaneous. Thus, CuAlLDH@BC showed a high reusability performance even after third cycle of adsorption-desorption process.

Keywords: Adsorption; biochar; composite; congo red; layered double hydroxide

ABSTRAK

Kajian ini bertujuan supaya hidroksida berganda berlapis CuAl (LDH) dimuatkan ke bioarang untuk membentuk komposit CuAlLDH@BC melalui kaedah kerpasan bersama. Komposit CuAlLDH@BC telah disedia dan dicirikan oleh pembelauan sinar-X (XRD), spektroskopi inframerah transformasi Fourier (FTIR), kaedah BET analisis khusus luas permukaan, gravimetrik terma dan mikroskop elektron pengimbasan (SEM) untuk analisis morfologi. Komposit CuAlLDH@BC digunakan sebagai penjerap untuk penyingkiran merah Kongo. Keupayaan penjerapan komposit CuAlLDH@BC dinilai oleh model kinetik kedua pseudo dengan $Qe_{calculated}$ dan $Qe_{experimental}$ komposit telah ditutup (masing-masing 47.619 dan 46.143 mg/g). Tambahan pula, kelakuan penjerapan lebih tekal dengan model isoterma Langmuir, berbanding model isoterma Freundlich. Data penjerapan isoterma memperoleh kapasiti penjerapan maksimum ialah 61.350 mg/g. Kajian termodinamik menggambarkan sifat endotermik CuAlLDH@BC serta hakikat bahawa proses penjerapan adalah spontan. Oleh itu, CuAlLDH@BC menunjukkan prestasi kebolehgunaan semula yang tinggi walaupun selepas kitaran ketiga proses penjerapan-desorpsi.

Kata kunci: Bioarang; hidroksida berganda berlapis; komposit; Kongo merah; penjerapan

INTRODUCTION

Synthetic dye wastewater is considered to be an environmental hazard that can contaminate water for a long time (Ma et al. 2015). The major sources of synthetic dye in wastewater are the textile, paper, pulp, paint, and cosmetic industries (Schwarzenbach et al. 2010). Commonly, synthetic dyes such as Congo red have a high resistance to oxidizing agents, are non-biodegradable, highly toxic, and an eye and skin irritant. Congo red dye is diazo- benzidine-based anionic dye. Congo red become popular as synthetics dye due to a bright color, does not wear off easily, sold freely for textile industry and after use carelessly thrown away without any treatments (Raval et al. 2016). Therefore, the elimination of Congo red from wastewater has become a necessity (Chakraborty & Nagaraja 2015). Techniques including adsorption (Soleimani et al. 2018), bioremediation (Vikrant et al. 2018), chemical decomposition (Gholami et al. 2020), and membrane (Shenvi et al. 2015) have been used to remove dyes from aqueous solutions. Based on its cost-

effectiveness, ease of use, and high efficiency, adsorption is considered to be the leading technique for the removal of pollutants in water. Potential adsorbents include bentonite (Mohammed & Baytak 2016), zeolite (Abdelrahman 2018), activated carbon (Foroutan et al. 2019), and layered double hydroxide (LDH) (Lesbani et al. 2020).

LDH is an anionic-synthetic layered material which can be used as an adsorbent due to its highly flexible structure. The general formula of LDH is $[M2+1-xM3+x(OH)2]x+[Amx/m\cdot nH2O]x-$, where M2+ is a divalent cation, M3+ is a trivalent cation, and Am is an interlayer anion (Wu et al. 2011). Its strong adsorption performance can be attributed to anion exchange from the interlayer. LDH can be synthesized in some ways, including precipitation, hydrothermal synthesis, and ion exchange. It can adsorb various pollutants from wastewater, including metal cations, dyes, and organic compounds. Palapa et al. (2020a) reported that CuCr-LDH adsorbed malachite green with a maximum uptake of 56 mg/g. Furthermore, Zhu et al. (2020) reported that a MgAl-LDH nanostructure could remove organic contaminants, such as non-ionic naphthalene, to a maximum capacity of 43.7 mg/g, while Tran et al. (2018) found that MgAl-LDH adsorbed copper and lead in an aqueous solution with a maximum uptake of 84.7 and 59.9 mg/g, respectively. However, LDH powder has a limited adsorption capability due to its tight layer stacking (Inumaru et al. 2007). Researchers have attempted to improve the adsorption capabilities of LDH using intercalation (Lesbani et al. 2020), composite (Malak-Polaczyk et al. 2010), and calcination (Peng et al. 2015) processes. According to Mahjoubi et al. (2017), Ni-CLDH calcined have good adsorption capacity up to 438 mg/g for malachite green removal. The intercalation process of CuAl LDH by polyoxometalate was enhancing adsorption capacity malachite green removal from 55.866 to 149.253 mg/g (Palapa et al. 2020a). However, in this era, the modification material using carbon enrichment has become the preferred choice due to its high surface area, stable structure, and effectiveness as a supporting material (Cui et al. 2020). On the other hand, the utilization of carbonaceous from waste biomass is a new reuse method of waste management (Firdaus et al. 2017). Biochar (BC) is a carbon-based compound produced by the pyrolysis of biomass at high temperatures. BC is an attractive carbon-rich material from agricultural waste and industrial byproducts that can be used in material modification (Xia et al. 2019). According to Huang et al. (2019) reported that LDH modified with BC can enhance adsorption capacity of dyes. Meili et al. (2019) reported that the MgAl LDH modified by BC from an animal's bone had been used to remove methylene blue from water solution. The maximum adsorption capacity attains 406 mg/g. Wang et al. (2016) also reported that the removal of Ar using NiFe modified by BC from pine has a maximum adsorption capacity of 438 mg/g. Zuhr et al. (2020) reported that date palm BC loaded to MgAl-LDH were employed for enhanced aqueous uptake of methylene blue 302.75 mg/g after 180 min. Accordance with previous studies showed that LDH modified using BC has good potential, effectivity and high performance as adsorbent.

