Synthesis of Chitosan Silica Membrane from Petung Bamboo (*Dendrocalamus asper*) Leaves and Its Application as Pb(II) Metallic Adsorbent

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Abstract: *Membrane synthesis through a phase inversion method using chitosan and sodium silicate solutions has been conducted. This research aims to characterize the silica chitosan membrane (SCM) of petung bamboo leaves and determine the synthesized product's adsorption capacity for Pb(II) ions. The XRF characterization showed the silica content of petung bamboo leaves with a percentage of 78.03%. SEM analysis before adsorption is around 13.0 μm, and the pore diameter after adsorption is around 9.7 μm. The results of adsorption analysis of Pb(II) metal using AAS showed that the SCM variation A at an initial concentration of 10.0000 ppm Pb(II) metal adsorbed was 9.8101 ppm, and at an initial concentration of 25.0000 ppm Pb(II) metal was 22.3421 ppm. The variation B at an initial concentration of 10.0000 ppm Pb(II) metal adsorbed was 9.8870 ppm and at an initial concentration of 25.0000 ppm Pb(II) metal adsorbed was 23.5806 ppm. The variation C at an initial concentration of 10.0000 ppm Pb(II) metal adsorbed was 9.9639 ppm, and at an initial concentration of 25.0000 ppm Pb(II) metal was 24.1855 ppm. The results of this research conclude that the highest SCM adsorption power is variation C (2%:22.95%) with a percentage of 99.63%.*

Keywords: *adsorbent; Pb(II) metal; petung bamboo leaves;* Dendrocalamus asper*; silica chitosan membrane*

INTRODUCTION

Membrane is a barrier that selectively lets some parts through and does not let others through. Membrane technology has several advantages, namely the separation process takes place at room temperature, its properties vary, it can be adjusted according to needs and most of the membranes produced can be reused. If the membrane is damaged, it can be recycled so it produces relatively no new waste so it is classified as clean technology [1]. This process depends on the size of the pores and the material forming the membrane. The membranes are widely used in water and wastewater treatment, gas separation in the food and beverage industry, medicine, and pharmaceuticals [2]. One material that can be used as a membrane is silicon dioxide. Some plants contain specialized aquaporins that bind silicon. Silica gel in plants performs another function: it replaces cellulose and increases the strength of plant structures [3].

Composite membranes are asymmetric membranes consisting of dense porous and supporting layers with different materials. This membrane can provide optimal performance against selectivity, permease rate, and thermal stability [4]. Membranes can be made from organic materials, such as polymers, generally non-porous polymer membranes are made with an asymmetric or composite structure. One of the materials used in making membranes is silica which is obtained from petung bamboo leaves [5].

Bamboo leaf waste is one of the biomass wastes that has not been utilized yet optimally [6]. Hence it needs to be developed to increase its economic value and reduce its negative environmental impact. Bamboo leaves contain many chemical compounds such as silica. Using the sintering method, the silica content obtained from bamboo leaves reaches 50% [7]. Most of the silica content is 17–23% by mass, which is higher than the silica content of rice husk (9.3–13.5% by mass). Bamboo leaf ash has a high SiO content of 75.90–82.86 wt.% [8-10]. Silica is one of the materials that can be used as a membrane because it has the property of forming a pore membrane so that the resulting membrane will have pores. The use of silica in membranes can also increase the affinity of the membrane toward the metals [11-12]. Another material that can be used to improve the quality of the resulting membrane is chitosan.

A naturally occurring renewable basic polysaccharide with no harmful side effects is chitosan. The only naturally occurring alkaline polysaccharide, chitosan, is an extract of shrimp, crab, and insect shell skeletons that has undergone chitin deacetylation. It is a naturally occurring polymer substance with abundant supplies. Some of chitosan's qualities are good biocompatibility, simple biodegradation, non-toxicity, and environmental friendliness. Chitosan and its derivatives are widely employed, particularly in the biomedical industry, where they can be utilized to create fake skin and other soft tissue materials as well as drug carriers [13].

