Low-Cost Yet High-Performance Hydrochar Derived from Hydrothermal Carbonization of Duku Peel (*Lansium domesticum)* for Cr(VI) Removal from Aqueous Solution

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Abstract: *Carbon-based adsorbent as a hydrochar (Hc) material with Duku (*Lansium domesticum*) peel precursors has been successfully synthesized as evidenced by XRD, FT-IR, BET, and SEM analysis. XRD analysis showed the presence of diffraction peaks around 16° and 22° which indicated the presence of carbonaceous material. This is confirmed by FTIR analysis which shows the presence of vibration at 2931 cm^{-1} of cellulose. SEM data results showed that heterogeneous and has an irregular shape and surface area increased twice from Duku peel to Hc. Duku peel and Hc adsorbent materials were applied to adsorb heavy metal ions Cr(VI). Kinetic parameters of Cr(VI) using Duku peel and Hc showed that the optimum time reached was at 120 min. The adsorption kinetics model of Cr(VI) using Hc tends to follow the PFO model and Langmuir isotherm adsorption. Duku peel material used to adsorb Cr(VI) reached an adsorption capacity of 42.19 mg/g, while in Hc material there was an increase that reached 80.64 mg/g. The thermodynamic parameters of both materials show that the adsorption process is spontaneous.*

Keywords: *hydrothermal carbonization; hydrochar;* Lansium domesticum *peel; adsorption; Cr(VI)*

■ INTRODUCTION

Environmental pollution is a serious problem that can be a health threat to living things and the environment [1]. The types of pollution that are mostly found are in the form of dyes, organic compounds, and heavy metal ions. Heavy metals are dangerous contaminants when they enter the environment through the water. Even heavy metal ions at low concentrations have been considered highly toxic [2]. Heavy metals can accumulate in the food chain and their resistance in the ecosystem will harm the environment. Heavy metals can come from various industrial activities such as metallurgy, textiles, batteries, mining, ceramics, and so on [3]. Cr(VI) is one of the most common heavy metal ions in wastewater. Cr(VI) is the most dangerous oxide form of Cr. The ability of Cr(VI) to form oxoanions in highly soluble water such as chromate and dichromate can be potentially harmful to human health. Cr(VI) which is toxic and carcinogenic can cause several respiratory, liver, and kidney problems [4]. This is because Cr(VI) cannot be degraded by the body and has high solubility and mobility in the environment [5] based on these various negative impacts, an efficient method is needed to overcome heavy metal ion contamination [6]. Various existing technologies such as photodegradation, coprecipitation, electrochemical degradation, electrocoagulation, and adsorption.

Adsorption is the most widely used method. High efficiency, easy to perform, low cost, and allows the adsorbent to be regenerated, making the adsorption method the right choice [6]. The adsorbent in a solid-state has a good ability to adsorb. Several of the most widely used adsorbents are zeolite, carbon, silica gel, and biosorbents [7]. Among all adsorbents, carbon-based materials have shown several advantages over other adsorbents. Its higher resistance to moisture and good thermal stability make this material continue to be developed, one of which is the hydrothermal carbonization method [8].

The hydrothermal carbonization method produces a product in the form of hydrochar (Fig. 1). Several studies have made the hydrochar material derived from raw materials such as orange peel, rice husk, pomelo skin, pea shells, pineapple peel, coconut husk, sawdust wood, and duku (*Lansium domesticum*) peel [9]. Duku (*Lansium domesticum*) peel was chosen because it contains carbon compounds and their abundance that is easy to find. *Lansium domesticum* is a species of the Meliaceae family that can grow to 40–50 feet. The fruit is locally known as langsat, long-kong, duku, lang-sook, or langsat-khao [10]. Hua et al [11] research explains that hydrochar prepared from microbial aging can adsorb Cd(II) with an adsorption capacity of 4.19 mg/g. On the other hand, the use of hydrochar as an adsorbent from pinewood biomass showed the ability of Pb(II) adsorption with an adsorption capacity of 46.70 mg/g [12]. Research conducted by Wang et al used the skin of the pomelo fruit as an adsorbent for Cr(VI). The surface area of the pomelo skin is 3.85 m^2/g with an adsorption capacity of 0.57 mg/g [13]. On the other hand, Li et al. [14] conducted a study on overcoming Cr(VI) contamination by the adsorption method using hydrochar made from bamboo sawdust. The resulting adsorption capacity of Cr(VI) reached 3.20 mg/g. The adsorption process of Cr(VI) using hydrochar has also been proven by Shi et al. [15] which uses corn cobs to have a maximum adsorption capacity of 7.23 mg/g. These data confirm that the hydrochar material has a good ability in the adsorption process due to its low-cost and efficiency than nanocomposites and synthesis materials. Therefore, this research was conducted