In this study, CuAl-LDH was developed as a composite with BC to enhance the adsorption efficiency of Congo red in an aqueous solution. We evaluated the kinetic and thermodynamic parameters of the adsorption process by varying time, temperature, and initial concentration. The reusability of the adsorbent was studied using three cycles of adsorption-desorption using several reagents.

MATERIALS AND METHODS

CHEMICALS AND INSTRUMENTATIONS

The analytical grade chemicals used in this study included copper nitrate (99.5%, 241.60 g/mol, Merck), aluminum nitrate (95.0%, 375.13 g/mol, Merck), sodium hydroxide (99.9%, 40.0 g/mol, Sigma Aldrich), and sodium carbonate (99.9%, 105.99 g/mol, Merck). Rice husk biochar was obtained and used as received from a local supplier with pyrolysis treatment in a furnace under constant N_2 flow for two hours at 500 ℃ (10 ℃/min). The Congo red (CR) solutions were prepared by dissolving the calculated amounts of CR into deionized water. The x-ray diffraction (XRD) characterization was performed using XRD Rigaku Miniflex-600 and the sample was measured at a scan rate of 1°/min. Infrared spectra were obtained from FTIR Shimadzu Prestige-21 measurements using a KBr disc and the samples were scanned at wavenumber 400 - 4000 cm^{-1}. The specific surface area was calculated using Multipoint Brunauer-Emmett-Teller (BET) based on data collected by ASAP Micromeritics 2020 at 77 K. The surface morphology of materials was characterized using a scanning electron microscope (SEM) Quanta-650 Oxford instrument. The thermogravimetric curve was determined using a Shimadzu DTG-60H instrument. The dye concentration was analyzed using a UV-visible spectrophotometer Bio-Base BK-UV1800 at a 498 nm wavelength of maximum absorbance.

PREPARATION OF CUALLDH@BC

The CuAl-LDH starting material was obtained as per Palapa et al. (2020b). The preparation of CuAl-LDH loaded

by BC to form CuAlLDH@BC was conducted using co-precipitation method. A solution of copper nitrate 10 mL 0.75 M was mixed with 10 mL 0.25 M aluminum nitrate. The mixture was stirred at a constant rate for an hour until the starting materials were completely dissolved. A beaker containing 1 g of the biochar was prepared and added to the mixture with continuous stirring. A solution of 1 M sodium hydroxide was added dropwise until a pH of 10 was reached. The mixing solution was kept at 80 °C for three days. Composites were then washed and dried at room temperature for a day.

ADSORPTION EXPERIMENTS

The adsorption process was carried out in batch systems. A 50 mg of adsorbents was added into 50 mL CR solution with various initial concentration. The adsorption process was conducted by variation of adsorption time, and temperature. As much as 0.05 g adsorbents (i.e. CuAl LDH, BC and CuAlLDH@BC) was added into 0.05 L CR solution, respectively, with various concentration 50 - 90 mg/L and shaken for 5 - 150 min at temperature 303 - 333 K. The desorption study was performed using several reagents, including NaOH, HCl, water, and ethanol. The adsorbed material (0.250 g) and reagent (25 mL) were mixed and the mixture was shaken for 180 min. The filtrate was separated by centrifugation at 100 rpm and measured using UV-Vis spectrophotometer. The reusability was carried out under optimal condition obtained from adsorption studies in batch adsorption. As much as 0.250 g of CuAlLDH@BC composite was added into 100 mL of CR with concentration 100 mg/L within 2 h at 30 °C. Then, the

CuAlLDH@BC was collected, washed by deionized water, dried at 90 °C for 1 h and reuse as adsorbent. The reusability of CuAlLDH@BC was examined by the repetition of CR adsorption for three cycles. Similar procedure was conducted using CuAl LDH and BC for reusability study.

