REMOVAL OF ION NITRATE AND PHOSPHATE USING COCOA SHELL SKIN MODIFIED WITH FUNCTIONAL POLYMER

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Abstract: Cocoa is a plant that is widely cultivated in Indonesia, one of which is in the Yogyakarta area. On the outside of the cocoa fruit, it is known as the cocoa shell skin. Cocoa shell skin is an agricultural waste that is a simple, cheap, and environmentally friendly development that is used as an adsorbent for nitrate and phosphate removal. This article discusses the observation of the ability of the cacao shell against ion nitrate and phosphate adsorption and then compares it after being modified with a functional polymer. Modification of the surface of cacao shell skin with 2-*[(methacryloyloxy)ethyl]trimethylammonium chloride* (META) resulted in an improvement; the percentages of removal of ion nitrate and phosphate were 89.67% and 92%, respectively. In addition, this study compared the characterization of materials resulting from the absorption of Cocoa Shell Skin (CH) and Cocoa Shell Skin Modified META (CH-META) for nitrate and phosphate ions using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The modification with META could improve the C-N group and N-H groups on the surface of cacao shell skin.
Keywords: *cocoa shell skin; ion nitrate; ion phosphate; functional polymer; quaternaru ammonium*

Abstrak: Kakao merupakan tanaman yang banyak dibudidayakan di Indonesia salah satunya di daerah Yogyakarta. Bagian luar buah kakao dikenal dengan kulit cangkang kakao. Kulit cangkang kakao merupakan limbah pertanian yang merupakan pengembangan sederhana yang murah dan ramah lingkungan serta digunakan sebagai adsorben penyerap nitrat dan fosfat. Artikel ini membahas tentang observasi kemampuan kulit cangkang kakao terhadap adsorpsi ion nitrat dan fosfat kemudian adanya perbandingan dengan cangkang cacao setelah dilakukan modifikasi dengan polimer fungsional. Modifikasi permukaan kulit cangkang kakao dengan META menghasilkan peningkatan persentase penyerapan ion nitrat dan fosfat masing-masing sebesar 89,67% dan 92%. Selain itu, penelitian ini membandingkan karakterisasi bahan hasil penyerapan *Cocoa Shell Skin* (CH) dan *Cocoa Shell Skin – Modifikasi* META (CH-META) untuk ion nitrat dan fosfat menggunakan *Fourier-Transform Infrared* (FTIR) dan *Scanning Electron Microscopy* (SEM). Modifikasi dengan META dapat meningkatkan gugus C-N dan gugus N-H pada permukaan kulit cangkang kakao.
Kata kunci: kulit cangkang kakao, ion nitrat, ion fosfat, polimer fungsional, ammonium kuartenari

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Introduction

Water pollution is currently the biggest environmental problem in the world that must be addressed with sustainability as a priority. The main problem is the provision of clean water for household and industrial use. In addition, waste containing pollutants such as nitrate and phosphate is discharged from various sources that are not treated or treated properly, causing rapid degradation of clean water resources (Rahayu et al., 2023). Global bioethanol production continues to increase and is estimated to reach 165,000 million liters in 2026. One waste that is of concern is vinasse waste or liquid waste from the bioethanol industry. This waste is characterized as a liquid residue in acidic conditions with a pH of less than 4, a brownish color, a distinctive odor, and contains a high chemical oxygen demand (COD) value of more than 100,000 mg/L. It is estimated that in the production of one liter of bioethanol, 12 to 15 times as much liquid waste is produced (Chowdhary et al., 2018; Rodríguez-Félix et al., 2018). This waste also contains complex inorganic and organic ion compositions with high pollution potential, such as phosphate and nitrate. Phosphate is a polyatomic ion or radical with the HOPO(OR) functional group consisting of one phosphorus atom and four oxygens with a molecular mass of 48 g/mol and is denoted PO_4^{3-}. Nitrate is a polyatomic ion with the molecular formula NO_3^- and a molecular mass of 62.0049 g/mol. Nitrate also describes the functional group of RONO2. Nitrate is an inorganic ion that is included in the nitrogen cycle which is formed from the catalytic oxidation process. Under normal conditions, nitrate is a stable compound but will easily explode at high temperatures and pressure.

