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Fabrication of Adsorbent using Nano-Sized Lignocellulosic Biochar Coated on *Luffa aegyptiaca* Sponge to Remove Heavy Metal Chromium VI

(Pembuatan Penjerap menggunakan Bioarang Lignoselulosa Bersaiz Nano Disalut pada Span *Luffa aegyptiaca* untuk Menyingkirkan Logam Berat Kromium VI)

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ABSTRACT

Eliminating heavy metal Cr (VI) in liquids is challenging. Developing adsorbents using sustainable, cheap, and biodegradable materials is still a concern. Therefore, this study aims to synthesize a heavy metal adsorbent by transforming forest residue into nano-sized lignocellulose biochar. This nano-sized lignocellulosic biochar, with the assistance of chitosan and alginate, was coated onto the *Luffa aegyptiaca* sponge surface to complete the structure of the proposed heavy metal adsorbent. This adsorbent is easy to apply in adsorbing heavy metals, is durable, and can be reused. The adsorbent products were characterized to observe the functional groups by Fourier Transform Infrared (FTIR) and surface morphology by Scanning Electron Microscopy (SEM). The adsorbents were also experimented with contact times of 120 and 1200 minutes in the adsorption process. The decrease in heavy metal concentration was analyzed by Atomic Absorption Spectroscopy (AAS). Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy (SEM-EDX) observed the adsorbent surface that has absorbed heavy metal ions. FTIR characterization of surface functional groups showed the presence of hydrogen, aliphatic C-H group, C=C aromatic ring, carboxyl groups, and carbonate ion, capable of binding heavy metal Cr (VI). The morphology of the adsorbent coated on luffa showed that the adsorbent was well attached. The results of the adsorption process showed a decrease in Cr (VI) concentration, with adsorption efficiency reaching 94% for 1200 min and adsorption capacity of 0.36 mg/g. SEM-EDX results validated the attachment of Cr (VI) heavy metal ions to the adsorbent surface.

Keywords: Adsorbent coating; forest residual; lignocellulosic biochar; *Luffa aegyptiaca*

ABSTRAK

Menyingkirkan logam berat Cr (VI) dalam cecair adalah satu cabaran. Membangunkan bahan penjerap menggunakan bahan yang mampan, murah dan boleh terurai masih menjadi kebimbangan. Oleh itu, kajian ini bertujuan untuk mensintesis bahan penjerap logam berat dengan menukar sisa hutan menjadi bioarang lignoselulosa bersaiz nano. Bioarang lignoselulosa bersaiz nano ini, dengan bantuan kitosan dan alginat, telah disalutkan ke atas permukaan span *Luffa aegyptiaca* untuk melengkapkan struktur bahan penjerap logam berat yang dicadangkan. Bahan penjerap ini memberikan kelebihan dalam penggunaannya yang mudah dalam menjerap logam berat, tahan lama dalam larutan dan boleh digunakan semula. Produk penjerap ini telah dicirikan untuk mengesan kumpulan berfungsi dengan Infra-Merah Transform Fourier (FTIR) dan morfologi permukaan dengan Mikroskopi Elektron Pengimbasan (SEM). Bahan penjerap juga diuji dengan masa sentuhan 120 dan 1200 minit dalam proses penjerapan. Penurunan dalam kepekatan logam berat dianalisis dengan Spektroskopi Serapan Atom (AAS). Mikroskopi Elektron Pengimbasan bersama Spektroskopi Serakan Tenaga Sinar-X (SEM-EDX) mengesan permukaan penjerap yang telah menyerap ion logam berat. Pencirian FTIR bagi kumpulan berfungsi permukaan menunjukkan kehadiran hidrogen, kumpulan

alifatik C-H, cincin aromatik C=C, kumpulan karboksil dan ion karbonat yang mampu mengikat logam berat Cr (VI). Morfologi bahan penjerap yang disalutkan pada luffa menunjukkan bahawa bahan penjerap melekat dengan baik. Keputusan proses penjerapan menunjukkan penurunan kepekatan Cr (VI), dengan keberkesanan penjerapan mencapai 94% untuk 1200 minit dan kapasiti penjerapan sebanyak 0.36 mg/g. Keputusan SEM-EDX mengesahkan sangkutan ion logam berat Cr (VI) kepada permukaan bahan penjerap.

Kata kunci: Bioarang lignoselulosa; lapisan penjerap; *Luffa aegyptiaca*; sisa hutan lignoselulosa

Introduction

Chromium is a transition metal commonly found in nature, and its toxicity is primarily associated with the hexavalent form, Cr (VI). Cr (VI) compounds find extensive applications in various industries, including textile production (Biju et al. 2022), batik dyeing (Sri Lestari et al. 2020), and tanned leather (Arellano-Sánchez et al. 2021). Cr (VI) exposure causes multiple adverse health effects to various adverse health effects (Aminatun et al. 2019; Aslam, Yousafzai & Javed 2022), including respiratory and gastrointestinal problems, kidney damage, and even carcinogenicity. Cr (VI) poses significant ecological threats by accumulating in soil and water, affecting flora and fauna within affected ecosystems (Arellano-Sánchez et al. 2021; Biju et al. 2022; Briffa, Sinagra & Blundell 2020; Mohiuddin, Mdleleni & Key 2018; Zhang & Li 2021). The adsorption process is a promising and reliable method to bind heavy metals by adsorbing contaminants through the adsorbent surface. This research focuses on fabricating adsorbents for Cr (VI) removal with environmentally friendly chemistry, sustainable techniques, cost-effectiveness, and renewable resources.