RESULTS AND DISCUSSION

CHARACTERIZATION OF MATERIALS

The Fourier-transform infrared spectroscopy (FTIR) spectrum and XRD pattern of CuAl-LDH, BC, and the CuAlLDH@BC composite are shown in Figure 1. The broad vibration of hydroxyl groups (O-H stretching) in brucite layers and the interlayer was confirmed at 3420 cm^{-1} for both LDH samples. The lower vibration at 1635 cm^{-1} was attributed to O-H bending. The nitrate anion from the CuAl-LDH and CuAlLDH@BC interlayer was confirmed by an intense peak at 1381 cm^{-1}. The BC spectra shows a low intense peak that denotes the stretching vibration of C-O at 1645 cm^{-1}. The FTIR spectrum of both BC and CuAl-LDH appears in the CuAlLDH@BC composite and indicates that the composite material was successfully prepared. Figure 1 also shows the powder diffractogram of adsorbents. The CuAlLDH@BC diffractograms are composed of the characteristic diffraction pattern for CuAl-LDH and BC. CuAlLDH@BC show peaks at 10°, 28°, 35°, and 60° corresponding to reflections from (003), (006), (012), and (110), indicating that the material has a layered structure. The broad peak at 24° corresponds to the reflection plane (002) on the surface of the LDH due to the presence of BC. The interlayer space of the CuAlLDH@BC composite was 7.66 Å.
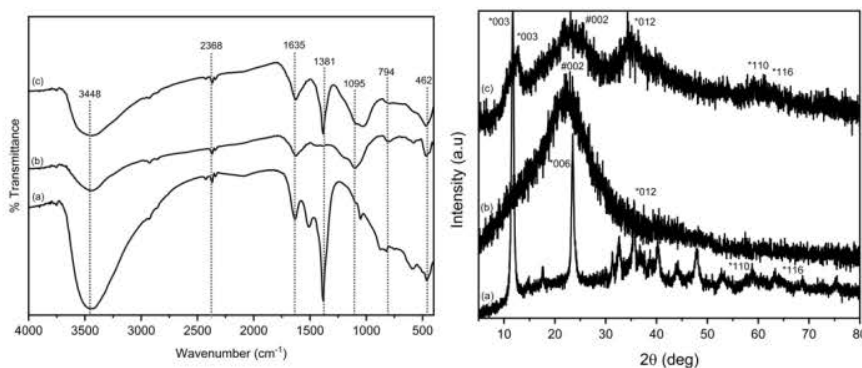

FIGURE 1. FTIR spectra and XRD pattern of (a) CuAl LDH, (b) BC, (c) CuAl-LDH@BC composite

The nitrogen adsorption-desorption isotherms of CuAl-LDH, BC, and CuAlLDH@BC are shown in Figure 2. The nitrogen adsorption-desorption curve indicates type IV, indicating a mesoporous material. The hysteresis loop of the materials is H3-type, consistent with a cavitation-induced desorption branch lower limit of $(P/Po) > 0.42$. The H3 hysteresis explain [7] the binding strength of anions located in the interlayer. Table 1 shows the BET surface areas, pore-volume, and pore size of CuAl-LDH, BC,

and CuAlLDH@BC. According to IUPAC classifications, the pore size of CuAlLDH@BC can be characterized as mesopore (Thommes et al. 2015). The surface area of CuAlLDH@BC according to the BET calculation is 200.9 m^2/g. Although the pore size of the composite is lower than CuAl-LDH, its pore volume increased three-fold. The decrease in pore size can be attributed to the loading of biochar into layers and the LDH surface. Azargohar and Dalai (2006) reported that carbon rich BC possesses no pores and has a low surface area.
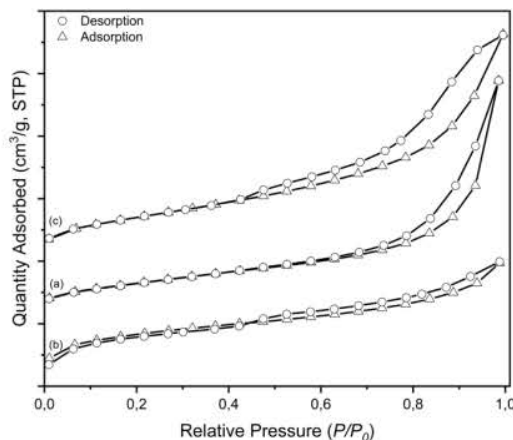

FIGURE 2. N_2 adsorption-desorption curve of (a) CuAl LDH, (b) BC, (c) CuAl-LDH@BC composite