The sugar residue of chitosan has an acetylamino or amino group on C2 and a hydroxyl group on C. From a conformational point of view, they are all planar groups with a unique structure that allows them to chelate metal ions with a certain ionic radius [14]. Chitosan contains amine groups that function as ion exchangers [15-16]. Many excellent characteristics of cellulose nanocrystals include their non-toxicity, potent biocompatibility, high hydrophilicity, high tensile strength (up to 7500 MPa), high transparency, high crystallinity, and high Young's modulus (up to 140 GPa). Furthermore, hydroxyl groups are abundant in cellulose molecules and can be subjected to a variety of processes, including etherification, esterification, and oxidation reactions [17]. Because these hydroxyl groups enable molecules to form hydrogen bonds, cellulose can be easily grafted and copolymerized with other materials. These qualities guarantee that cellulose will find widespread use in food packaging [18], paper [19], biomedical [20], adsorbent, new energy, and other industries. When used as a dispersion phase, nano-cellulose with a high aspect ratio can enhance mechanical characteristics, water and heat resistance, and other attributes of natural or synthetic polymers. Specifically, superior-quality composite materials can be produced [21]. On the other hand, the use of chitosan in making membranes is less effective, and this is due to the property of chitosan, which cannot form pores. Hence it is necessary to combine the composition of the membrane between chitosan and silica.

The combination aims to reduce the membrane's pore size so that the separation takes place more effectively and increases the adsorption capacity of the membrane due to the presence of active groups in silica [15-16]. The use of membranes as adsorbents has several advantages compared to other adsorbents. These advantages are membranes that can be used repeatedly, membrane separation that takes place continuously, and the ability to separate particles to nanometer size [1,22]. Damaged synthesized membranes can be recycled, so they relatively do not produce a new waste and are classified as clean technology [23].

To improve the practical aspect, silica can be embedded into the chitosan membrane matrix. Chitosan can be obtained from chitin through a deacetylation reaction to produce a multifunctional polymer with functional groups containing N and O atoms. These functional groups are responsible for the excellent performance of an adsorbent in the separation process [24-26]. In several reports, chitosan has shown its ability to remove heavy metals [25,27], biodiesel impurities [28], dyes [29] and pesticides [30]. Moreover, chitosan can be easily dissolved in acetic acid, thus enabling a simple and environmentally friendly process of membrane matrix preparation [31].

Oxide materials typically have hydroxyl groups covering their surface, typically represented as S–OH during the impregnation stage. These groups can exchange protons with the liquid solution to behave as bases or Bronsted acids, which allows them to interact with certain active phases based on surface ionization reactions, as illustrated in Eq. (1) and (2).

S–OH + H_2O → S–O^- + H_3O^+ (1)

S–OH + H_3O^+ → S–OH_2^+ + H_2O (2)

The presence of SO^- anions and S–OH_2^+ cations on the surface is a function of pH. At the critical pH value, the number of negative charges (S–O) exactly equals the number of positive charges of S–OH_2^+, resulting in a zero net charge [32-33].

Several studies on membrane combinations using chitosan-silica have been carried out. Silica-based membranes that have calcined for two hours show an increase in water uptake from 37.9% to 51.97% (Stober) and from 40% to 56.21% (sol-gel) [34]. The silica chitosan membrane (SCM) has good accuracy with an average %recovery of 100.96% and precision with an average %relative standard deviation of 1.43 and 3 min of response time as well [35]. SCM materials were synthesized from sugarcane bagasse ash to adsorb methylene blue dye with a removal efficiency of 97.3% and an uptake capacity of 9.73 mg/g [36]. The chitosan-silica hybrid aerogel was successfully synthesized using sol-gel and ambient drying methods [37]. Based on this description, this study aims to determine the characteristics of the SCM of petung bamboo leaves (*Dendrocalamus asper*) and their adsorption capacity on Pb^{2+} metal ions.

■ EXPERIMENTAL SECTION

Materials

Seven materials were used in this experiment. The materials used in this experiment were 4 M of sodium hydroxide (NaOH) solution, chitosan powder, 2% of acetic acid solution (CH_3COOH), 5% of NaOH solution, distilled water (H_2O), 10 and 25 ppm of $Pb(NO_3)_2$ solutions, and filter paper.

Instrumentation

Nine tools were used in this experiment. The tools used in this experiment were a set of glassware, hotplate, magnetic stirrer, analytical balance, oven, petri dish, XRF instrument (Thermo Fisher Scientific), SEM (Hitachi Flexsem 1000), and AAS (AA-7000 Shimadzu).

Procedure

Preparation of sodium silicate (Na_2SiO_3) solution

Silica (0.05 g) was dissolved in 2 mL of 4 M NaOH solution. This dissolving process was carried out at 50 °C until dissolved, thus 5.73% Na_2SiO_3 solution was obtained. The same treatment was carried out for two masses of 0.1 and 0.2 g silica.

Preparation of 2% chitosan solution

Chitosan (2 g) was dissolved in 100 mL of 2% CH_3COOH solution with the help of a magnetic stirrer. Thus, 2% of the chitosan solution was obtained.