These traditional methods cannot cover the range of decontamination required to meet precise and affordable requirements. New solutions for wastewater treatment include UV photocatalysis, e.g. photolysis, activated carbon adsorption, ozonation, oxidative decomposition and electrochemical processes. However, they are still not cost effective (Ahmadi et al., 2023). In the last decade, this method has been replaced by inexpensive adsorbents for biomass, especially biomass from agricultural wastes. However adsorption methods such adsorption have a positive side efficiency and the cost-effectiveness of the process is quite limited (Wiroesoedarmo et al., 2018). Therefore, nowadays many researchers are looking for low-cost alternative materials. Research in recent years has shown that several natural biomaterials including agricultural products and by-products can accumulate high concentrations of ion nitrate and phosphate, one of which is skin cocoa shell skin (Aini et al., 2023).

Cocoa is one of Indonesia's main export commodities, contributing 12.7% of the world's total cocoa production. Over the past decade, Indonesia's annual cocoa production has averaged about 683 kilotons, and several research endeavors have showcased the potential of cacao pod husk as a valuable adsorbent (Adjin-Tetteh et al., 2018; Jaya et al., 2020; Kilama et al., 2019). Cacao production involves extracting seeds from its pods, resulting in four primary by-products: cocoa husk, placenta, cocoa mucilage, and cocoa bean skin. In the last ten years, Indonesia has produced around 683 kilo tons of cocoa per year (Directorate General of Estates, 2019). Various studies have provided evidence of the potential of cocoa pods to be valorized as an adsorbent (Tsai et al., 2020), bioenergy (Adjin-Tetteh et al., 2018; Kilama et al., 2019), anti-biofouling agents (Wibisono et al., 2021), and food additives: antioxidants (Santos et al., 2014), pectin emulsifiers based on their bioactive compounds.

Cocoa shell skin contains 36.23% cellulose, 1.14% hemicellulose, and 20-27.95% lignin. The high cellulose content in cocoa pods has the potential to be further processed as an adsorbent to treat water pollution waste. The results of the FT-IR analysis showed the presence of CH, OH (hydroxyl), and C = CH (aromatic-H) groups (Wijaya.M & Wiharto, 2017). Utilization of cocoa shell skin as an alternative source of nutrition in animals by fermentation (Sa & Abike, 2016). Anthropogenic activities resulting from population growth and industrial development have worsened the environment and, consequently, water quality (Bansal et al., 2021; Cerrahoğlu Kaçakgil & Bingöl, 2020). Industrial wastewater can contain ions such as Nitrate and phosphate depending on the source (O. Ighalo et al., 2020). These ions are harmful to human health in various ways (Mahvi et al., 2023). Therefore, the treatment process using cocoa shells needs to be done to overcome the dangers of Nitrate and phosphate.

Adsorption is a technique that is general used in water treatment because it is clean, easy to control, efficient and inexpensive technology (Balarak et al., 2021; Cherdchoo et al., 2019; O. Ighalo et al., 2020). Popular adsorbent materials are clays (Awad et al., 2019; Uddin, 2017), polymers (Zhang et al., 2020), nanomaterials (Diab et al., 2020; Eltaweil et al., 2021; Omer et al., 2021), biosorbents (Annadurai et al., 2020; S et al., 2018, 2021) and activated carbon (Eletta et al., 2021). Biomass such as cocoa shell skin are excellent precursors for the development of adsorbents for water purification applications (Eletta et al., 2021). This study aims to investigate the ability of cocoa shell skin as an adsorbent for nitrate and phosphate from aquos solutions.

Material And Methods

Materials and Apparatus

Materials used during research in the analysis were cacao shell, HCl, 2-[(Methacryloyloxy)ethyl]trimethylammonium chloride solution (META) were purchased from Wako 1st Grade, Japan, as a modifier and reagent used in testing the content of nitrate: $C_{46}H_{52}N_4O_8.H_2SO_4.{}_7H_2O$ and NaCl were purchased from Trade TCI Mark, Japan and reagent for testing phosphate is $K_2Sb_2C_8H_4O_{12}\cdot 3H_2O$, $(NH_4)_2MoO_4$ dan $C_6H_8O_6$ were purchased from Trade TCI Mark, Japan, according to SNI procedure No. 06- 6989.9-2004 and SNI No. 6989.31-2005. The equipment used to detect nitrate, nitrite and phosphate ions is spectrophotometry UV-Vis (Thermo Scientific-Genesys) was carried out. Furthermore, identifying the functional group in the polymer was carried out using Fourier Transform InfraRed (FTIR) Spectrum 400 Series Perkin Elmer.