TABLE 1. BET calculation results of LDH and BC adsorbents

Adsorbents	Pore volume cm³/g	BET surface m²/g	Pore size nm
CuAl LDH	0.116	46.2	10.39
BC	0.060	72.25	3.33
CuAlLDH@BC	0.350	200.90	7.03

The thermogravimetric curves of CuAl-LDH, BC, and CuAlLDH@BC precursors shown in Figure 3 have two dehydration steps; the dehydration of water molecules physisorbed at the external surface of the crystallites, and the dehydration of intercalated water molecules more strongly attached to hydrogen bonds. Figure 3(b) shows that the derivative thermogravimetric

(DTG) curve for BC also has two steps. The first denotes the oxidation of organic compounds and the differential thermal analysis (DTA) curve indicates an exothermic process. The second peak may be attributed to the oxidation of cellulose and bonding of organic molecules. Figure 3(c) shows that the DTG curve for CuAlLDH@BC shows a similar decomposition and weight loss curve for both materials.
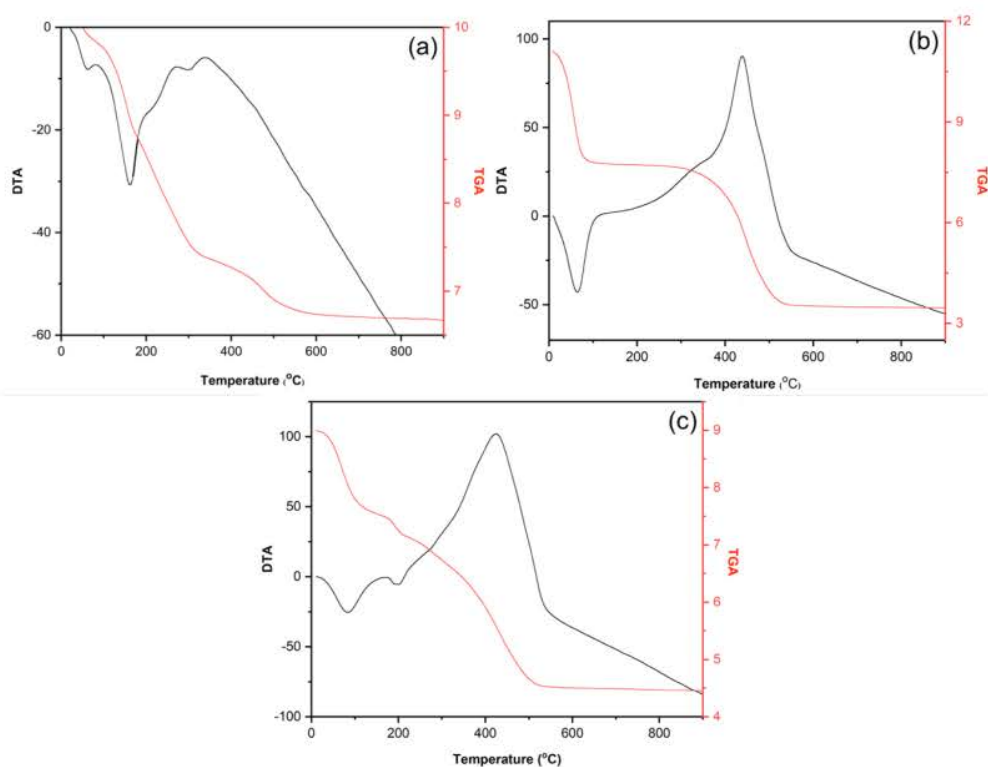
FIGURE 3. Thermogravimetry curve of (a) CuAl LDH, (b) BC, (c) CuAl-LDH@BC composite

The morphologies of CuAl-LDH, BC, and CuAlLDH@BC were investigated and the results are shown in Figure 4. CuAl LDH is characterized by heterogeneity with a round shape and aggregated particles on the surface. This is similar to the morphology reported by Mao and Jiao (2018), who attributed the aggregated morphology to high temperatures during the synthesis process. According to Bukhtiyarova (2019) and Parida and Mohapatra (2012), co-precipitation synthesis of LDH resulted in a plate-like morphology with agglomerated particles on the surface. Figure 4(c) shows that the surface morphology of CuAlLDH@BC has no particular BC-like structure and predominantly shows the presence of the LDH phase.

EFFECT OF CONTACT TIME ON CR REMOVAL

The effect of contact time on CR removal by CuAl-LDH, BC, and CuAlLDH@BC are depicted in Figure 5.