*Synthesis SCM petung bamboo leaves (*D. asper*)*

Chitosan solution was measured and then added with 2 mL of 5.73% sodium silicate. It was homogenized using a magnetic stirrer for 1 h. The mixture of solutions was poured into a petri dish and dried in the oven at 65 °C until half-dry and allowed to rest in the open air until completely dry. The formed SCM was immersed in an alkaline solution for 24 h until the membrane was lifted to the surface and then neutralized with distilled water. The same treatment was carried out with two percentages of 11.47% and 22.95% Na_2SiO_3 solutions (Fig. 1).

Preparation of Pb(II) metal ion solution

A total of 1.599 g of solid $Pb(NO_3)_2$ was put into a 1 L measuring flask. Next, the solid was dissolved in distilled water to the limit mark and homogenized to obtain a stock solution of Pb(II) metal ions with a concentration of 1000 ppm. Next, it was diluted until a solution with a concentration of 10 and 25 ppm was obtained.

*SCM adsorption power test of petung bamboo leaves (*D. asper*) against metal Pb(II)*

The resulting SCM of petung bamboo (*D. asper*) leaves were placed on a funnel that has been covered with filter paper. A volume of 50 mL Pb(II) solution with a concentration of 10 ppm was poured into the membrane so it was able to pass through the membrane. The solution that had passed through the membrane was analyzed using AAS, and the residual Pb(II) metal was measured. The treatment was carried out three times. The same treatment was also carried out for a 25 ppm Pb(II) solution.

*SCM characterization of petung bamboo leaves (*D. asper*)*

The SCM of petung bamboo leaves (*D. asper*) which had the highest adsorption capacity was analyzed

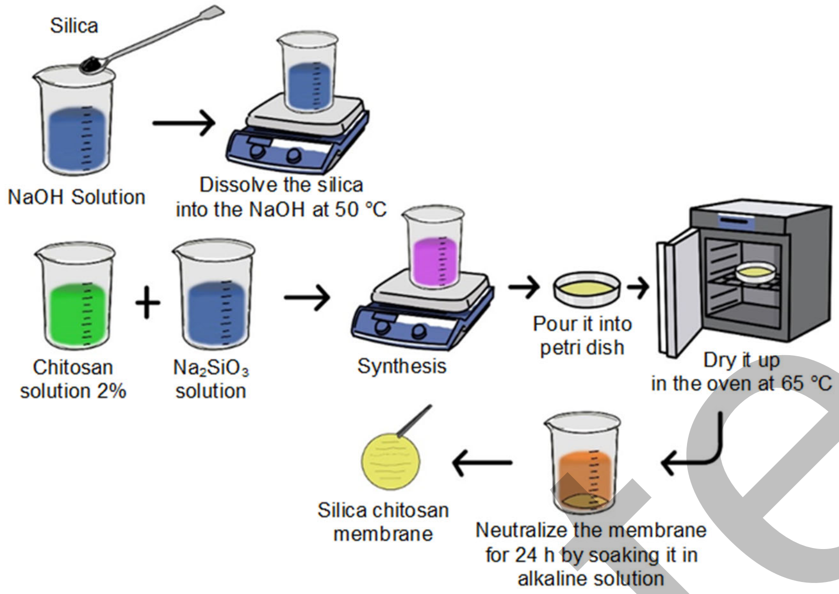


Fig 1. SCM synthesis scheme

for its morphology. SCM of petung bamboo leaves analyzed by SEM was one sheet of SCM petung bamboo leaves before the adsorption took place and one sheet of SCM petung bamboo leaves after the adsorption occurred. The pore diameter of the membrane can be measured based on the results of SEM analysis at 5000× magnification.

RESULTS AND DISCUSSION

Result of Petung Bamboo Leaf Analysis (*D. asper*) with XRF

Based on Table 1, the results of the analysis using The XRF result was as follows: SiO_2 with 78.03%, CaO 15.23%, K_2O 5.4%, Si 36.48%, P 6.10%, Ca 3.27%, and other oxides of < 1% respectively. XRF showed that the silica contained in the ashes of petung bamboo (*D. asper*) leaves was 78.03%. This is not much different from the research conducted by Udaibah and Priyanto [38] which revealed that the silica content of petung bamboo leaf ash was 77.06%. The high silica content of petung bamboo leaf ash can be used as the main ingredient in the manufacture of petung bamboo leaf (*D. asper*) SCM. Heat treatment of bamboo leaves at a certain temperature affects the ash's mineralogical composition and changes in morphology [32]. In the process of thinning bamboo leaves, a combustion reaction can occur as in Eq. (3).

$$\text{Elements of C, H, Si} + CO_{2(g)} \rightarrow CO_{2(g)} + H_2O_{(g)} + SiO_{2(s)} \quad (3)$$