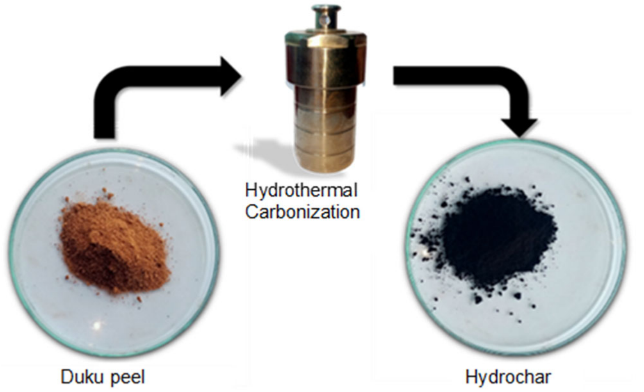

Fig 1. Schematic illustration of hydrochar formation using hydrothermal carbonization method

to maximize the use of Duku peel waste and its application as a waste-based adsorbent. This study proves that the development of Duku peel into hydrochar (Hc) material through the hydrothermal carbonization method has a good ability to adsorb heavy metal ions Cr(VI). Fruit peel waste is quite abundant but still lacking in utilization is Duku peel waste. According to Fig. 1, hydrothermal carbonization method is carried out as an easy and inexpensive method. This is certainly very beneficial in terms of research and utilization of a waste-based adsorbent. Shankar et al. [16] revealed that Duku peel contains phenolic compounds. The content of these compounds allows Duku peel to bond with metals. According to Lam et al. [17], the abundance of Duku peel with unique chemical content, non-toxic and reusable makes Duku peel potential to be a biosorbent. The success of Hc material synthesis was characterized by XRD, FTIR, and a surface area analysis. The ability of the two materials is determined by kinetics, isotherm, and thermodynamic parameters.

■ EXPERIMENTAL SECTION

Materials

The chemicals used in this experiment were $K_2Cr_2O_7$ (Merck, 99.8%), 1,5-diphenylcarbazide (Sigma Aldrich, 98%), H_2SO_4 37% by MallinckrodtAR®. The hydrochar source was made from *Lansium domesticum* peel. Water was obtained using a Purite® water purification system from the Research Center of Inorganic Materials and Complexes.

Instrumentation

The material characterization was performed using X-Ray Diffraction (XRD) Rigaku mini flex-6000, Fourier-Transform Infrared Spectrocopy (FTIR) Shimadzu Prestige-21, surface area analyzer Quantachrome Instruments, and Scanning Electron Microscopes (SEM) analyzer SU800 Series. The concentration of Cr(VI) complexed with diphenylcarbazide was analyzed using a spectrophotometer UV-Visible Biobase BK-UV 1800PC.

Procedure

Duku peel biosorbent preparation

Duku peel is cut into small pieces and washed using water until clean, and dried under the sun, then oven at 100 °C for 8 h, mashed, and sieved using a 40 mesh filter.

Hydrothermal carbonization

A total of 2.5 g of duku peel and 50 mL of water were put into a 100 mL Hydrothermal Stainless-steel Autoclave, then oven at 200 °C for 12 h. After that, the Hc precipitate was cooled at room temperature for 12 h and washed with distilled water, then dried in an oven at 105 °C for 24 h to obtain the Hc product, which was further characterized using XRD, FTIR, BET, and SEM analysis.