Procedure

Treatment of Cocoa Shell Skin (CH)

Starting from the initial preparation of cocoa shells obtained from the Nglangeran area which is one of the cocoa processing centers in D.I. Yogyakarta. Cocoa shell skin (CH) is then processed by hulling and washing with HCl to remove organic compounds contained in the cacao shell. Then air it for about 3-5 days and bake it in the oven at 70°C for 24 hours to produce cocoa shell skin treatment (CH-T). Furthermore, CH-T was processed using various variations of mass, temperature, concentration, and time and obtained the optimum value of each variation as seen in Table 1.

Table 1. Variation of Removal Ion using Cocoa Shell Skin Modified with Functional Polymer

Parameter	Variation
Mass (g)	0.1, 0.2, 0.3, 0.4, 0.5
Temperature (°C)	25, 30, 40, 50, 60
Concentration (ppm)	10, 15, 20, 25, 30
Contact Time (min)	10, 15, 30, 60, 120

The optimum yield CH-T is a monomer containing quaternary ammonium groups that function as anion exchangers. CH-T which has been processed in certain variations is then filtered, and followed by heating in the oven at 50°C for 24 hours. After that, CH-T was contacted with the synthesis compound and found how the difference in Ion absorption using CH-T.

Batch biosorption

The third stage is followed by observing and applying the ability of CH-T materials to adsorp nitrate and phosphate contained in sugar and synthesis industrial wastewater (nitrate and phosphate). An analysis of nitrate and phosphate content was carried out based on SNI No. test. 06-6989.9-2004 and SNI No. 6989.31-2005. The application of the ability of CH is removing phosphate and nitrate ions from aqueous solutions. Evaluation of the performance of CH was carried out on variations in equilibrium time, temperature, stirring speed, and mass of CH. In addition, adsorption was carried out using 0.3 grams as an initial mass of adsorbent with 25 mL of adsorbate solution. Adsorption isotherm balance was carried out to determine the maximum adsorption capacity (qmax) for PO_4^{3-} and NO_3. After that, the results will be compared with CH-META to determine the effectiveness of CH in ion adsorption. The adsorption efficiency (%Removal) value is represented by Equation 1.

$$\%Removal = \frac{(Co-Ce)}{Co} \times 100\% \ldots\ldots\ldots\ldots(1)$$

where: Co – represents the initial concentration of the adsorbate solution (mg/l), and Ce stands for its equilibrium concentration (mg/l), respectively; W is the weight of the adsorbent (g) and V is the volume of solution (L).

Discussion

Effect of Concentration

In this variation, phosphate and nitrate solution with initial concentrations of 10, 15, 20, 25 and 30 ppm were agitated with 0,1 g of cocoa shell skin pod shells at 25°C for 30 minutes. As shown in Figure 1, the effect of phosphate and nitrate concentration will affect the percentage of removal.