Biomass renewable resources such as forest residues have great potential as adsorbents for contaminant removal (Kwapinski et al. 2010; Vieira et al. 2022; Xiang et al. 2020). Forest residues offer an eco-friendly alternative to conventional adsorbents, sustainable sources, abundant availability, reduced dependence on non-renewable resources, and minimized environmental impact (Crini et al. 2019; Inyang et al. 2016; Vieira et al. 2022). Renewable resource-based adsorbents such as biochar show promising potential for Cr (VI) removal (Xiang et al. 2020), but several challenges are present in their practical implementation. These include optimizing adsorbent preparation methods, improving adsorption capacity, and cost-effectiveness.

Forest residual-derived lignocellulosic biochar has gained significant attention as a potential adsorbent for heavy metals (Vieira et al. 2022). The main composition of lignocellulosic biomass is cellulose, hemicellulose, and lignin (Chemerys et al. 2018b). Pyrolysis methods can convert this lignocellulosic into biochar, a carbon-rich material with minerals (Baharim et al. 2023; Mukherjee et al. 2022). These biochar materials possess desirable characteristics, including functional groups that bind heavy metal ions, high surface area, and porosity (Chemerys et al. 2018a; Lu et al. 2012). Functional groups that can bind ion contaminants include hydrogen (O-H) bonds, C-H bonds, C-C bonds, carboxyl (C=O) functional groups, C=C bonds, N-H bonds, and carbonate ions (Arana et al. 2017; Deng et al. 2017; Inyang et al. 2016; Mukherjee et al. 2022; Xiang et al. 2020). An illustration of heavy metal binding by biochar surface functional groups is shown in Figure 1. The adsorption properties of lignocellulosic biochar can be improved through physical, chemical, and thermal modifications (Elfi Yulia, Estiyanti & Bambang 2023). In this investigation, physical modification of lignocellulosic biochar was performed using ball milling techniques, which involved reducing its particle size to the nanoscale (previous research) (Elfi Yulia et al. 2023). Biochar as an adsorbent is widely applied in powder form, like banana biochar (Chemerys et al. 2018b). This research developed a nanopowder biochar adsorbent attached to a luffa sponge that will be easily applied to a contaminated solution.

Luffa aegyptiaca, a minor vegetable commodity that sub-tropical plant belonging to the *Cucurbitaceae* family, is recognized as a biodegradable material, non-toxic, low-cost, a natural, and falls under the category of natural and renewable resource (Liu et al. 2015; Nadaroglu, Cicek & Gungor 2017; Wang et al. 2021). Products from luffa sponge are accessible in the pharmaceutical, cosmetics, and other industries

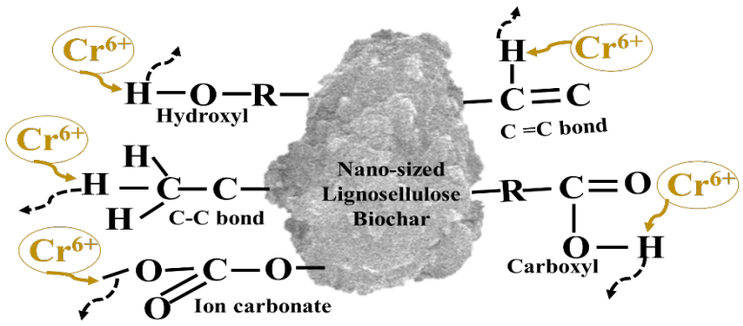

FIGURE 1. Illustration of biochar adsorption mechanism on heavy metals

(Anastopoulos & Pashalidis 2020). The fibrous structure of the natural luffa sponge primarily consists of 60% cellulose, 30% hemicelluloses, 10% lignin, and crisscrossed fibers form a three-dimensional reticular (Anastopoulos & Pashalidis 2020; Liu et al. 2015). Luffa fibers exhibit excellent mechanical properties, high permeability, high specific hole capacity, a complex macroscopic architecture structure, and multifunctional groups (Liu et al. 2015; Nadaroglu, Cicek & Gungor 2017). Various modification techniques have been applied to luffa sponge fibers to enhance adsorption capacity, including activated carbon (Kong et al. 2017; Wang et al. 2021), polymer grafting (Liu et al. 2015), and ionic liquid modification (Wang et al. 2018). These modifications positively affected adsorption capacity but were challenging to separate from aqueous solutions in practical applications. Because of this, other researchers tried to maintain the luffa sponge's shape by making modifications, such as crosslinking the luffa sponge and chitosan (Schio et al. 2021), modified with Zn nanoparticles (Nadaroglu, Cicek & Gungor 2017). This research also used the original shape of the luffa sponge to facilitate the application of the adsorbent in the contaminant solution.

The attachment of lignocellulosic biochar to the luffa sponge in this study was assisted by chitosan and alginate. The use of chitosan or alginate as natural polymers in the production of green adsorbents has been widely produced (Ahmad, Manzoor & Ikram 2017; Wang et al. 2016). Natural polymers have the advantages of renewability, biodegradability, reproducibility, biocompatibility, and low production cost compared to synthetic polymers (Ablouh et al. 2019). As done in many previous studies, chitosan or alginate can be used separately as one of the natural polymers.