The effect of contact time on CR adsorption onto CuAl-LDH, BC, and CuAlLDH@BC showed the rapid diffusion of adsorbate molecule in mixing solution with active sites of adsorbent within 40 min. Thus, the adsorption interaction becomes gradual after equilibrium is reached. CuAl-LDH, BC, and CuAlLDH@BC reached equilibrium at 100, 70 and 40 min, respectively. The increased adsorption capacity was attributed to the driving force of the concentration gradient. The CR adsorption rate is associated with the interaction of adsorbate and adsorbent's surface. These findings indicated that a low adsorption rate is associated with the internal surface diffusion and pore-filling behavior. The kinetic model of CR removal by various adsorbents is also shown in Figure 5.
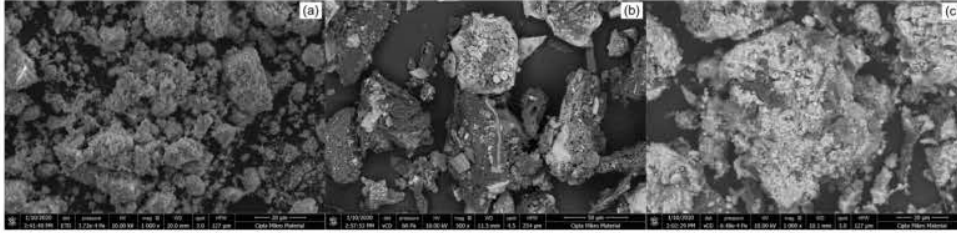
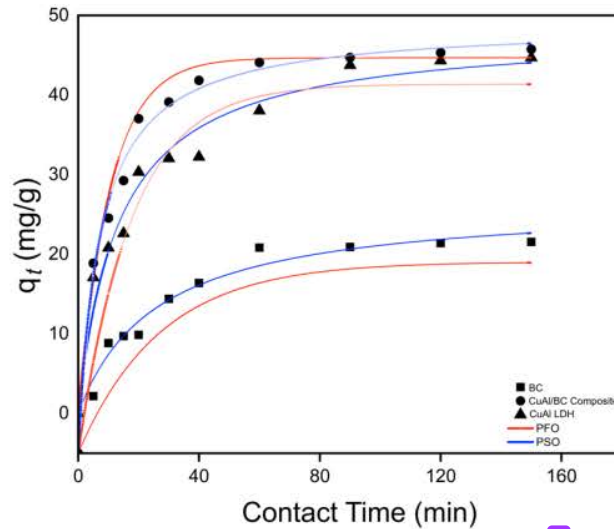FIGURE 4. SEM images of (a) CuAl LDH, (b) BC, (c) CuAl-LDH@BC composite

FIGURE 5. The curve of fitted kinetics model against the experimental data by CuAl LDH, BC, and CuAl-LDH@BC composite

Adsorption kinetics were investigated using pseudo-first order (PFO) and pseudo-second-order (PSO) models to predict the process mechanism for adsorbents. The PFO and PSO equations can be expressed by (1) and (2), respectively:

$$\log(qe - qt) = \log qe - \frac{k_1 t}{2.303} \qquad (1)$$

$$\frac{t}{qt} = \frac{1}{k_2 \, qe^2} + \frac{1}{qe} t \qquad (2)$$

where q_e and q_t represent the adsorption capacity at equilibrium and time; k_1 is the PFO rate constant; and k_2 is the PSO rate constant. Rate constants were obtained by plotting the equations to derive the correlation coefficients, and are listed in Table 2.

TABLE 2. Summary data for pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models fitted to Congo red (CR) adsorption by CuAl-LDh, BC, and CuAlLDH@BC

Adsorbent	$Qe_{experiment}$ (mg/g)	PFO			PSO		
		Qe_{Calc} (mg/g)	R^2	k_1	Qe_{Calc} (mg/g)	R^2	k_2
CuAlLDH@BC	46.143	24.400	0.988	0.037	47.619	0.998	0.097
CuAl LDH	44.705	39.763	0.974	0.038	49.261	0.995	0.007
BC	21.450	14.160	0.975	0.047	27.173	0.992	0.016

The parameters and correlation coefficients (R^2) obtained from linear plotting of log(qe-qt) versus t (PFO) and t/qt versus t (PSO) are shown in Table 2. In all cases, $R^2 > 0.992$ and results indicate that PSO is preferred over PFO. According to PSO model assumption, the adsorption rate-controlling steps can be attributed to the chemisorption process. This is further supported by the PSO $qe_{(calc)}$, which is close to the $qe_{(experiment)}$. These findings indicate that adsorption which suggests electrostatic attraction from adsorbate-adsorbent mixing. The increased k_2 value of the CuAlLDH@BC composite reflects the reduced time needed by the systems to achieve equilibrium. In other words, a higher k_2 value indicates that the adsorbate molecule is in a reactive condition (Nisar et al. 2016).