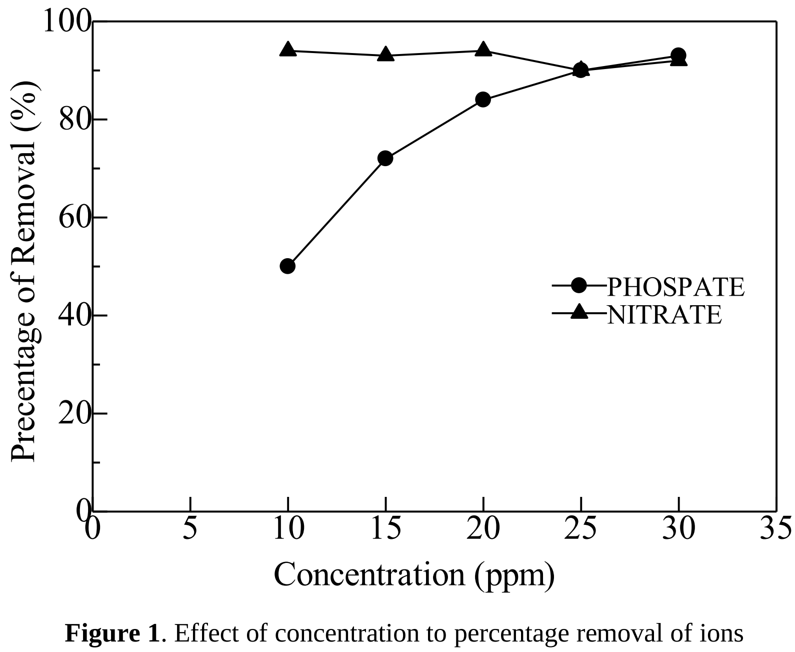

Figure 1. Effect of concentration to percentage removal of ions

Figure 1 shows that the percentage of removal of CH increases in proportion to the concentration of Phosphate ions with the highest absorption percentage of 93% for a concentration of 30 ppm. However, the percentage of removal can decrease as in Nitrates, where the highest percentage of removal is at a concentration of 10 ppm of 94% and continues to decrease with increasing concentration. That is, if the ion concentration is too high it can cause the cocoa shell skin to experience a decrease in its ability to absorb. This may occur as a result of an increased surface charge of CH leading to saturation of the active site and a consequent decrease in dye efficiency (Balarak et al., 2021). The reason for the increase in the adsorption capacity of CH with an increase in the initial concentration of adsorbate can be attributed to the increased interaction between the adsorbent and the dye (Inyinbor et al., 2016).

Effect of Contact Time

In this variation, phosphate and nitrate 15 ppm solution with initial contact times 10, 15, 30, 60 and 120 minutes were agitated with 0,1 g of cocoa shell skin at 25°C. As shown in Figure 2, the effect of contact time agitated will affect the percentage of removal.

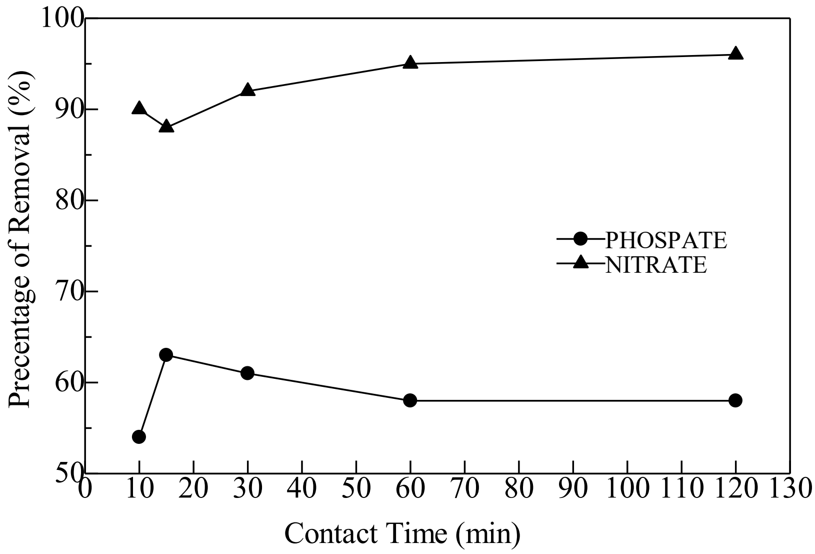

Figure 2. Effect of contact time to percentage removal of ions

Contact time is a factor that plays an important role in the biosorption process. It can be seen in Figure 2 that the percentage of Nitrate ion removal has increased in proportion to the length of contact time CH with Nitrate ions with the highest absorption percentage of 96% for a contact time of 120 minutes. This means that the longer the contact time, the metal ion has the potential to experience an increase in adsorption power.

However, the percentage of removal can decrease as in Phospate, where the highest percentage of removal value is at 15 minutes of contact time of 63% and continues to decrease with the length of the contact time because more and more Phospate ions are absorbed into the CH biosorbent. The absorption of metal ions causes the formation of ions which crowd on the surface of the biosorbent, thereby reducing the surface area of the CH biosorbent. This causes a decrease in the adsorption power of Phosphate ions resulting in metal ions that have been bound to the biosorbent tend to be desorbed back into the solution (Irawan et al., 2015; Setiawan et al., 2019).