Kinetics, isotherm and thermodynamic study

Kinetic studies were carried out to determine the adsorption kinetics model by adding 0.02 g of adsorbent to 20 mL of Cr(VI) solution with time variations 0, 10, 20, 30, 40, 50, 60, 70, 90, 120, 150, and 180 min. The effect of temperature and concentration was carried out to determine isotherm parameters and thermodynamic adsorption of Duku peel and Hc. Addition of 0.02 g of adsorbent to 20 mL of Cr(VI) solution with a concentration of 25, 50, 75, 100, and 125 ppm, then stirring for 60 minutes with temperature variations of 30, 40, 50, 60 and 70 °C. The complexation of Cr(VI)-diphenylcarbazide was carried out by Cr(VI) solution (10 mL) added diphenylcarbazide solution (2 mL, 1000 mg/L) and H_2SO_4 (1 mL, 1 M). The mixing solution was homogeneous within 5 min. Measurement of the concentration of Cr(VI)-diphenylcarbazide adsorption was carried out using a UV Vis spectrophotometer at a wavelength of 543 nm.

RESULTS AND DISCUSSION

The characteristics of the Duku peel and Hc adsorbent materials were analyzed by XRD, FTIR, BET, and SEM. XRD analysis is one of the main characterizations of the Duku peel to Hc preparation in Fig. 2. XRD analysis is used to determine changes in the crystal structure in Duku peel biomass to Hc during the hydrothermal carbonization process. Fig. 2 shows the diffractogram of the Duku peel at diffraction angles of 16.90° and 21.80°. The hydrothermal carbonization process carried out on Duku peel to produce Hc did not significantly change the XRD pattern. It is proven that Fig. 1 shows the XRD pattern of Hc which is at the diffraction angle of 16.00° and 22.47°.

According to Yadav et al [18], the peaks around 16° indicate that the material is in the crystalline phase and 22° are specific regions for cellulose compounds. This indicates that the Hc synthesis of the Duku peel does not change the structure of cellulose. The hydrothermal carbonization process affects the intensity of the diffractogram peak of the Duku peel which tends to be amorphous but after the process it produces Hc which tends to have better crystallinity.

In addition to XRD analysis, the success of Hc material synthesis is also supported by FTIR analysis in Fig. 3. This analysis is used to detect functional groups