EFFECT OF TEMPERATURE AND ISOTHERM ADSORPTION

The effect of temperature and the initial concentration of CR on dye uptake was evaluated for CuAl-LDH, BC, and CuAlLDH@BC. Temperature was investigated between 303 - 333 K. Figure 6(a) represents the CR uptake for several concentrations of CuAl-LDH. The highest CR removal (49.31 mg/g) was observed at 333 K and a CuAl-LDH concentration of 90 mg/L. Figure 6(b) shows the highest CR uptake (32.08 mg/g) by BC was at 333 K and Figure 6(c) shows that the highest CR uptake (58.76 mg/g) by the composite was also at 333 K. Increased dye uptake with temperature can be attributed to decreased viscosity of the solution and increased porosity of the interlayer, resulting in the enhancement of active adsorbent sites.
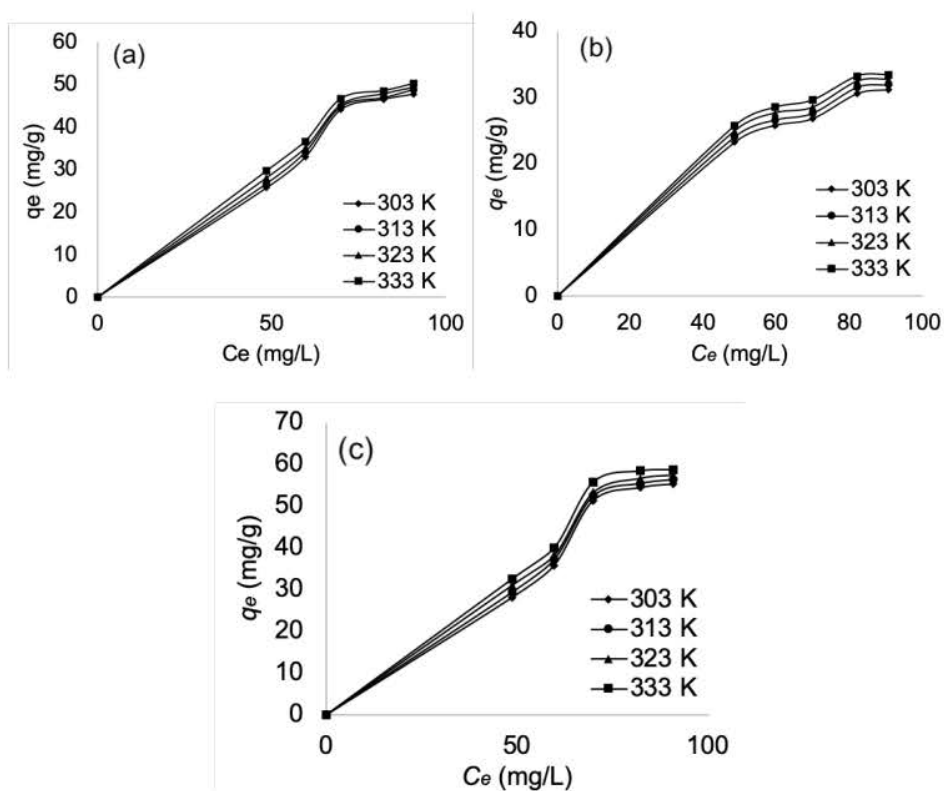
FIGURE 6. Effect of initial temperature of CR adsorption onto CuAl LDH (a), BC (b), CuAl LDH@BC composite (c)

The adsorption isotherm models are important to describe the adsorption mechanism for CR interaction on adsorbent surface. The equilibrium studies are useful to obtain the adsorption capacity of CR adsorption using CuAl-LDH, BC, and CuAlLDH@BC. The equilibrium isotherm model was tested is Freundlich and Langmuir. The Freundlich isotherm adsorption model usually describes a multilayer process on a heterogeneous surface and the Langmuir isotherm describes the interaction of adsorbent-adsorbate and the extent to which a layer or site is occupied on the homogeneous surface (Boutemak et al. 2019). The linear forms of the Langmuir and Freundlich isotherm models can be expressed by (3) and (4), respectively:

$$\frac{Ce}{qe} = \frac{1}{q_{max}}C_e + \frac{1}{q_{max}k_L} \quad (3)$$

$$\ln q_e = \ln k_F + \frac{1}{n}\ln C_e \quad (4)$$

where q_{max} and k_L represent Langmuir constant and and n are Freundlich constants with n providing an indication of a favorable adsorption process and to verify the type of adsorption. The isotherm adsorption parameters are shown in Table 3. In all cases, results show that the R^2 for the Langmuir model is higher than those of the Freundlich model, suggesting that CR adsorption is monolayer adsorption. The maximum adsorption capacities of CuAlLDH, BC, and CuAlLDH@BC were 56.818, 42.735, and 61.350 mg/g, respectively. Similar results of CR adsorption using several adsorbents have been reported by previous researches. According to Sriram et al. (2019), CR adsorption using diatomaceous earth (DE) obtained an adsorption capacity 23.2 mg/g at