Chitosan, a natural polymer rich in functional groups such as hydrogen and amine, is effective for metal ion adsorption (Ahmad, Manzoor & Ikram 2017; Gao et al. 2022; Zhou et al. 2013). Chitosan's amine functional groups have been used as a surface modification agent impregnated onto supporting surfaces as adsorption sites (Zhou et al. 2013). Amino groups facilitate chemical modification, yielding polymeric networks with improved mechanical robustness and adsorption efficiency (Mahmoud & Ibrahim 2023). Numerous studies have explored chitosan-modified biochar composites for heavy metal adsorption, including those using chitosan Schiff-base (Wang et al. 2023), chitosan-modified rice straw biochar (Hamid et al. 2023), chitosan-modified mimosa biochar (Perera et al. 2023), chitosan–biochar hydrogel beads (Zhao et al. 2023), chitosan-biochar composite derived from agricultural waste (Son Tran et al. 2023), coating chitosan on biochar (Zhou et al. 2013), the chitosan-modified biochar composite (Gao et al. 2022), and chitosan to modify gasifier biochar (Burk et al. 2020). Overall, these modifications resulted in the creation of amine coordination sites on biochar, enhancing heavy metal adsorption with notable improvements in stability, adsorption properties, and surface functionalities (Burk et al. 2020; Gao et al. 2022; Zhou et al. 2013).

On the other hand, alginate, a binary heteropolymer, offers thickening properties and easy gel formation (Cataldo et al. 2016; Sutirman, Sanagi & Wan Ibrahim 2021; Wang et al. 2016). The presence of carboxylic and hydroxyl groups in alginate can bind metallic ions (Cataldo et al. 2016; Wang et al. 2016). Although soluble in water, alginate is often combined with other ingredients to improve stability (Wang et al. 2016). Alginate helps to synthesize biochar into composites due to alginate's gelling and clumping properties (Cataldo et al. 2016;

Chun et al. 2022; Wang et al. 2016). Using alginate as an adsorbent has been widely researched to form bead-shaped granules (Cataldo et al. 2016), fibroid gels (Kong et al. 2020), aerogel (Wang et al. 2016), hydrogels (He et al. 2022) and biochar alginate composite (Chun et al. 2022).

The combination of lignocellulosic biochar nanoparticles, chitosan, and alginate coated on a luffa sponge has been prepared to have a mixed sorbent, which is much more efficient than a single sorbent. In the process of making adsorbents, the attachment of biochar in the process of synthesis adsorbents to the luffa sponge requires chitosan and alginate to be attached and mechanical solid properties during the adsorption process in water. Alginate can crosslink biochar and chitosan to form a more substantial material. This combination allows the organic functional groups on the biochar surface to be effectively developed (He et al. 2022). Ablouh et al. (2019) used a combination of chitosan microspheres/sodium alginate hybrid beads to absorb Cr and Pb, showing that the correlation between the original chitosan microspheres and sodium alginate improved the properties of the resulting hybrid beads. It is believed that the performance of adsorbents based on lignocellulosic biochar nanoparticles will be enhanced by combining chitosan and alginate. In addition, the adsorbent attached to the luffa sponge is also expected to be accessible in heavy metal sorption applications.

This study aimed to fabricate an adsorbent with a coating of nano-sized lignocellulosic biochar on the Luffa aegyptiaca sponge (luffa-NLB coated adsorbent) with natural polymers like chitosan and alginate. Combining forest residue-derived lignocellulosic biochar and luffa sponge can add value to its potential applications. In practical application, adsorbents modified by coating onto luffa fibers facilitate their separability from aqueous solutions and make them easy to reuse. The raw materials and final adsorbent were characterized to observe functional groups using Fourier Transform Infra-Red (FTIR), morphology before and after synthesis adsorbent using Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy (SEM-EDX), and the heavy metal Cr (VI) adsorption capacity using Atomic Absorption Spectroscopy (AAS) was investigated and presented in this paper.

Materials and Methods

Materials and Preparation of Adsorbent

The lignocellulosic forest residue near Institut Teknologi Bandung was collected as the raw material for biochar production. According to Figure 2, the collected lignocellulosic material was dried and chopped into small pieces. These pieces were treated using low-temperature pyrolysis (100-300 °C) under limited oxygen conditions. The resulting biochar was processed by grinding it using a grinder machine (FCT-Z200) and then sieving it through a 212 um mesh. Next, the biochar was dried in a furnace at a temperature of 60 °C until the moisture content reached 4%. In the last step, the powdered biochar was milled for 4 h using the High Energy Ball Milling–Ellipse 3 Dimension (HEM-E3D) technique. This milling process yielded a fine and uniform biochar powder with an average particle size of 282.7 nm, as determined in previous research (Elfi Yulia et al. 2023).

Luffa aegyptiaca sponges came from a local farmer in Bandung, Indonesia. This study used a two-cm-high horizontally cut luffa sponge. The luffa sponge pieces were cleaned and washed under a continuous stream of water to remove any dirt or dust particles. Subsequently, the luffa sponge was immersed in distilled water for four hours, changing the water every hour. Afterward, the luffa sponge was dried in an oven at 60 °C for approximately 2.5 h.