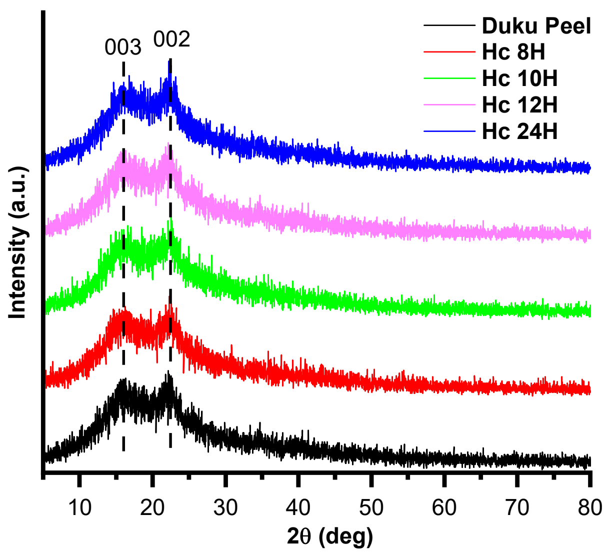

Fig 2. XRD pattern of the Duku peel and Hc

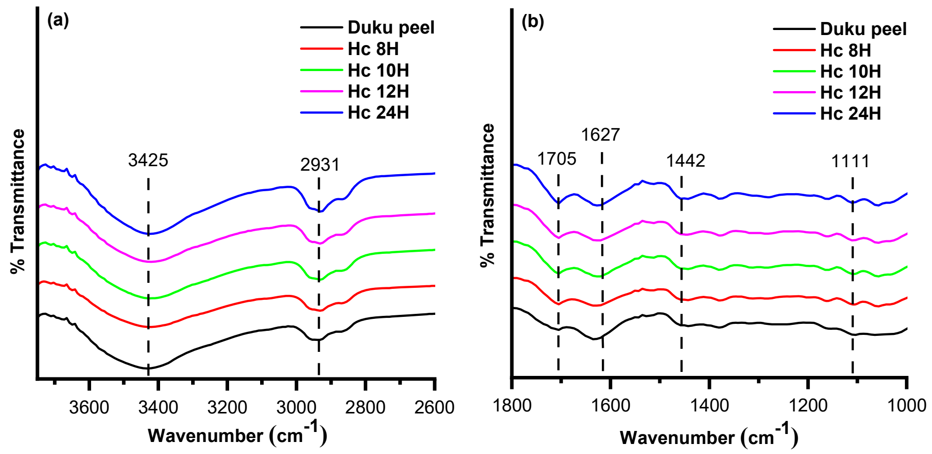

Fig 3. FTIR spectra of Duku peel and Hc at 200 °C in different times of hydrothermal process at wavenumber (a) 2600–3750 cm^{-1} and (b) 1000–1800 cm^{-1}

contained in Duku peel and Hc. Fig. 3(a) shows the spectra of the Duku peel, while Fig. 3(b) shows the Duku peel spectra that have gone through the hydrothermal carbonization process to Hc.

The spectra showed the similarity of vibrations at 3425 and 1627 cm^{-1} which indicates the –OH from hydroxyl and carbonyl groups [19] group of alcohol in both materials. Another vibration also appeared at 2931 cm^{-1} which indicated the presence of C–H cellulose [20]. The sharp vibration at 1635 cm^{-1} indicates the C=O group of the primary amide vibrations. Meanwhile, another vibration in 1442 cm^{-1} indicates C=C stretching from aromatic compounds [21]. Based on He et al. [22] it has been confirmed that there are vibrations of C=O at 1705 cm^{-1}.

One of the advantages of the hydrothermal carbonization process is that it increases the surface area of the material. To prove this, a surface area analysis was performed to measure the increase in surface area from Duku peel to Hc. This surface area analysis also displays the measurement results of pore volume and pore diameter. Surface area analysis was carried out by the N_2 adsorption-desorption process which produced the isotherm pattern in Fig. 4.

The Hc isotherm pattern in Fig. 4(b) tends to resemble the pattern of the Duku peel isotherm. According to IUPAC, Type III isotherm shows the characteristic of weak interaction between adsorbent and adsorbate, where the affinity between the adsorbent molecules is greater

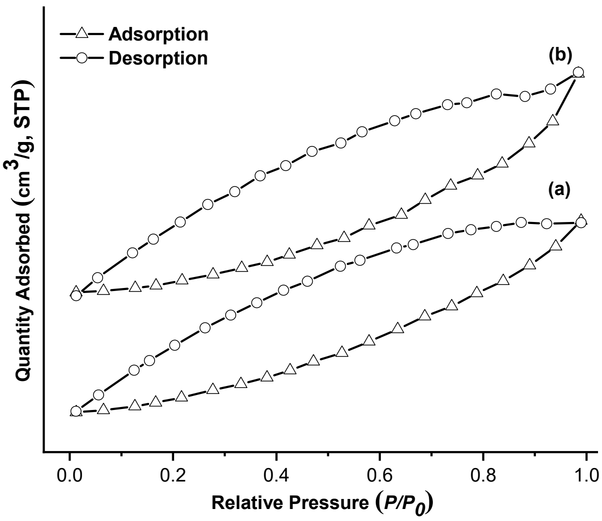

Fig 4. N_2 adsorption-desorption isotherm of the (a) Duku peel and (b) Hc

than the affinity for the surface of the adsorbent. The type III isotherm pattern is an indication that the material has low adsorption energy [23]. BET measurement data on the surface area, pore-volume, and pore diameter for both adsorbents are presented in Table 1.

The data in Table 1 shows the results of measuring the surface area of the Duku peel of 12.34 m^2/g. After the carbonization process took place, there was an increase in the surface area of the hydrochar material which almost doubled to 22.63 m^2/g. This indicates that the hydrothermal carbonization process succeeded in increasing the surface area of the material.