TABLE 3. Isotherm adsorption parameters of CR adsorption using CuAl LDH, BC and CuAlLDH@BC

Adsorbent	Adsorption isotherm	Adsorption constant	T (K)			
			303	313	323	333
CuAlLDH@BC	Langmuir	Q_{max}	60.241	60.976	62.500	61.350
		k_L	0.034	0.053	0.092	0.234
		R^2	0.999	0.999	0.999	0.999
	Freundlich	n	1.393	1.459	1.921	3.183
		k_F	2.655	3.966	6.925	11.844
		R^2	0.998	0.986	0.999	0.995
CuAl-LDH	Langmuir	Q_{max}	54.348	56.180	56.556	56.818
		k_L	0.167	0.156	0.159	0.218
		R^2	0.999	0.998	0.999	0.998
	Freundlich	n	0.759	0.873	0.981	1.199
		k_F	2.359	1.246	1.321	2.610
		R^2	0.994	0.986	0.993	0.990
BC	Langmuir	Q_{max}	40.537	42.918	41.112	42.735
		k_L	0.044	0.031	0.057	0.064
		R^2	0.979	0.990	0.982	0.989
	Freundlich	n	2.820	1.427	1.159	1.263
		k_F	7.323	2.734	1.943	2.690
		R^2	0.959	0.990	0.962	0.958

pH 7. Lafi et al. (2016) have been reported that CR adsorption using MgAl LDH obtained 60.813 mg/g after shaken 180 min from an initial concentration was 100 mg/L. MgFe-carbonate is also reported as adsorbent of CR from aqueous solution. The result of adsorption capacity is 104.60 mg/g at pH 4 (Ahmed et al. 2020). NiCo2O4-NiO has been studied to remove CR in the aqueous phase, NiCo LDH modified using zeolitic imidazolate framework-67 (ZIF-67) by ultrasonic treatment. The adsorption result was showed the high adsorption capacity of up to 543.5 mg/g (Hu et al. 2019). Lian et (2009) also reported that Ca-bentonite was prepared to remove CR from wastewater. The adsorption capacity was slightly increased up to 23.25 mg/g, which was higher than bentonite pristine. Coal-based mesoporous modified activated carbons also reported a low adsorption capacity. The adsorption capacity result is 52 mg/g at pH 7.5 (adsorbent dosage 5 g, initial dye concentration 150 mg/L) (Lorenc-Grabowska & Gryglewicz 2007). On the other side, activated carbon prepared from coir pith has been studied to adsorb CR and has adsorption capacity up to 6.7 mg/g at pH 3 (Namasivayam & Kavitha 2002). These adsorption capacity results are very low if it compared to adsorption capacity of LDH's. According to previous results studies, the adsorption capacity of CuAlLDH@BC is middle-high value compared to other adsorbents.

THERMODYNAMIC STUDY

Thermodynamic parameters, including enthalpy (ΔH), entropy (ΔS), and Gibbs energy (ΔG) were determined using the Van't Hoff formula as shown in (5) and (6):

$$\Delta G = -RT \, ln \, (K_d) \qquad (5)$$

$$ln \, (K_d) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (6)$$

where R represents the universal gas constant and K_d is the adsorption distribution coefficient. The thermodynamic parameters were determined by calculating Van't Hoff linear regression as $1/T$ vs $ln \, (K_d)$ as seen in Figure 7. Table 4 lists the values of the thermodynamic parameters based on Figure 7's data. The negative value of ΔG at various temperatures confirms the spontaneity of the adsorption process and that it is more favorable at higher temperatures. The positive values of ΔS for CR adsorption using CuAl-LDH and CuAlLDH@BC correspond to the randomness of the solid-liquid phase interface during the adsorption process. The positive ΔH indicates that the adsorption process is endothermic, and this is supported by the fact that CR adsorption increases with temperature.

TABLE 4. The thermodynamic parameter of CR adsorption using CuAl LDH, BC and CuAlLDH@BC

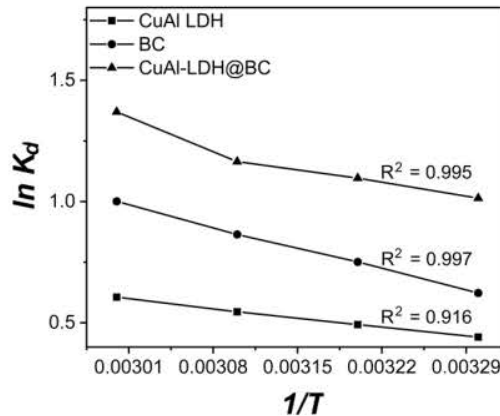| Adsorbents	$C_{initial}$	T (K)	Q_e (mg/g)	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)
CuAl LDH		303	51.270	39.967	0.134	-0.722
		313	52.381			-1.556
		323	53.254			-2.390
		333	55.714			-3.224
CuAlLDH@BC	90.698 mg/L	303	55.190	24.545	0.083	-0.752
		313	56.302			-2.096
		323	57.413			-3.440
		333	58.683			-4.784
BC		303	45.429	4.853	0.016	-0.004
		313	46.778			-0.165
		323	47.968			-0.325
		333	49.397			-0.485