In addition, the percentage reduction in removal can also be due to the initial adsorption stage of the concentration gradient between the liquid film around the adsorbent particles and the large available pore sites, because of this the adsorption rate is faster. In the next step, the adsorption rate decreases due to slow pore diffusion of dissolved ions into some of the adsorbent (Bhuvaneshwari et al., 2021).

Effect of Cacao Shell Mass

In this variation, phosphate and nitrate 15 ppm solution were agitated with variations of cocoa shell skin with initial 0.1, 0.2, 0.3, 0.4, and 0.5 grams at 25°C for 30 minutes. As shown in Figure 3, the effect of Cacao Shell Mass will affect the percentage of removal.

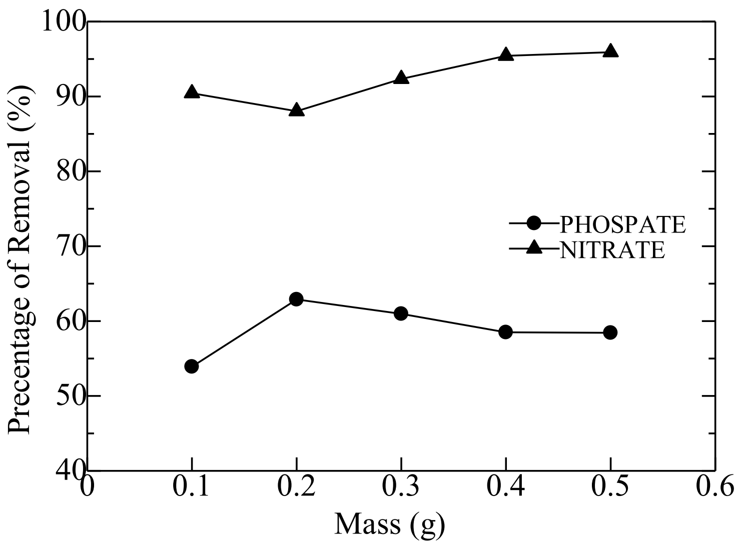

Figure 3. Effect of mass cacao shell skin to percentage removal of ions

The weight of the biosorbent is a significant factor in the process of biosorption. The result shows that an increase in the mass of the biosorbent causes an increase in the mass of the biosorbent in solution causes an increase in the number of groups that are active in absorbing ion Nitrate and Phosphate (Bhuvaneshwari et al., 2021).

The effect of adsorbent mass on the removal of Phosphate and Nitrate ions was investigated and shown in Figure 3. The results show that the absorption percentage of Nitrate ions increases in proportion to the increase in CH mass with the highest absorption percentage of 96% for 0.5 g CH. This shows that the mass of the adsorbent increases the more available surface area so it has more active sites for tying metal ions (Balarak et al., 2021). However, the percentage of removal tends to decrease with Phosphate, this is because the CH biosorbent used is unsize. So it is possible that between mass variations one another has a different surface area which results in an unstable graph. This is because the ionic size of the phosphate is larger so it only has the active group in cacao (Aini et al., 2023; Gorzin & Bahri Rasht Abadi, 2018).

Effect of Temperature Agitated

In this variation, phosphate and nitrate 15 ppm solution with initial temperatures of 25, 30, 40, 50 and 60 ^{o}C were agitated with 0,1 g of cocoa shell skin for 30 minutes. As shown in Figure 4, the effect of agitated temperature will affect the percentage of removal.

