

Exploring Cacao Husk Waste – Surface Modification, Characterization, and its Potential for Removing Phosphate and Nitrate Ions

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ABSTRACT

Environmental pollution by phosphate and nitrate ions has become a serious problem. The innovation of cacao husk as an adsorbent and sustainable material can be a solution for absorbing phosphate and nitrate ions. Cacao husk (CH) derived from the matured cocoa fruit's remaining pod material that often discarded as waste. The aim of this research is to develop an environmentally friendly and economical cacao husk (CH) based material for the absorption of phosphate and nitrate ions from aqueous solutions. CH surface modification is made by reacting the cationic polymer 2-[(methacryloyloxy)ethyl]trimethylammonium (META), into CH treatment (CH-T). Successful surface modification of CH-T with cationic polymers was confirmed to improve the surface properties for the removal of phosphate and nitrate ions. The surface charge morphology, structure, pore distribution and stability of the modified CH-T were investigated by Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET) and elemental analysis. 0.3 grams of CH-T modified with 75% cationic polymer with stirring at 70 rpm for 180 minutes at 50°C was reported as the best modification condition. Removal efficiencies of phosphate and nitrate ions increased after adding quaternary ammonium to CH-T to 96% and 93.4%, respectively. These results indicate that CH modification has prospective as a low-cost catalyst for wastewater treatment.

Keywords: adsorption, cacao husk, 2-[(methacryloyloxy)ethyl]trimethylammonium, nitrate, phosphate.

INTRODUCTION

Environmental contamination is one of the problems of current concern and an urgent problem for living creatures. The continuing of waste disposal carried out by industry and non-industry is a fundamental problem of environmental pollution [1]. The challenge of managing large amounts of organic waste or secondary materials requires environmentally friendly technological advances [2]. For maintaining ecosystem balance and human health, clean water quality is the main factor that needs to be considered. Water frequently gets contaminated by the introduction of harmful ions like phosphate and nitrate. Contamination caused by phosphates and nitrates is anionic

contamination of surface and underground water sources. Large concentrations of anions can have a negative impact on human health and the quality of natural ecosystems [3]. These anions primarily enter to the environment through the weathering of phosphate rock and various anthropogenic activities such as agriculture, industry, and domestic task. Although several techniques are exploited for removing phosphates and nitrite from wastewater. Extensive research has been conducted on bio-sorbents that a promising alternative to commercial solutions. Biosorption is the process where inactive or deceased biological substances absorb pollutants via various physicochemical processes [3, 4]. Various technological innovations have been employed to effectively eliminate

anionic contaminants from aqueous solutions, including adsorption [5], chemical reaction, phytoremediation, and bioremediation [6]. Nevertheless, traditional approaches may encounter challenges in terms of limited treatment effectiveness and expensive operational expenses. Consequently, there is still a need to advance uncomplicated and cost-effective treatment technologies to eliminate anionic contaminants from water sources.

Adsorption is as a method For wastewater treatment due to its environmentally friendly nature, simplicity in operation, efficiency, and economic feasibility. The familiar absorbent material used by researchers are clay [5, 7], polymers [8, 9], nanomaterials [10, 11], biosorbents [12, 13], and activated carbon [14, 15]. Adsorbents derived from agricultural sources or lignocellulosic materials are gaining traction in research circles, attributed to their unique properties [16]. Adsorbents are renewable, biodegradable, environmentally friendly, low cost, and abundantly available [17–19].

Recently, activation techniques can produce activated carbon (AC) with superior surface area, extensive porosity, and enhanced adsorption capabilities. Activated carbon has been produced and is widely used for wastewater absorption and pollutant elimination. The use of agricultural food residues as an adsorbent to remove synthetic dyes is gaining attention in research because of its efficacy and cost effectiveness [20]. There has been increasing recognition of the affordability of industrial, forestry and agricultural waste due to its abundant availability and minimal processing requirements, adding to the appeal of waste [21, 22]. The biomass derived from such waste has been harnessed to create extracts that act as adsorbents and to develop nanomaterials with similar applications [23].