FIGURE 7. Van't Hoff Plot of CR adsorption onto CuAl LDH,
BC and CuAl-LDH@BC

DESORPTION AND REUSABILITY

Desorption was evaluated by contacting the adsorbed dye on the solid surface with water, assuming that the interaction between the adsorbent-adsorbate was weak. Another study regarding adsorbent-adsorbate interaction, the adsorbed dye was desorbed by using HCl, or alcohol i.e. ethanol (Zhang & Gao 2013). Some eluents were tested in order to get suitable eluent for the desorption process. Figure 8 shows that HCl becomes suitable eluent for desorption process of CR onto CuAl-LDH, BC and CuAlLDH@BC with desorption percentage are 98.6, 98.3 and 94.1%, respectively. This finding indicated that in acid condition, the surface of the LDH becoming positively charged so that the electrostatic attraction of adsorbent-adsorbate and H-bonding were weak (Mittal et al. 2009). Furthermore, desorption was also high in the base solution due to hydrophobic interaction and OH- ions having a higher affinity for the anion exchange. The reusability process leads to determine the effectiveness of the potential adsorbent. The results of the reusability after the three cycles showed slight decreases in the effective adsorption process. Successively, the efficiency of CR removal decreased from 80.93 to 62.60% for the CuAlLDH@BC composite, from 76.37 to 53.57% for CuAl LDH, and from 54.32 to 44.24% for BC. Thus, in accordance with these results, CuAlLDH@BC composite can be promising as an adsorbent to remove CR.
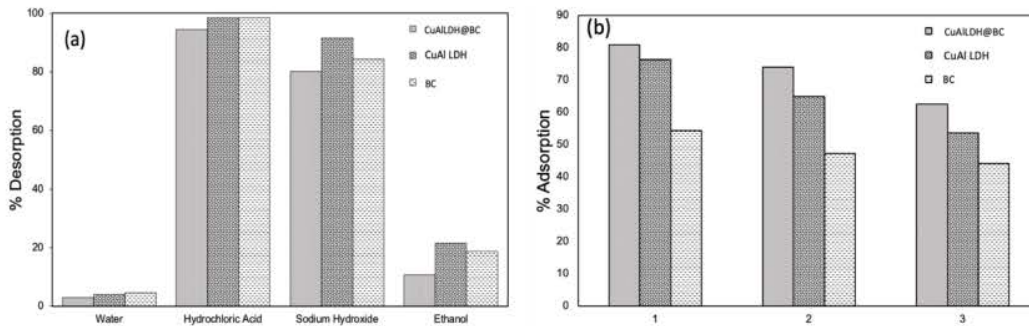

FIGURE 8. (a) CR desorption study and (b) regeneration of adsorbents

CONCLUSION

In this study, we prepared a composite based on copper-aluminum and biochar (CuAlLDH@BC) for CR adsorption. X-ray analysis showed that diffraction peaks of biochar and copper-aluminum layered double hydroxide appeared at 24° (002) and 10° (003), 28° (006), 35° (012), 60° (110), identical to those of the CuAlLDH@BC composite. The IR spectrum showed that the composite has the vibration of both starting materials at 1645/cm and 1381/cm. The surface area of CuAlLDH@BC increased markedly to 200.90 m²/g. Thermal analysis indicated that the patterns of the starting materials also appeared on the composite, as reflected by its heterogeneous shape.

The CuAlLDH@BC composite was used to adsorb CR, and adsorption parameters were determined using kinetic, isotherm, and thermodynamic methods. The PSO kinetic model was fitted for the CuAlLDH@BC composite, and the resulting $q_{e\ calculation}$ (47.619 mg/g) was close to the $q_{e\ experiment}$ (46.143 mg/g). Adsorption isotherm data suggested that adsorption followed the Langmuir model via monolayer adsorption processes with a maximum capacity of 61.350 mg/g for CuAlLDH@BC at 333 K. This capacity was larger than composite source materials; BC and CuAl-LDH demonstrated maximum adsorption capacities of 42.735 and 56.818 mg/g at 333 K, respectively. Thermodynamic analysis indicated that adsorption was spontaneous ($\Delta S > 0$) and endothermic ($\Delta G < 0$) for all adsorbents. The reusability efficiency concluded that the adsorption capacity of CuAlLDH@BC composite exceeded from 80.93 to 62.60% following three reusability cycles. We conclude that the composite is a high efficiency and reusable adsorbent for the removal of CR from an aqueous solution.

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