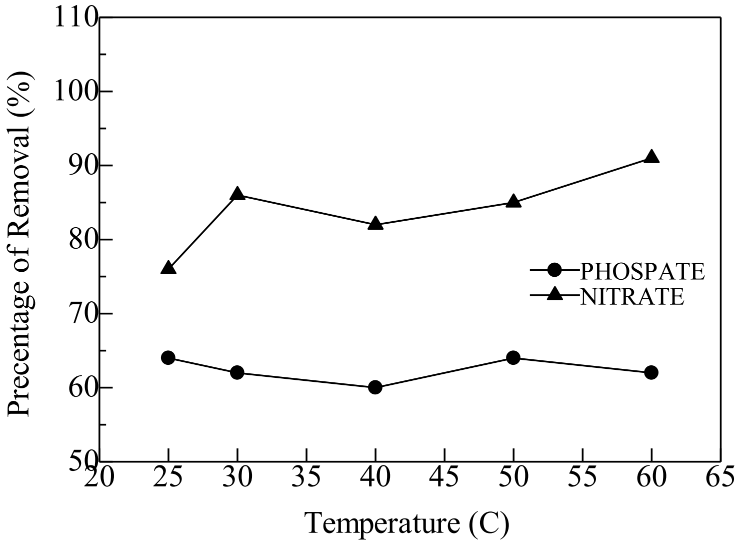

Figure 4. Effect of temperature on percentage removal of ions

The effect of temperature agitated between CH and ion solutions on the percentage removal was investigated and shown in Figs. 5. The results showed that the percentage of absorption of nitrate ions increased in proportion to the increase in agitated temperature with the highest absorption percentage of 91% for a temperature of 60°C while the results for phosphate ions tended to be stable. This shows that the temperature of the solution affects the effectiveness of biosorption. It can be seen that the amount of metal ion uptake tends to increase in proportion to the increase in temperature so that the biosorption is endothermic (Ahmad & Danish, 2018). Adsorption of metal ions may involve not only physical but also chemical absorption. The effect may be due to the increase in active sites because of bond breaking at higher temperatures (Fotsing et al., 2020).

Comparison CH with CH -META

Optimum results were obtained from each variation, in the variation of the optimum condition using 0.4 gram, the optimum temperature used was 50 °C, the absorption time used was 60 minutes and the optimum concentration was obtained at 15 ppm. The optimum condition of CH will be compared with CH-META like Figure 5.

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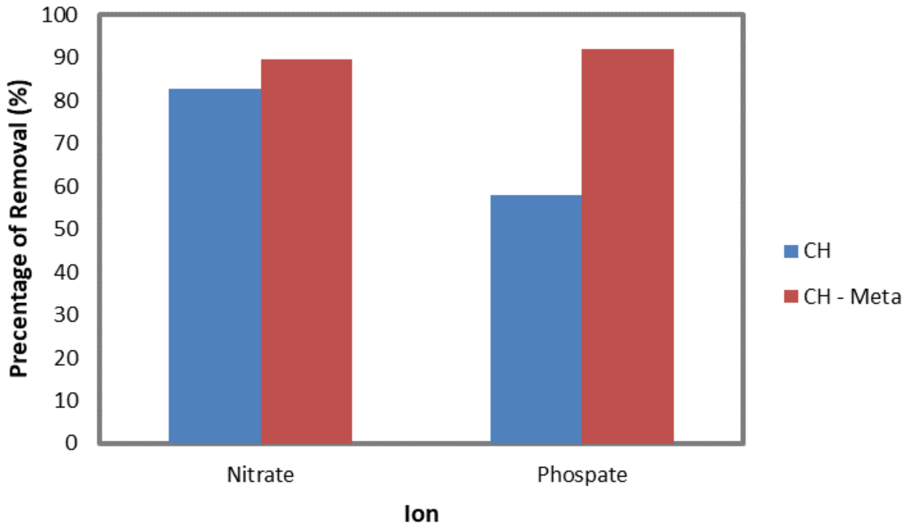


Figure 5. Comparison of Optimum Absorption Results between CH and CH-META

Figure 5 shows that the per cent removal of nitrate and phosphate ions after modification with CH-META is greater than the per cent removal before modification. The removal percentage of Nitrate before modification is 82.8% and after modification is 89.67%, meanwhile removal percentage of Phosphate before modification is 58% and after modification is 92%. This indicates that the ability to absorb CH-META in binding nitrate and phosphate ions is more effective than without META modification.

Characterization CH and CH-META

CH and CH-META were characterized using Fourier Transform Infra-Red (FTIR) to determine and confirm the type of organic compound group bonds formed in them after adsorption. FTIR characterization was carried out using the mid-infrared wavelength range, namely 4000-400 cm^{-1}, as shown in Figure 6.