Cacao (*Theobroma cocoa*) stands as a chief export product from Indonesia, accounting for 12.7% of global cocoa output. Over the past decade, Indonesia's annual cocoa production has averaged about 683 kilotons [24], and several research endeavors have showcased the potential of cacao husk (CH) as a valuable adsorbent [25–27]. Cacao production involves extracting seeds from its pods, resulting in four primary by-products: cocoa husk, placenta, cocoa mucilage, and cocoa bean skin. The CH makes up approximately 70–75% of the entire fruit. It's a significant source of fibrous elements such as lignin, cellulose, hemicellulose, and pectin [28, 29] as well as a reservoir of bioactive substances [30, 31]. Often, decaying CH in cocoa plantations poses environmental challenges and

becomes a hotspot for fungi that cause diseases like black pod rot [31]. Extracts from the cocoa bean's husk are valuable due to their richness in antioxidant flavanols (including catechins and epicatechins), theobromine, caffeine, and cocoa butter. This husk is a treasure trove of lignocellulosic content, abundant in elements like potassium, lignin, cellulose, hemicellulose, pectin, and antioxidants [32]. Recently, the modification of cacao husk has been dedicated for enhancing its physical and chemical characteristics by utilizing diverse materials such as cationic polymer. In addition, the modification of cacao husk using cationic polymer can increase the adsorption capacity for negatively charged solutes such as heavy metals and organic substances. 2-[(methacryloyloxy)ethyl]trimethylammonium (META) is a monomer that has a cationic group and a methacrylate functional group that can carry out polymerization reactions with other monomers. META can be applied in polymerization reactions to produce cationic polymers [33].

This work used a cationic polymer containing quaternary ammonium from 2-[(methacryloyloxy)ethyl]trimethylammonium to modify the surface of CH treated (CH-T) in order for improving the material performance. The goal of this study was to characterized and examine the performance of this modified CH-T with cationic polymer for adsorption ion phosphate and nitrate from aqueous solutions. It conducted a series of adsorption studies under different experimental settings to understand the mechanisms involved in the adsorption of phosphate and nitrate. To the best of our knowledge, this could be the first time that modification of cacao husk modified with cationic polymer introduced from 2-[(methacryloyloxy)ethyl]trimethylammonium for adsorption ion phosphate and nitrate from aqueous solutions.

EXPERIMENTAL

Preparation of cacao husk treated

In this study, cacao husk obtained from the Nglangeran area as one of the centres for processing cacao in D.I. Yogyakarta, Indonesia. CH is one of the agricultural wastes produced by cocoa plants. CH can be used as an adsorbent for various chemical species and water media [34, 35]. The initial treatment is to cut CH into small sizes and wash CH using HCL to remove organic compounds in the cacao husk. The drying process is carried out

using the mix by sun and oven method. Initial drying is done under sunlight for 3–5 days. This procedure aims to decrease the moisture level in the cocoa husk and cut down on the energy required for drying. Subsequently, the cocoa is baked in an oven at 70 °C for a day, resulting in cacao husk treated. Next, CH-T was reacted with 2-[(methacryloyloxy) ethyl]trimethylammonium.

Optimization of cacao husk treated with [(methacryloyloxy) ethyl] trimethylammonium

CH-T was reacted with 2-[(methacryloyloxy) ethyl]trimethylammonium, which is a monomer containing quaternary ammonium groups that acts as an anion exchanger using variations in temperature, concentration, mass, contact time, and stirring. CH-T was reacted with META at a specific concentration for 3–5 hours. Subsequently, the mixture was filtered and washed with distilled water, followed by oven-drying at 50°C for a duration of 24 hours. Prior to utilization, the CH-T-META substance was treated with HCl to activate the anionic exchange group [36]. The expected setup schematic of CH-T-META is displayed in Figure 1.

CH-T-META characterization

The CH-T-META’s physicochemical attributes were examined using methods like Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR), and Branueur-Emmet-Teller (BET). The characterization of the developed CH-T-META includes analysis of surface morphology, the surface’s pore region, and the active groups present within the CH-T-META as an adsorbent. The SEM was utilized to study the

surface profile of the monolithic polymers (META-EDMA), while the FTIR aided in the analysis of functional groups. Elemental Analysis was employed to gauge the weight percentages of C, H, and N in a specimen. Additionally, the BET assessment assisted in discerning the material’s surface traits, such as area and pore volume.