Table 1. BET surface area analysis

Materials	Surface area (m^2/g)	Pore size (nm), BJH	Pore volume ($(cm^2/g)_{BJH}$)
Duku peel	12.34	0.02	2.64
Hc	22.63	0.04	2.76

Table 2. Parameter of adsorption kinetic model on Duku peel and Hc

Parameter		Adsorbent	
		Duku peel	Hc
1st order	qPFO	56.46	58.23
	k_1 (1/min)	0.05	0.05
	R^2	0.99	0.99
2nd order	q-PSO (mg/g)	58.13	63.29
	k_2 (mg/min)	0.001	0.001
	R^2	0.911	0.96
Elovich	a (g/mg)	386.00	25.16
	b (g/mg.min)	0.08	0.07
	R^2	0.89	0.93

Scanning Electron Microscopy (SEM) analysis is used to see the surface morphological structure, and particle size and to show the crystallographic structure of the observed material object. Fig. 5(a) presents the SEM analysis results of Duku peel adsorbents which tend to clump in the same phase or what is commonly referred to as aggregation. Fig. 5(b) shows the particle morphological pattern of the Hc adsorbent which tends to be heterogeneous and has an irregular shape: this is due to the hydrothermal carbonization treatment given, causing the particles to experience a breakdown or what is commonly known as deaggregation.

The ability of the adsorbent material was tested through the isotherm and thermodynamic parameters of adsorption. Based on the physical adsorption process, allows the adsorbent material to be regenerated because the weak bond between the adsorbent and the adsorbate is easily released so that the adsorbate is easily desorbed. The kinetics parameters were carried out by varying the adsorption contact time, the results of which were presented in Fig. 6. The graph shows that the Cr (VI) adsorption process using both adsorbents reached the optimum time of 120 min. The results of determining the kinetics of Cr(VI) adsorption parameters are presented in Table 2.

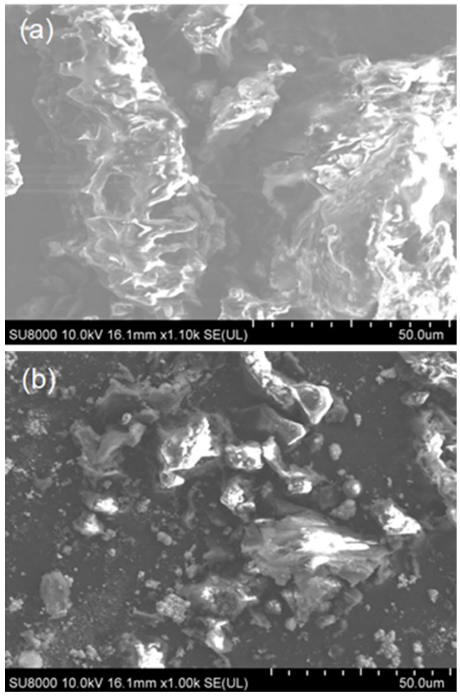

Fig 5. SEM of (a) Duku peel and (b) Hc

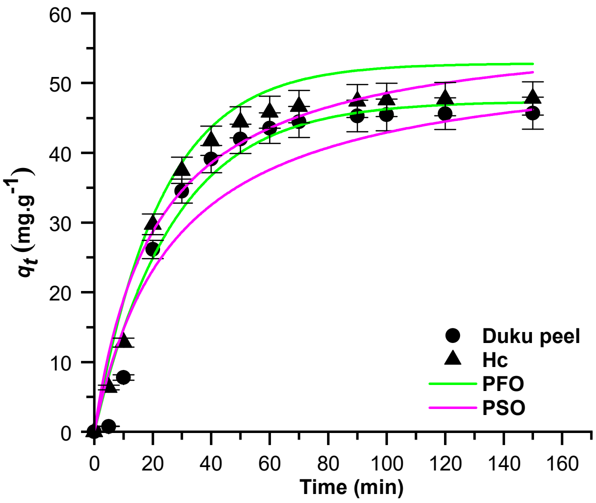

Fig 6. The effect of variations in the adsorption time of Cr(VI)