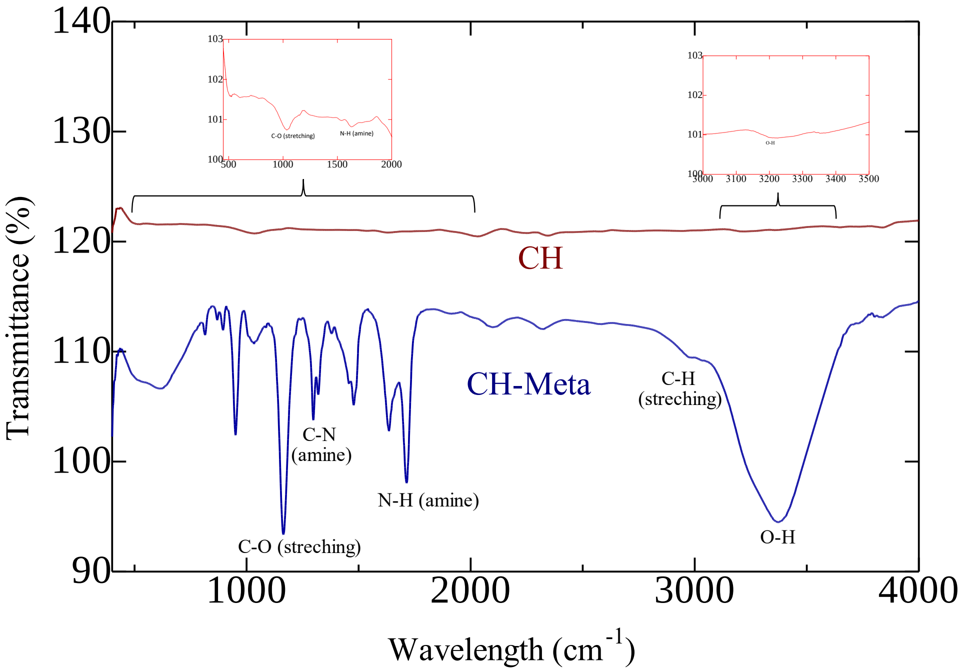


Figure 6. Fourier Transform Infrared (FTIR) spectrum of CH and CH-META

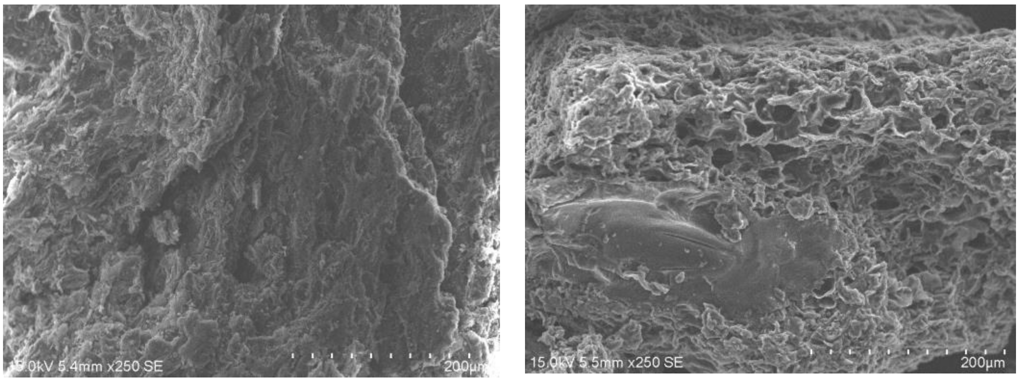
Fourier Transform Infrared (FTIR) was carried out to determine the presence of amine compounds. The amine group itself was used as a strong anion exchanger. The FTIR spectrum of organic polymer monolith is shown in Figure 6. In Figure 6, it can be seen that there are three peaks in CH and five peaks in CH-META.

These three peaks in CH were the first peaks at wave number 1035 cm^{-1}. the second peak at wave number 1633 cm^{-1} and last peak at wavenumber 3214 cm^{-1}. Then, these five peaks in CH-META were the first peak at wave number 1150 cm^{-1}. the second peak at wave number 1250 cm^{-1}, the third peak at wavenumber 1721 cm^{-1}, the fourth at wave number 2965 cm^{-1}, and the fifth peak at wavenumber 3378.6 cm^{-1}. In this graph, the peak at CH is not too sharp and strong.