Phosphate (PO₄³⁻) and nitrate (NO₃) adsorption experiment

The application of the ability of CH has been reacted with META to become CH-T-META for removing phosphate and nitrate ions from aqueous solutions. Evaluation of the performance of CH-T-META was carried out on variations in equilibrium time, temperature, stirring speed, and mass of CH. In addition. adsorption was carried our using 0.3 grams as initial mass of adsorbent with 25 mL of adsorbate solution. Adsorption isotherm balance was carried out to determine the maximum adsorption capacity (q_{max}) for PO₄³⁻ and NO₃⁻. Calculation of adsorption capacity uses equation 1 and adsorption efficiency uses equation 2. The adsorption capacity (q_e) and adsorption efficiency (RE) value at equilibrium (mg/g) and (%) respectively:

$$q_e = \frac{(C_0 - C_e) \times V}{W} \tag{1}$$

$$RE = \frac{(C_0 - C_e) \times 100\%}{C_0} \tag{2}$$

where: C_0 – represents the initial concentration of the adsorbate solution (mg/l), and C_e stands for its equilibrium concentration (mg/l), respectively; W is the weight of the adsorbent (g) and V is the volume of solution (L).

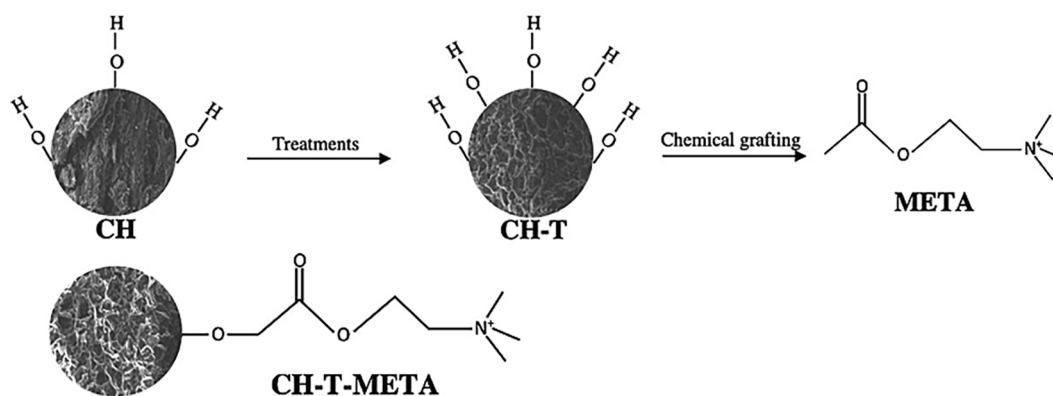


Fig. 1. Expected setup schematic of CH-T-META

RESULT AND DISCUSSION

Structure of the material and surface morphology

The Fourier Transform Infrared Spectroscopy (FTIR) facilitates the qualitative analysis of functional groups in chemical compounds found within the cocoa husk. FTIR is recognized as an analytical method suitable for pinpointing components in organic, inorganic, and polymeric materials, among others. This technique employs infrared radiation to examine the test samples, revealing their chemical attributes. The radiation absorbed by the sample transforms into rotational energy of its molecules. Subsequently, the detector captures this signal, which is then translated into a spectral format. The FTIR outcomes for CH and CH-T-META can be viewed in Figure 2, with the wavenumber for CH-T-META detailed in Table 1.

According to Figure 1 has clearly changed after modification. Wavelengths are measured from 400 to 4000 cm^{-1} . The wavenumber of CH looks smooth and has a peak around 2428 cm^{-1} which falls into the C-H group. The peaks produced from CH in this study are related to research conducted by (Maribel Alexandra) who reported that the FTIR peak results on CH were around 1470 cm^{-1} , 1930 cm^{-1} , and 2130 cm^{-1} which fell into the C-H group. Next, a CH reaction was carried out with 2-[(methacryloyloxy)ethyl]trimethylammonium called CH-T-META, a change in the peak of the chemical compound group occurred. Based on the Table 2, the IR Spectra of CH-T-Meta is dominated