Afterward, the lignocellulosic biochar is coated to the luffa sponge using the natural polymers chitosan and alginate. The chitosan solution came from technical-grade chitosan powder derived from shrimp shells, and the alginate solution came from technical-grade sodium alginate powder. The chitosan powder was dissolved in 10 mL of acetic acid (Merck, 100% for analysis) and 490 mL of distilled water to produce the 2% chitosan solution. Meanwhile, 20 mg of alginate powder was dissolved in 1000 mL of distilled water to create the 2% alginate solution.

Adsorbent Fabrication

The adsorbent synthesis using lignocellulosic biochar on the luffa sponge involved several sequential stages, according to Figure 2. Initially, 1.5 grams of biochar nanoparticle powder was dissolved in 30 mL of distilled water using a magnetic stirrer at 40 °C for 15 min, resulting in a homogeneous biochar solution. Subsequently, 15 mL of a 2% alginate solution was added to the biochar solution and stirred for 30 min to ensure thorough mixing. Following this step, 45 mL of a 2% chitosan solution was introduced and stirred for 30 min at 40 °C. It is crucial to avoid the simultaneous addition of the chitosan and alginate solutions to the biochar solution, as it may lead to agglomeration. Next,

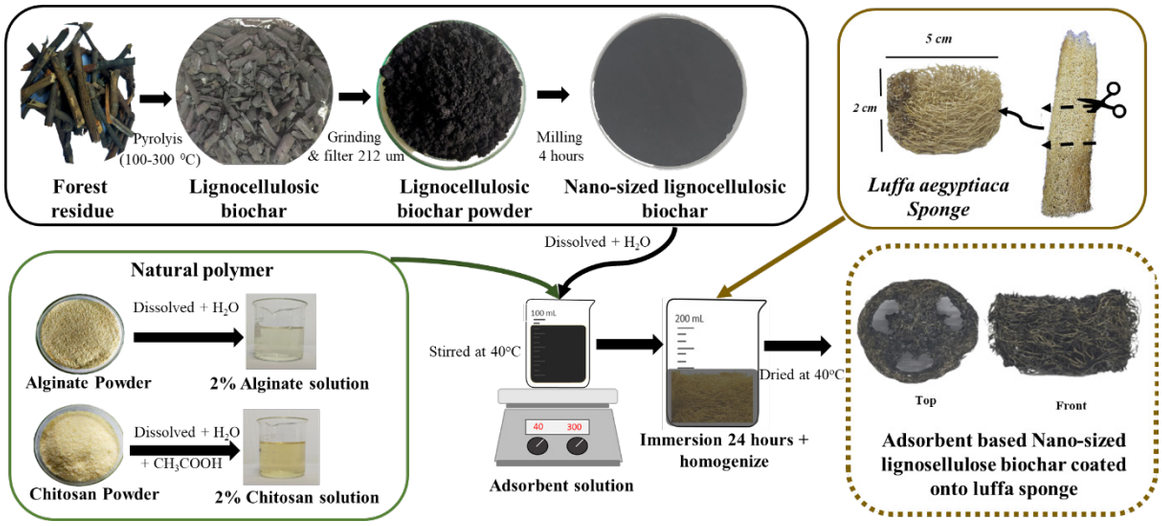

FIGURE 2. Illustration of the process of coating lignocellulosic biochar onto luffa surface

the luffa sponge was inserted and fully immersed in the prepared mixture for 24 h. Ultrasonic batch treatments were conducted during the first and last hour of immersion to promote uniform coating of the adsorbent material on the luffa sponge. Finally, the coated adsorbent was dried at 60 °C for 3 h, ensuring complete adsorbent drying.

CHARACTERIZATION OF MATERIALS

Fourier Transform Infra-Red (FTIR)

FTIR identifies chemical structure, specifically the functional groups in raw materials, including nano-sized lignocellulose biochar, chitosan, alginate, luffa sponge, and the final adsorbent luffa coating. This study uses Shimadzu, Prestige 21 FTIR with spectrum measurements at 400 to 4500 cm-1 wavelengths. Specific chemical bonds and groups were determined by examining the FTIR spectra, providing valuable insights into the composition of the materials (Usman et al. 2013). In heavy metal absorption, several functional groups need to be identified: O-H bonds, C-H single bonds, C=O double bonds, and C=C double bonds (Arana et al. 2017; Deng et al. 2017; Inyang et al. 2016; Mukherjee et al. 2022; Xiang et al. 2020).

Morphology of Materials

The morphological surface of nano-sized lignocellulosic biochar, luffa sponge original, and adsorbent nano-sized lignocellulosic biochar coating onto luffa sponge was analyzed using Scanning Electron Microscopy (SEM-Hitachi SU3500) with an acceleration voltage of 15 kV. The sample is made conductive by sputtering with gold. This comprehensive analysis provides a better understanding of morphology, structure, and information adsorbent about the attached chemical compounds. The SEM images recreated the membrane surface in three dimensions, and the roughness profile was viewed using ImageJ software.