The absorption area in the wavenumber between 1150 - 1025 cm^{-1} refers to the C-O (stretching) absorption area. The high intensity of the principal peak in organic polymer monolith describes many oxygen-containing groups after the polymerization process. The absorption area in the wavenumber between 1250 – 1020 cm^{-1} refers to the C-N (amine) absorption area. Subsequently, the absorption area in the wavenumber around 1650 – 1580 cm^{-1} refers to the N-H (amine) absorption area. These amine groups are contributed by functional monomers that are used. The absorption area in the wavenumber between 2853 – 2962 cm^{-1} refers to the C-H (stretching) absorption area. Then, in the wavenumber between 3000 – 3600 cm^{-1}, it relates to the O-H functional group. It can be concluded that existing bonds and functional groups are thought to come from the presence of a polymerization reaction involving an initiator, monomer, crosslinker, and porogen (Rahayu et al., 2021).

The peak reflected on the FTIR, shows that all of the CH functional groups (C – O, N – H and O – H) are part of CH -META, but not all the functional groups seen in CH-META are visible in CH (C – N and C – H). Meanwhile, the thing that differentiates the two is related to the steepness of the peak of the amine functional group, where CH-META looks clearer and stronger. This indicates that the effect of CH-META modification in the adsorption of Nitrate ions has a better efficiency than CH.

In addition to characterization using FTIR, CH and CH-META were also characterized using a Scanning Electron Microscope (SEM) to identify their morphological forms as shown in Figure 7 (a) and (b).



(a) (b)

Figure 7. Scanning Electron Microscope (SEM) photo of **(a)** CH **(b)** CH-META

Figure 7 (a) and (b) are the morphology of CH and CH-META after the adsorption of Nitrate and phosphate ions. Figure 7 (a) shows that CH has a fairly smooth surface. CH shows a lamellar structure with a smooth cell wall without macropores and mesopores. The lamellar structure of CH is associated with irregularly shaped lignocellulosic layers of the cellulose. SEM image of CH-Meta in Figure 7 (b) shows a rough surface, a little white substance, and small and large pebbles indicating that the adsorbent has a heterogeneous surface. In this modification, the adsorbent shows obvious shrinkage and its porous structure collapses due to shrinkage (Eletta et al., 2021; Fotsing et al., 2020).

In the previous research, the determined specific surface areas for CH and the CH-T-META blend were 48.34 m^2/g and 63.66 m^2/g, respectively, as measured using the Brunauer-Emmett-Telle (BET). Such a surface area is commendably high, making it suitable for adsorbent materials. Nonetheless, adsorption is multifaceted, encompassing a plethora of physicochemical interactions. Relying solely on the specific surface area doesn't provide a comprehensive assessment of a substance's aptitude for adsorbing pollutants. The total pore volumes for CH and CH-META were found to be 0.1631 CH/g and 0.2181 cc/g, respectively. The resulting pore sizes for CH and CH-META were 13.38 nm and 13.52 nm, pointing to a mesoporous structure. Notably, a significant proportion of the material lies in the

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mesoporous range, exceeding 2 nm. An abundance of mesoporous pores can notably enhance the adsorption capacity (Aini et al., 2023).

Conclusions

Based on the results of the research that has been done, absorption data and absorption concentrations were obtained using pure cocoa shell skin and modifications of the various variations used. From the results obtained, the optimal absorption value of each variation using random particle sizes at optimal conditions obtained a mass of 0.4 grams, a temperature of 50 °C, a time of 60 minutes, and a concentration of 15 ppm. The removal percentage of Nitrate before modification is 82.8% and after modification is 89.67%, meanwhile removal percentage of phosphate before modification is 58% and after modification is 92%. This indicates that the ability to absorb CH-META in binding nitrate and phosphate ions is more effective than without META modification. The FTIR characterization results show that the CH-META modification is more efficient in removing Nitrate ions than CH. The results of the SEM characterization show that CH has a fairly smooth underlying surface and CH-META has a heterogeneous surface. Based on these results, the future perspective is to modify CH to CH-META.

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