by the amine functional group. The peak at 3366.4 cm^{-1} is associated with the N-H group with the amine functional group, the peak at 1624.1 cm^{-1} is associated with the N-H group with the amine functional group, while the peak at 1716.8 cm^{-1} is associated with the C=O group with the carboxylic acid functional group and at the peak of 1297.2 cm^{-1} corresponds to the C=N group with the aromatic amine functional group, the peak identified in the broad signal without a defined peak at around 3366.4 cm^{-1} . On the cocoa husk, the strong absorption band at 3366.4 cm^{-1} defines the amino functional groups. The modification of cacao shell as a biomaterial produces amino groups [37–39]. According to Vieillard, 2018 [38] modification of cacao shell through amino grafting shows a higher CO_2 retention capacity compared to metal-free products, although its alkalinity and porosity are lower. SEM images of CH and CH-T-META was explained in this part. The morphological characteristics of the adsorbent were carried out using the SEM analysis tool using the proximity of 500 SE images with a magnification of 100 nm and are shown in Figure 3. The unmodified cacao husk is shown in Figure 3a and the modified cocoa husk with META (CH-T-META) is shown in Figure 3b.

According to Figure 3a observed that the CH showed a rough surface and hollow particles with uniform sizes. In addition, the CH surface has high porosity. However, after the reaction with 2-[(methacryloyloxy)ethyl]trimethylammonium called CH-T-META, it was found that the morphology of CH underwent significant changes.

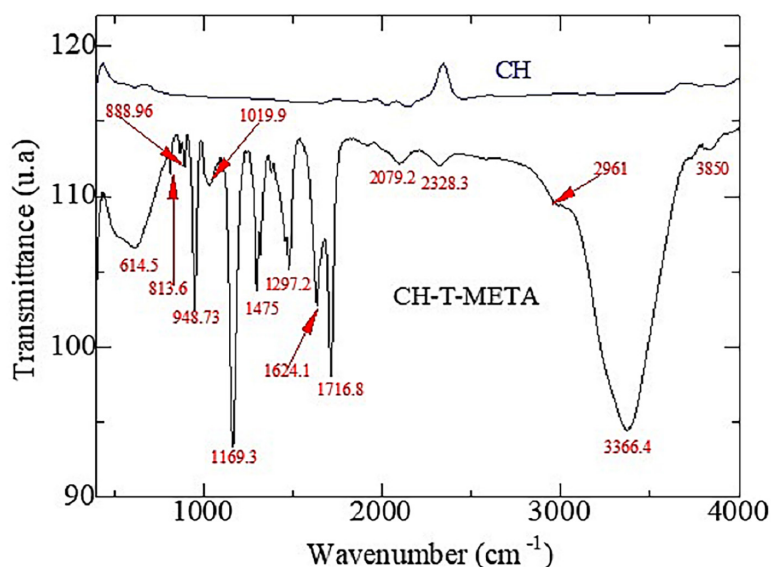
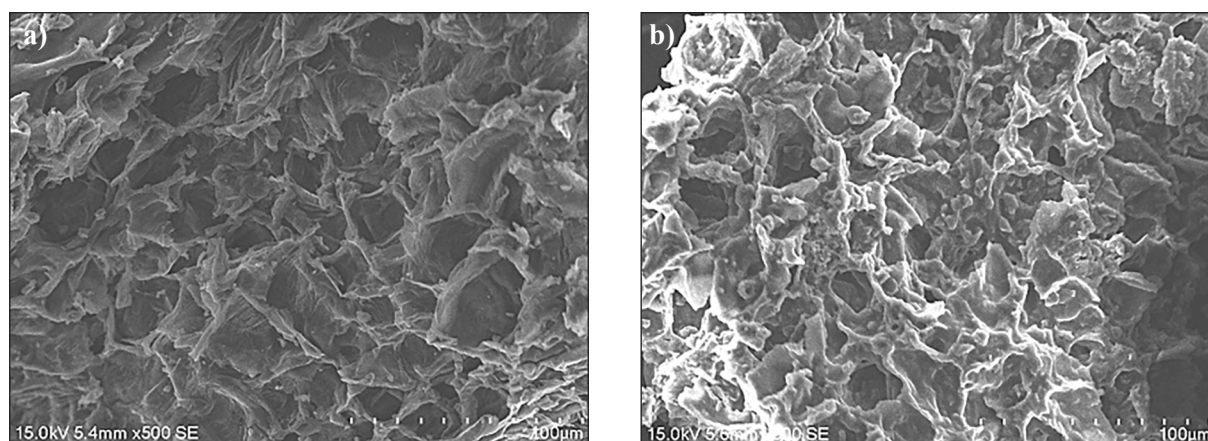