The Ion Distributions of Adsorbent Luffa Coating after Adsorption

The ion distribution on the surface of the Luffa-NLB coated adsorbent that has bound heavy metal Cr (VI) was observed using Scanning Electron Microscopy with Energy Dispersive X-ray spectroscopy (SEM-Hitachi SU3500) with an accelerating voltage of 15 kV, a magnification of 250 and resolution 125,7 eV. This characterization aims to show how contaminant ions bound to the adsorbent surface include Cr (VI), C, N, and O.

ADSORPTION PROCESS

This research aims to develop adsorbent materials that reduce heavy metal Cr (VI) levels. The batch method was used as an experimental approach to investigate the adsorption ability of the adsorbent. The Cr (VI)

concentration was initially adjusted to approximately 10 ppm by dissolving 0.0283 g of potassium dichromate ($K_2Cr_2O_7$ -Pudak Scientific) into 1000 mL of distilled water. The adsorption capacity test involved immersing 1.6716 g of the adsorbent in 65 mL of Cr (VI) (with a mass/volume ratio of 2.5%). The contact time of the adsorption process is 120 and 1200 min, respectively. Heavy metal Cr (VI) concentrations were tested using Atomic Absorption Spectroscopy (AAS).

The adsorption capacity is determined using Equations (1) and (2). The number of heavy metal ions adsorb per unit of adsorbent is specified in Equation (1) in an equilibrium q_e (mg/g) and in time q_t (mg/g). Equation (2) defines the percentage of binding of contaminant ions in the adsorption process. Where c_0 is the initial concentration of heavy metal ions in solution (mg/L); c_e and c_t are the concentration of heavy metal ions in an equilibrium state and in solution at time t (mg/L), respectively; V is the solution's volume (L); and m is the adsorbent's mass (g) (Deng et al. 2017; Q. Kong et al. 2017).

$$q_{e,t} = \frac{(c_0 - c_{e,t})}{m} \times V \quad (1)$$

$$\%\ adsorpsi = \frac{(c_0 - c_e)}{c_0} \times 100\% \quad (2)$$

Results and Discussion

Functional Groups of Raw Materials and Adsorbents

FTIR characterization can analyze the functional groups in the adsorbent raw materials, luffa sponge, and final luffa-NLB coated adsorbent. The FTIR spectrum in Figure 3(a) shows the spectra from nano-sized lignocellulosic biochar powder (orange line), chitosan powder (blue line), and alginate powder (magenta line). The spectra of the original luffa sponge (red line) and luffa-NLB coated adsorbent (black line) are shown in Figure 2(b).

All spectra of raw material adsorbent in Figure 3(a) confirmed -OH stretch in the absorption band 3650-3200 cm^{-1} with a peak between 3415-3440 cm^{1}. The 2950-2800 cm^{-1} absorption band shows a confirmed absorption peak at 2922 cm^{-1} as an aliphatic C-H group (methylene C-H asymmetric stretch) (Asep, Rosi & Risti 2019; Arana et al. 2017). Next, in 1615-1580 cm^{-1}, there are absorption peaks for C=C-C aromatic and C=O Carboxyl in 1610-1550 cm^{-1} or 1420-1300 cm^{-1}. In addition, ion carbonate absorption at 897 cm^{-1}. These functional groups can function to absorb heavy metals through the surface complexation process (Deng et al. 2017; Inyang et al. 2016; Lu et al. 2012).

The functional groups in biochar, such as hydroxyl, aliphatic, carboxylic, and aromatic, play a crucial role in their interactions with chitosan and sodium alginate in Figure 2(a). These interactions occur through different bonding mechanisms, including hydrogen bonding, ionic bonding, and covalent interactions, forming complex molecular structures. The hydroxyl groups (-OH) on biochar can form hydrogen bonds with the amine groups (NH bend) on chitosan at 1598 cm^{-1}. This interaction facilitates the attachment or binding of biochar to the chitosan matrix, leading to improved adhesion, and influences the physical properties and stability of the biochar-chitosan system.

The aliphatic groups present in biochar (at 2922 cm^{-1}) can undergo covalent interactions with chitosan and sodium alginate to the formation of strong chemical bonds. Such covalent bonding enhances the mechanical stability and durability of the composite system. The carboxylic groups on biochar can interact with the amine groups of chitosan through ionic bonding and the carboxylate groups of sodium alginate. These ionic interactions affect the mixture's overall stability and influence the composite's charge and solubility properties. The aromatic groups in biochar can interact with chitosan and sodium alginate, including hydrogen bonding, ionic bonding, and covalent interactions. These interactions impact the composite's structural arrangement and physical characteristics, reinforcing the bonds between biochar, chitosan, and sodium alginate.

The attachment of biochar, chitosan, and alginate to the luffa sponge is a process that involves the interaction between the three materials. Changes and reductions in peak wave intensity were observed in the luffa sponge before and luffa-NLB adsorbent (Figure 3(b)), which shows the chemical reactions that occur during the adsorbent coating process that can change or remove functional groups in the material. Spectral peak changes and reduction especially appear at C=C groups at 1100-1726 cm^{-1}. Luffa original has olefinic groups (C=C alkenyl stretch) between 1680-1620 cm^{-1} with a peak of 1654 cm^{-1} and carbonyl groups in the form of esters confirmed in the 1750-1725 cm^{-1} range with a peak of 1726 cm^{-1}. However, both spectra still have a double bond C = C aromatic ring, which has an absorption