The parameters of the kinetics model are calculated from the slope and intercept of each plot. The kinetics model was determined based on the regression coefficient R^2 [24]. Table r shows the Duku peel and Hc materials in the PFO kinetics model which are closer to 1, with values of 0.99 and 0.99, respectively. Moreover, the Qe_{calc} value of the two materials at PFO is closer to the Qe_{exp} value. This proves that the adsorption of

Cr(VI) using Duku peel and Hc follows the PFO kinetics model. According to Jiang et al. [25], the PFO kinetics model assumes the adsorption rate is influenced by the active site of the adsorbent.

Both of these parameters were determined by varying the concentration and adsorption temperature, as shown in the graph in Fig. 7. The graph explains that the Cr(VI) adsorption process using Duku peel and Hc has an increased adsorption capacity as the concentration and temperature increase. The adsorption results on the graph also show that the adsorption ability of Hc is better than Duku peel. The adsorption isotherm parameters determined were Langmuir and Freundlich isotherm models, in Table 3.

The value of the Cr(VI) adsorption capacity of the Duku peel in Table 3 reaches 42.19 mg/g, while the Hc adsorption capacity is as wide as 80.64 mg/g. This shows that the adsorbent synthesis by the hydrothermal method was successful in increasing the adsorption capacity significantly with increasing surface area which is evidenced in the N_2 adsorption-desorption analysis data in Table 1. Table 3 also shows the linear regression values of the Langmuir and Freundlich isotherm parameters.

Duku peel adsorbent material has an R^2 value of 0.99 in the Langmuir isotherm model and 0.891 in the Freundlich. The R^2 value of Hc on the Langmuir model is 0.98, while the Freundlich model is 0.96. According to Juleanti et al. [26], the determination of the adsorption isotherm model is based on a linear regression value that is close to 1, so that the Cr(VI) adsorption process using Duku peel and Hc materials tends to follow the Langmuir isotherm model. Langmuir isotherm model is used to describe the absorption process where there is no interaction between adsorbate molecules on the side that has the same absorption energy [27]. According to Bahar Nur Siregar et al. [28], Langmuir's isotherm model is based on the interaction between the adsorbent and the thermodynamic parameter data in the form of enthalpy (*ΔH*), entropy (*ΔS*), and Gibbs free energy (*ΔG*) are presented in Table 4.

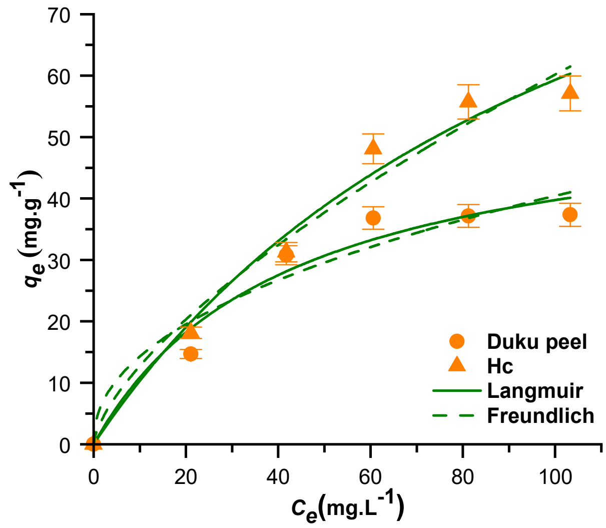

Fig 7. Effect of concentration and temperature on the adsorption of Cr(VI) onto Duku peel and Hc