Fig. 2. FTIR Spectrum of CH-T-META

Table 1. FTIR spectrum band assignment of CH-T-META

Wavenumber (cm ⁻¹)	Group	Compound class
614.5	C-Br Stretching	Halo compound
813.6	C-Cl Stretching	Halo compound
888.9	C=C Bending	Alkene
948.7	C=C Bending	Alkene
1019.9	C-N Stretching	Amine
1169.3	C-N Stretching	Amine
1297.2	C-N Stretching	Aromatic amine
1475	C-H Bending	Methylene group
1624.1	N-H Bending	Amine
1716.8	C=O Stretching	Carboxylic acid
2079.2	N=C=S Stretching	Isothiocyanate
2328.3	O=C=O Stretching	Carbon dioxide
2961	C-H Stretching	Alkene
3366.4	N-H Stretching	Amine

**Fig. 3.** SEM image of CH (a), CH-T-META (b)

CH-T-META is known to have a heterogeneous surface and has a smooth surface structure with small porosity. Heterogeneous surface morphology is of great interest to researchers because it is an indicator of the suitability of a material for use as an adsorbent. The results of SEM Images of CH and CH-T-META are in line with the results of research by Rodriguez-Arellano, 2021[40] which discusses the evaluation of cacao beans shell with the result that the surface of the cacao shell before the dye adsorption process and after adsorption undergoes a total transformation. The surface of the cacao shell before absorption has a very rough, heterogeneous surface and spherical particles of micrometric size.

The determined specific surface areas for CH and the CH-T-META blend were 48.34 m²/g and 63.66 m²/g, respectively, as measured using

the Brunauer-Emmett-Telle (BET) standard approach, detailed in Table 2. 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-T-META were found to be 0.1631 cc/g and 0.2181 cc/g, respectively. The resulting pore sizes for CH and CH-T-META were 13.38 nm and 13.52 nm, pointing to a mesoporous structure. Notably, a significant proportion of the material lies in the mesoporous range, exceeding 2 nm. An abundance of mesoporous pores can notably enhance the capacity for adsorption.

Table 2. Specific surface area of materials according to BET result

Characteristic	CH	CH-T-META
Surface area (m ² /g)	48.34	63.66
Pore volume (cc/g)	0.16	0.22
Pore size (nm)	13.38	13.53

Typically, particles with finer pore sizes exhibit greater absorptive capabilities.

Furthermore, the percentage of hydrogen, carbon and nitrogen contained in CH and CH-T-META can be seen in Table 3. The percentage of weight from materials was carried out using elemental analysis. The percentage of weight in terms of H, C, and N in CH-T-META were greater than CH before attaching cationic polymer from META. Based on the experiment result, the modification of CH using 2-[(Methacryloyloxy) Ethyl] Trimethylammonium (META) increased the amount C of 46.84%, H of 7.27% and N of 3.86%. 2-[(Methacryloyloxy)Ethyl] Trimethylammonium (META) is a compound containing a methacrylate functional group which can form covalent bonds with various polymers. In terms of chemical structure, 2-[(Methacryloyloxy)Ethyl] Trimethylammonium has a carbon structure that can provide additional sources of C and H atoms. META also has three methyl groups (CH₃) which contain additional C and H atoms.

Effect of percentage of cationic polymer

Cationic polymer is a polymer that has positively charged functional groups along the polymer chain. Based on chemical properties, cationic polymers have the ability to be soluble in water and compatibility with other materials. Hence, Cationic polymer is dissolve easily in water easily absorb other such as polymers, surfactants and other chemicals. The effect of cationic polymer on adsorption ion phosphate and nitrate is shown in the Figure 4. It was seen that the increasing phosphate and nitrate initial concentrations, a decrease in phosphate and nitrate adsorption was observed. Comparing