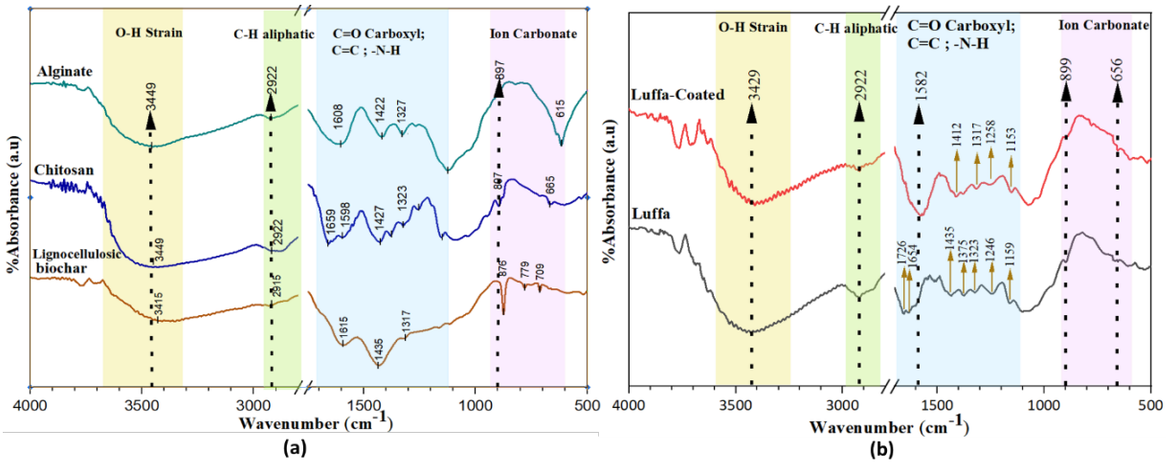

FIGURE 3. FTIR spectra result of (a) raw material adsorbent and (b) luffa-NLB coated adsorbent

band of 1615-1580 cm^{-1} with a peak of 1582 cm^{-1} and, simultaneously, shows the presence of a carboxyl group with an absorption band of 1610-1550 cm^{-1} and 1420-1300 cm^{-1}.

Furthermore, both spectra have aromatic tertiary amine groups confirmed in 1360-1310 cm^{-1} band, with the peak at 1323 cm^{-1} shifting to a peak of 1317 cm^{-1}. Absorption band 1490-1410 cm^{-1} with a peak of 1435 cm^{-1} shifted to 1411 cm^{-1} (Asep, Rosi & Risti 2019). While 898 cm^{-1} shows the extension of the carbonate ion bond (Arana et al. 2017). The interactions between biochar, chitosan, and sodium alginate functional groups in luffa sponge involve complex bonding mechanisms. These interactions are essential for forming stable and functional composite systems, contributing to the efficient reduction of heavy metals.

MORPHOLOGY OF ADSORBENTS

The morphology of lignocellulosic biochar powder characterized by Scanning Electron Microscopy (SEM-Hitachi SU3500) is shown in Figure 4(a)-4(c). The 100- and 5000-magnification SEM results show the distribution of lignocellulosic biochar particles like agglomerate particles.

The luffa sponge features a well-defined fibrous architecture characterized by regular arrangement, yielding a compact, resilient, and flexible network with excellent mechanical strength and resistance to pressure and impact (Figure 4(d)-4(f)). According to the results of morphological analysis using SEM, at a magnification of 320 and 1000 magnification, the spongy shape of the luffa resembles a fibrous morphology with irregularities that resemble lignocellulosic material. The luffa structure incorporates microscale cavities that facilitate efficient airflow and water absorption, contributing to its functional properties. The surface roughness profile of the luffa sponge with software reconstruction Figure 4(g) shows results between 800 µm × 1132 µm × 255 µm.

The attachment of lignocellulosic biochar to the luffa sponge was helped by chitosan and alginate. The sponge's color was changed from brown to black due to the color of the biochar. A biochar particle with a size of 272 nm can stick to the luffa sponge's surface. The role of chitosan and alginate as natural polymers is crucial in helping the biochar adhere to the luffa sponge and form a stable matrix. As a result, the luffa sponge coated with lignocellulosic biochar has a robust structure, strengthening the luffa structure while allowing the luffa sponge cavities to pass through the solution. Based on the results of morphological analysis using SEM at a magnification of 320 and 100 in Figure 4(i)-4(j), the luffa's surface has been thoroughly covered. On the surface of the luffa, in particular, particles of lignocellulose biochar appear to be evenly attached, and in general, the adsorbent material covers the microscopic gaps. The surface roughness profile of the luffa sponge after adsorbent-coating shows surface improvement between 851.3 µm × 1227 µm × 255 µm in Figure 4(k).