Table 3. Parameter of adsorption isotherm models on Duku peel and Hc

Adsorbent	Adsorption isotherm	Adsorption constant	T (K)			
			303 K	313 K	323 K	333 K
Duku peel	Langmuir	Q_{max}	20.61	30.30	34.01	42.19
		kL	0.33	0.08	0.19	0.14
		R^2	0.99	0.98	0.99	0.98
	Freundlich	N	1.14	1.23	1.97	2.43
		kF	1.69	1.33	1.38	1.43
		R^2	0.90	0.99	0.95	0.99
Hc	Langmuir	Q_{max}	51.81	57.14	76.92	80.64
		kL	0.02	0.03	0.04	0.10
		R^2	0.98	0.99	0.99	0.99
	Freundlich	n	0.37	0.44	0.51	0.74
		kF	1.32	1.36	1.37	1.42
		R^2	0.99	0.99	0.99	0.89

Table 4. Thermodynamic parameters for adsorption of Cr(VI) on Duku peel and Hc

Material	$\Delta H°$	$\Delta S°$	$\Delta G°$ (kJ/mol)			
	(kJ/mol)	(J/mol.K)	303 K	313 K	323 K	333 K
Duku peel	51.22	0.16	2.62	1.02	-0.58	-2.18
	49.31	0.15	1.97	0.41	-1.14	-2.71
	30.12	0.09	1.58	0.64	-0.29	-1.24
	27.29	0.08	2.90	-2.09	-1.29	0.48
	24.01	0.06	3.56	-2.89	-2.22	1.54
Hc	55.52	0.18	0.61	-1.20	-3.01	-4.82
	39.95	0.12	1.09	-0.19	-1.47	-2.75
	35.17	0.11	-0.10	-1.26	-2.42	-3.59
	23.97	0.07	0.25	-0.53	-1.31	-2.09
	18.38	0.05	1.10	0.53	-0.03	-0.61

The positive value of the entropy energy ($\Delta S°$) indicates that there is increased randomness at the solid/solution interface [29]. The enthalpy values of Duku peel which are in the range of 24.01–51.22 kJ/mol in Table 4 indicate a positive value. The same thing as Hc, the adsorption enthalpy value is around 18.38–55.52 kJ/mol with a positive value of enthalpy indicating that the adsorption process was endothermic. Palapa et al. [30] confirmed that the enthalpy range at 5–40 kJ/mol indicates the occurrence of physical adsorption, whereas if the enthalpy is more than 40 kJ/mol indicates the occurrence of chemical adsorption. Based on the enthalpy value of Duku peel and Hc, the overall adsorption process takes place physically, but some circumstances indicate that the adsorption takes place chemically because the enthalpy value is more than 40 kJ/mol [31]. According to these data, the adsorption process of Cr(VI) by Duku peel and Hc occurred in physical and chemical sorption. For comparison, Table 5 presents data from studies on Cr(VI) adsorption using several adsorbents. Based on Table 5, the results data of Cr(VI) adsorption using Hc is better than others researchers. This assumed that Hc from Duku peel has good ability for Cr(VI) removal.

In addition, the Cr(VI) adsorption mechanism (Fig. 9) is clarified through FTIR data after adsorption which is presented in Fig. 8. The spectra before and after

Tabel 5. Comparison of the adsorption of Cr(VI) using several adsorbents

Adsorbent	Adsorption capacity (mg/g)	Reference
Pineapple peel-derived biochars	41.67	[32]
Rice husk biochar	8.14	[33]
Tea waste biochar	9.12	[33]
Activated clay biochar composite	6.10	[34]
Holey graphene	5.48	[35]
Watermelon peel	72.49	[36]
Algal-bacterial aerobic granular sludge	51	[37]
Biochar derived from bamboo residues	40	[38]
Algae *Sargassum bevanom*	39.68	[39]
Biomass of *Sargassum dentifolium*, Seaweed	41.20	[40]
HA-Cell-RH	19.39	[13]
Bamboo sawdust hydrochar	3.20	[14]
Corn cobs hydrochar	7.23	[15]
Duku peel	42.19	This Research
Hc	80.64	This Research