the absorption of phosphate and nitrate, nitrate is more readily assimilated. The higher the concentration used, the more phosphate and nitrate ions will be absorbed. In this study, the highest absorption was at a concentration of 75% with an absorption of 67.43% phosphate, and at a concentration of 75% nitrate absorbed as much as 86.42%. The use of cationic polymers can increase adsorption efficiency and adsorption capacity because cationic polymers carry out electrostatic interactions between molecules of cationic and anion charged groups so that nitrate and phosphate which have anionic properties can easily interact with cationic polymers. According to Cho, 2011 [41] the presence of polymer groups is responsible for removing anions from aqueous solutions. Cho et al., 2011 reported the granular activated carbon modified by coating a polymer containing [3-(methacryloylamino)propyl]-trimethylammonium chloride with variations of 2.5% and 0.25% cationic polymer. The decreasing of removal efficiency affected by decrease in reactivity in the adsorbent pores [41].

Effect of stirring speed

The effect of varying the stirring speed of each sample can be seen in the Figure 5. The research results show that the absorption of nitrate ions, the faster the stirring is done, the more nitrate ions are absorbed, while the results of the absorption that occurs in phosphate ions are less stable so that the results obtained by the stirring speed are the maximum absorption of each ion is around 70 rpm with 93.13% nitrate absorption and 70 rpm stirring produces 64.93% phosphate absorption. The effect of stirring speed on the phosphate and nitrate adsorption process can be indicated that the stirring speed can increase the diffusion rate of phosphate and nitrate ions so that it can increase the contact process between ions and adsorbent. In addition, the high stirring process can ensure homogeneous distribution of the adsorbent and ions in the solution. The results of this research are related with Sarkar et al., 2021 research that stirring speed can affect adsorbent efficiency [42].

Table 3. The percentage of weight of CH and CH-T-META

Sample	Percentage of weight (%)		
	H	C	N
CH	4.09	33.81	0.91
CH-T-META	7.27	46.85	3.86

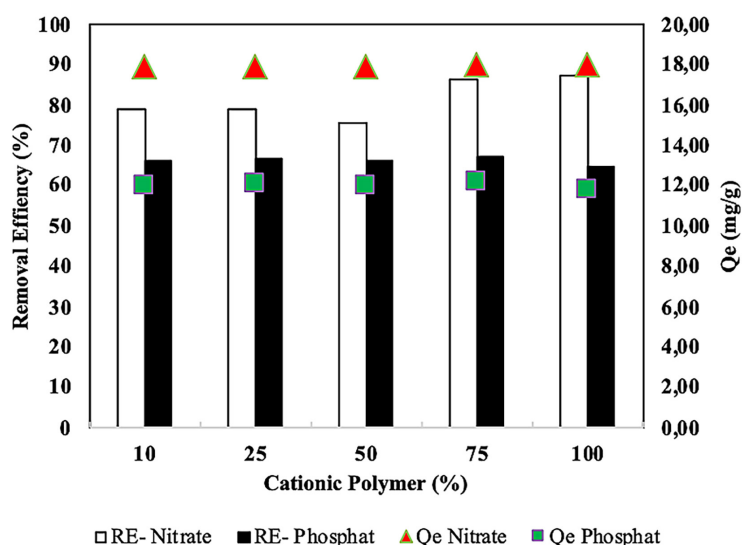


Fig. 4. Effect percentage of cationic polymer on adsorption of ion phosphate and nitrate