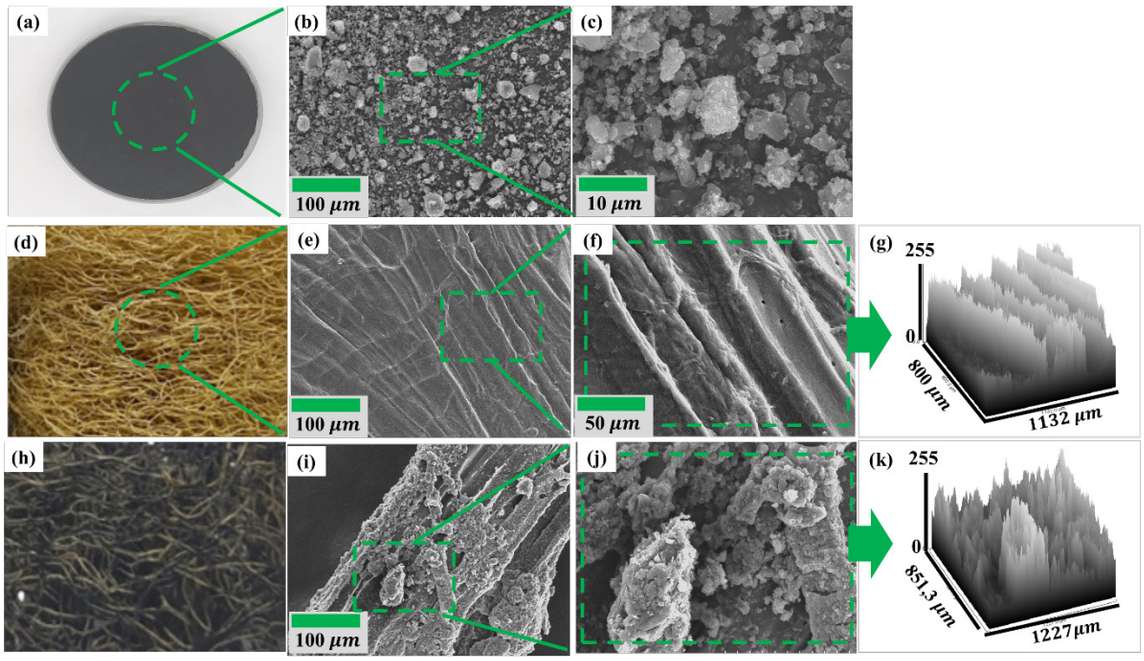

FIGURE 4. Morphology of SEM images of (a-c) lignocellulose biochar powder at 100M and 5000M, (d-f) original luffa sponge at 320 M and 1000M, (h-j) luffa-NLB coated adsorbent at 320M and 1000M, and (g and k) the surface profile analysis using reconstruction software processing

ADSORPTION CAPACITY

Heavy metal Cr (VI) in adsorption comes from a solution of $K_2Cr_2O_7$ with the initial concentration of Cr (VI) used at 9.74 mg/L. The ratio of adsorbent mass to heavy metal volume is 2.5%, which is 1.6716 g in 65 mL of Cr (VI) solution. The adsorption process on heavy metal Cr (VI) in Figure 5 shows that the adsorbent successfully binds heavy metal Cr (VI). At a contact time of 120 min, adsorbent luffa coating can reduce the concentration of Cr (VI) to 6.11 mg/L with an adsorption percentage of 37% and an adsorption capacity of 0.14 mg/g. Further testing with the contact time of the adsorption process was extended 10-fold to 1200 minutes. The final concentration of Cr (VI) solution was 0.55 mg/L, the adsorption percentage increased to 94%, as shown in Figure 5(a), and the adsorption capacity increased to 0.36 mg/g, as shown in Figure 5(b). The luffa coating adsorbent is in good condition and has robustness in the adsorption process for 1200 min. Therefore, this adsorbent can still be reused in binding heavy metals.

The surface morphology of the luffa adsorbent after the adsorption process characterized by SEM validated the attachment of Cr (VI) ions. Cr (IV) ions covered the surface of the luffa coating, as shown in Figure 6(a). The detailed appearance of Cr (VI) ions is shown in the SEM results in two spots in Figure 6(b) with 320 magnification and Figure 6(d) with 1000 magnification, further enlarged to 5000 magnifications in Figure 6(c) and 6(d). These characterization results validate that the nano-sized lignocellulosic biochar coated on the luffa sponge can bind heavy metals.

The ion distribution on the lignocellulose-based adsorbent layer biochar coating on luffa after the adsorption process of heavy metal Cr (VI) was characterized by SEM-EDX, evenly distributed, is shown in Figure 6(f). The content weight of each ion is 62,17% carbon, 27,62% oxygen, 0,12% nitrogen, and 11,09% Cr (VI), shown in Table 1. After adsorption, ion distribution on the adsorbent validates the attachment of Cr (VI) ions on the surface.