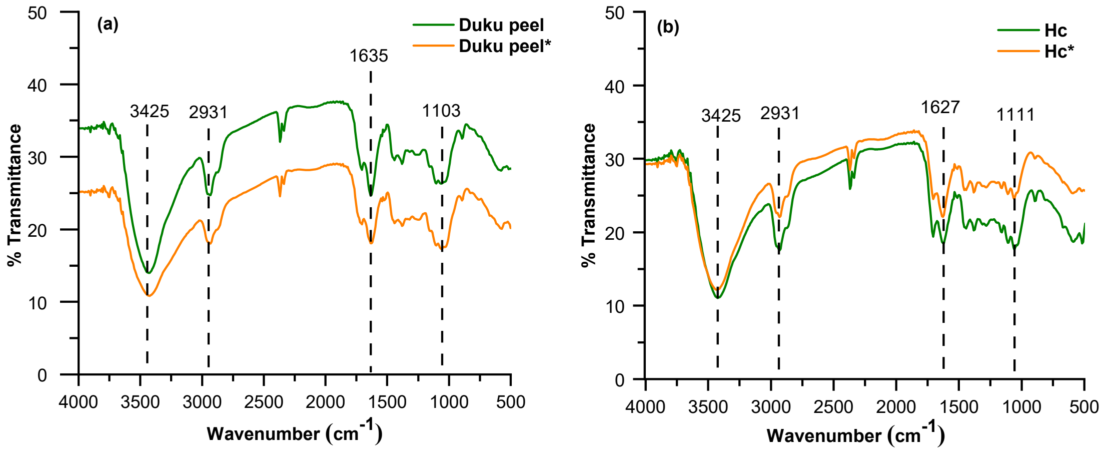

Fig 8. FTIR spectra of adsorbent after the Cr(VI) adsorption process using (a) Duku peel and (b) Hc

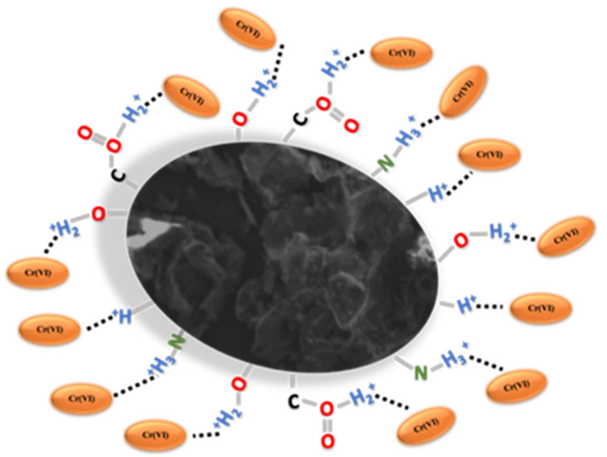

Fig 9. Illustration of the Cr(VI) adsorption mechanism

adsorption did not show much change. However, there is a band around 3700 cm^{-1} which indicates that the adsorbed Cr(VI) metal binds to the N–H group. On the other hand, the dominant band at 1600 cm^{-1} indicates that the adsorbed Cr(VI) binds to C=O. Based on the spectrochemical series which shows that C=O is a strong ligand, the chemical adsorption mechanism that dominates Cr(VI) may tend to bind with C=O compared to N–H.

CONCLUSION

The development of biosorbent material from Duku peel to Hc through the hydrothermal carbonization method has been successfully carried out. This is evidenced by the FTIR characterization data which shows the characteristic functional groups of Duku peel on Hc. In addition, the XRD data also shows distinctive diffraction at an angle of 21.18 (002) which is a characteristic of carbon materials with heterogeneous morphology particle. The superiority of the hydrothermal carbonization method which can increase the surface area of the adsorbent is proven by the nitrogen adsorption-desorption analysis data. The surface area of the Duku peel which was initially only 12.343 m^2/g, after going through the hydrothermal carbonization process into Hc material increased twice to 22.635 m^2/g. Furthermore, the increase of surface area is analogous to increasing adsorption capacity. From the adsorption study, this material has good performance for adsorption, from 42.194 mg/g (Duku peel) to 80.645 mg/g (Hc); followed by PSO kinetic study, Langmuir isotherm study. Hc material which has a surface area and adsorption capacity greater than Duku peel indicates that the hydrothermal carbonization method is effective for the synthesis of the adsorbent material.

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