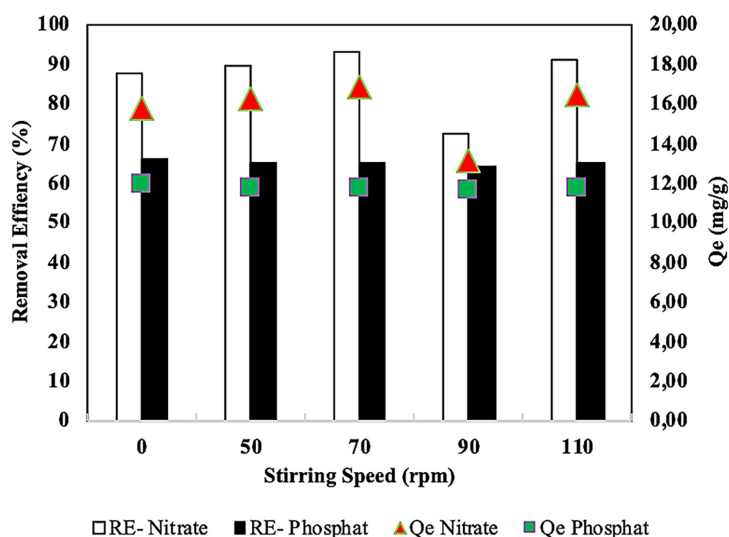


Fig. 5. Effect stirring speed on adsorption of ion phosphate and nitrate

Effect of reaction time

The effect of reaction time can be seen in Figure 6. It can be observed that the amount of adsorbed nitrate and phosphate increased over time for the two adsorbents and a high absorption result was obtained at a reaction time of 180 minutes, the absorption of nitrate ions obtained the highest absorption yield of 92.85% at the reaction time 180 minutes. while for phosphate, an absorption value of 66.52% was obtained at a reaction time of 180 minutes. It was proven that at a reaction time of 180 minutes it had good absorption of phosphate and nitrate ions. Reaction time for adsorption can affect the effectiveness of the adsorbent. Increasing the reaction time or contact time between the

adsorbent and ions in aqueous solution can increase the number of ions adsorbed. Apart from that, maximum reaction time can help the reaction reach the equilibrium point. Based on research Li, 2022 [43] increasing the reaction time from 1 hour to 5 hours can increase the percentage of nitrite removal from 51.18% to 58.15% and phosphate ions from 50.89% to 58.34%. The results of this research are comparable to research conducted by [44] that the reaction results in adsorption are almost unchanged or constant.

Effect of reaction temperature

Reaction temperatures are one of the variations that greatly affect the absorption of

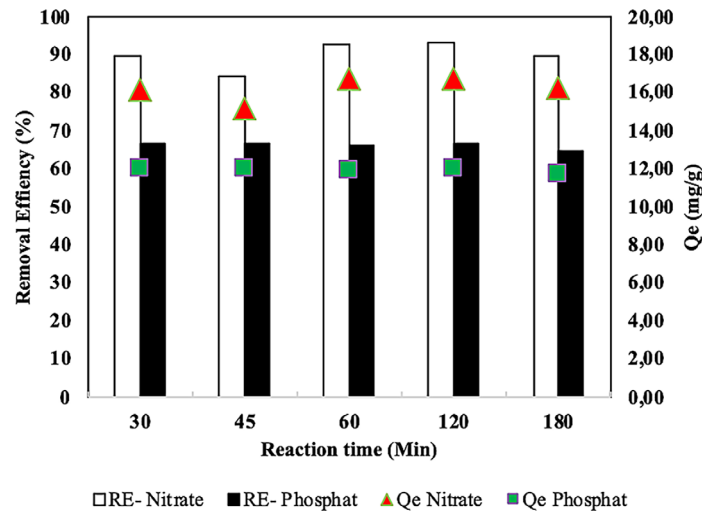


Fig. 6. Effect reaction time on adsorption of ion phosphate and nitrate

phosphate and nitrate ions that can be seen in Figure 7. The highest absorption is in nitrate 99.67% and in phosphate 98.51%, where the average temperature allows for the highest absorption of ions phosphate and nitrate around 50–60°C temperature. The effect of temperature on the absorption of phosphate and nitrate ions can be seen in the adsorption capacity where increasing temperature causes thermal energy to increase, thereby facilitating the diffusion of phosphate and nitrate ions. In addition, high temperatures in the adsorption process can increase the adsorption speed because the ion diffusion process is faster. The results of this research are relevant to previous research [45] which conducted research on the effect of temperature on denitrification in a case study in a nitrate study laboratory with the

result that nitrate removal was most efficient at a temperature of 40°C. It should be noted regarding the effect of temperature on the adsorption process that high temperatures are not recommended because it can damage the cocoa shell, reduce the benefits of absorption, and cause desorption. The results of this research are comparable to research conducted by Zhang and Li, 2021 that temperature variations of 25–75°C produced an adsorption rate above 60% [46].