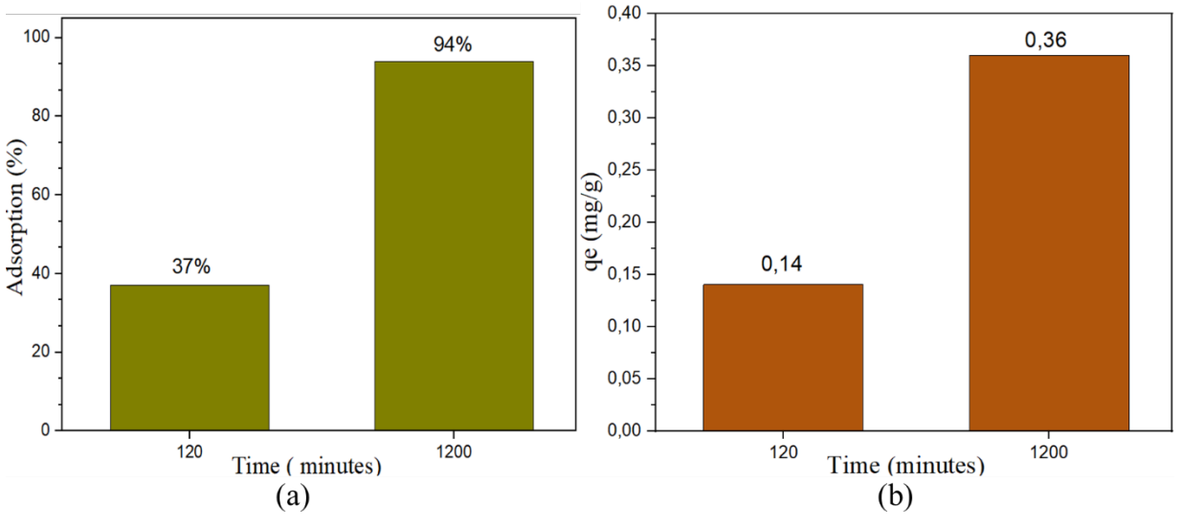

FIGURE 5. Result of the adsorption process (a) the adsorption percentage, (b) the adsorption capacity

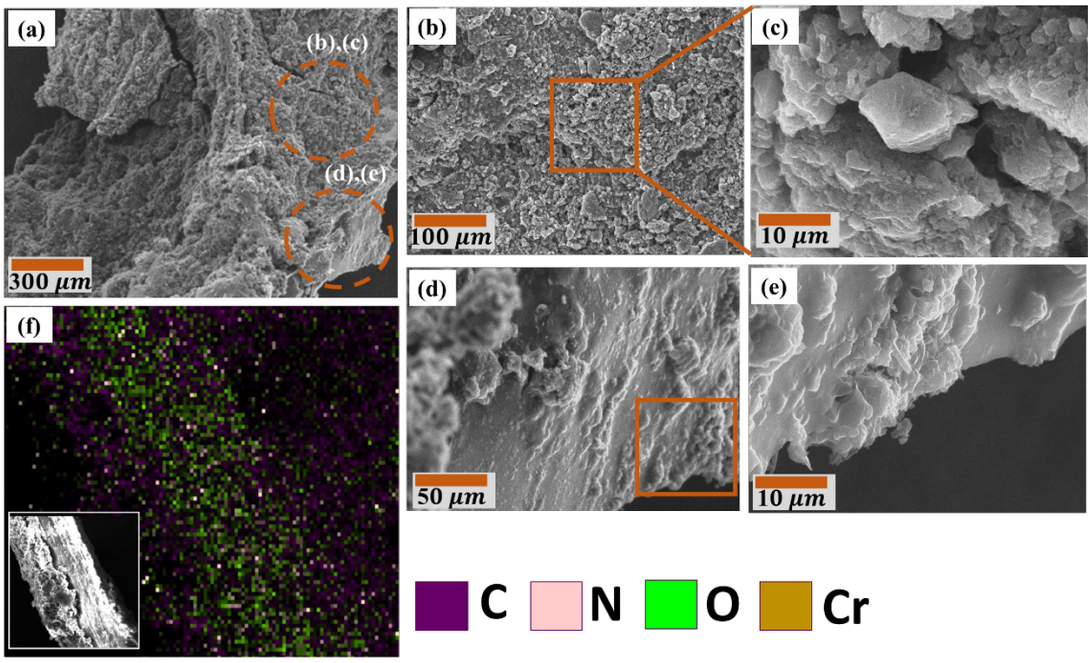

FIGURE 6. Morphology of adsorbent after adsorption process of Cr (VI) (a)150M (b) 320M (c) 5000M (d)1000M and (e) 5000M (f) the ion distribution of adsorbent after adsorption Cr (VI)

TABLE 1. The ion distribution after adsorption Cr (VI) from SEM-EDX

Element	Weight (%)	Atomic (%)
C	62,17	72,33
N	27,62	24,52
O	0,12	0,13
Cr	11,09	3,03

CONCLUSIONS

A new heavy metal adsorbent from forest residues transformed into nano-sized lignocellulosic biochar has been synthesized. The nano-sized lignocellulosic biochar is coated onto the *Luffa aegyptiaca* surface with the help of chitosan and alginate, making it an excellent adsorbent. The attachment of nano-sized lignocellulosic biochar to the surface of the luffa sponge changed the color of the luffa from brown to black, strengthening the luffa structure while allowing the luffa sponge cavities to pass through the solution. The FTIR spectra result of this adsorbent-coated luffa confirmed functional groups capable of binding heavy metals such as -OH stretch at 3429 cm^{-1}, aliphatic C-H group at 2922 cm^{-1}, C=C aromatic ring at 1582 cm^{-1} carboxyl groups at 1610-1550 cm^{-1} and 1420-1300 cm^{-1}, and carbonate ion at 898 cm^{-1}. The adsorbent binds metal Cr (VI), shown by decreased concentration of Cr (VI) and the attachment of Cr (VI) ions on the adsorbent surface. In 1200 min, the adsorption process reaches a 94% coefficient of adsorption with 0.36 mg/g adsorption capacity while maintaining the robustness of the adsorbent structure. This study can be extended for further research to analyze the effect of adsorbent dosage, initial heavy metal concentration, contact time, pH, and performance at a continuous flow rate.

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