Effect of cacao husk mass on the reaction

The use of cacao husk mass variations is used to determine effective mass variations. Variations in cacao husk mass can be seen in Figure 8. It shows that the use of large amounts of cacao husk

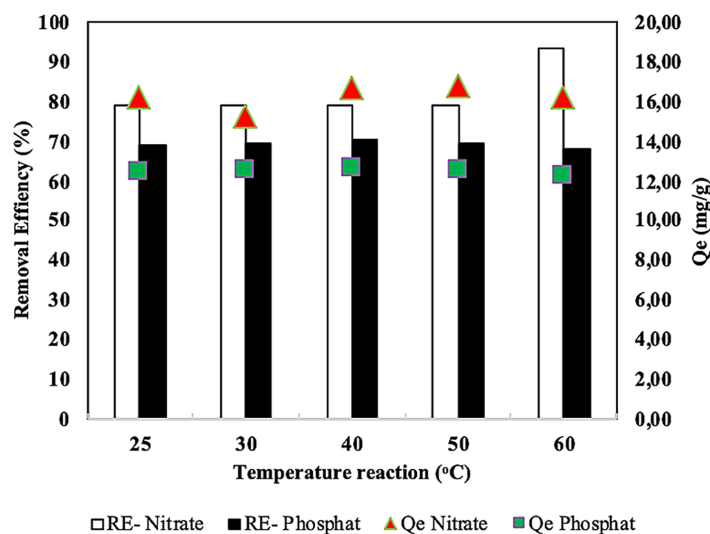


Fig. 7. Effect of temperature reaction on adsorption of ion phosphate and nitrate

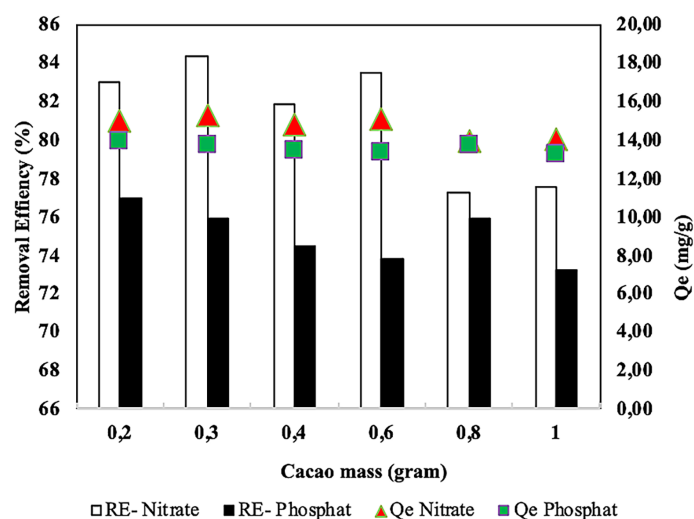


Fig. 8. Effect of cacao mass on adsorption of ion phosphate and nitrate

mass can cause a larger surface area and more active binding sites for nitrate and phosphate ions. Another influence is a decrease in adsorption capacity and adsorption efficiency. Based on the research results, the highest uptake of phosphate and nitrate ions was found at a mass of 0.3 gram, where the uptake for both phosphate and nitrate ions was 99.67%. Therefore, the effective mass used is to use 0.3 gram of cocoa husk. The relationship between variations in cocoa shell mass and absorption efficiency is not linear. In addition, variations in the mass of cocoa shells during the reaction can affect the attainment of the equilibrium time. The time required to reach equilibrium will vary. The results of this research are comparable to the results of research conducted by Gorzin et al., 2018 that equilibrium decreases when the adsorbent mass increases. However, in this study the decrease in equilibrium did not have a significant effect [47].

CONCLUSIONS

Surface modification of cacao husk and cationic polymer with 75% of 2-[(methacryloyloxy) Ethyl] Trimethylammonium (CH-T-META) was successfully conducted and applied for removal of phosphate and nitrate ions. Removal efficiency is achieved with 75% of cationic polymer that reacted with 0.3 gram of CH under 70 rpm of stirring speed for 180 minutes at 50°C. The removal efficiency was 99.67% both phosphate and nitrate ions. The SEM analysis shown that the surface was heterogeneous surface that indicator of the suitability of a material for use as an adsorbent.

Elemental analysis confirmed that the modification found in the percentage of C (46.84%), H (7.27%), and N (3.86%).

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