Na_2SiO_3 solution is a solution that functions as a precursor in membrane synthesis. Na_2SiO_3 solution is produced by dissolving silica with a mass variation of 0.05, 0.1, and 0.2 g in 4 M NaOH solution. The selection of these variations aims to determine the effect of the addition of silica on the characteristics of the resulting membrane. NaOH can dissolve SiO_2 because it is based on the physical properties of SiO_2, which can only dissolve in alkaline solutions. It also acts as a Na^+ ion supplier to produce Na_2SiO_3. The choice of NaOH was based on the results of research conducted by Castillo et al. [39], where NaOH has a low melting point, making it easier to form Na_2SiO_3 at temperatures that are not too high. The resulting Na_2SiO_3 solution is white. Reactions

Table 1. Composition of petung bamboo leaf ash

Compound	Percentage (%)	Elements	Percentage (%)
SiO_2	78.03	Si	36.48
CaO	15.23	P	6.10
K_2O	5.42	Ca	3.27
P_2O_5	0.66	K	0.28
Fe_2O_7	0.46	Fe	0.38
MnO	0.08	Mn	0.06
TiO_2	0.08	Ti	0.07
ZnO	0.01	Zn	0.01

that occur during the formation of Na_2SiO_3 can be seen in Fig. 2.

Based on the reaction mechanism in Fig. 2, the NaOH compound dissociates to form Na^+ and OH^- ions. When silica is reacted with a NaOH solution, it will form an unstable intermediate ion $(SiO_2OH)^-$. In the SiO_2 compound, the electronegativity of O is higher than Si, causing Si to be more electropositive, resulting in a hydrogenation process. The hydrogen contained in the hydroxyl group of the intermediate ion $(SiO_2OH)^-$ reacts with the hydroxyl group attached to NaOH to form a water molecule and two Na ions in NaOH will neutralize the negative charge of the intermediate ion $(SiO_2OH)^-$ formed, then interacts with the SiO ion to form Na_2SiO_3 [40].

SCM Petung Bamboo Leaves (*D. asper*)

The method used in membrane synthesis in this study is the phase inversion method, which is often used in membrane synthesis. The phase inversion method is a process in which a polymer is changed from a liquid phase to a solid phase [36]. Chitosan solution was added to the Na_2SiO_3 solution at the membrane synthesis stage. The addition of Na_2SiO_3 solution, which is a source of silica, into the chitosan solution aims to form membrane pores to increase membrane permeability and the membrane's affinity for metals. Silica will form pores with intermolecular oxygen silica bonds to form long SiO_2 chains and bonds between silica and oxygen in the –OH group [11-12].

Method addition of the Na_2SiO_3 solution little by little while stirring using a magnetic stirrer aims to ensure that the mixing of the chitosan solution and the Na_2SiO_3 solution does not produce lumps on the membrane. Clots in the membrane can cause holes and these clots can close the pores in the membrane which can affect the adsorption capacity of the membrane [36].

The membrane is printed in a plastic container, the use of a plastic container aims to avoid silica interaction with the mold. The printed membrane was dried in an oven at 65 °C until half dry, then it was dried at room temperature. Drying is done in stages to produce a perfectly dry and even membrane because the membrane is easily damaged when wet. Therefore, the membrane must be dehydrated from the solvent [39]. The dry membrane is soaked using 5% NaOH. The NaOH solution functions as a non-solvent solution that diffuses to the bottom of the membrane, which coincides with the mold so that the membrane is pushed up and detached from the mold [23]. In addition, NaOH immersion also aims to coagulate SCM to obtain a more stable membrane and convert NH_3^+ to NH_2 [36]. The SCM of petung bamboo leaves (*D. asper*) was washed repeatedly with distilled water. The washing aims to remove the remnants of NaOH in the membrane, so the resulting membrane is neutral. The SCM of petung bamboo leaves (*D. asper*) produced is in the form of colorless (transparent) thin sheets, stiff in the dry state and elastic in the wet state (Fig. 3).

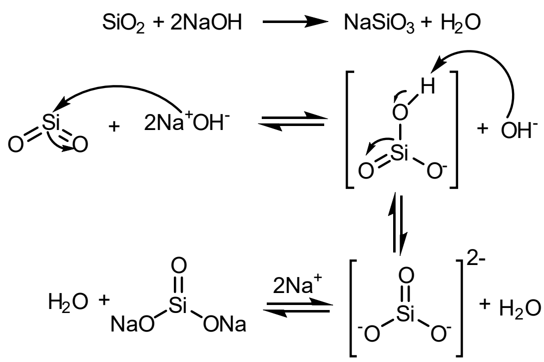


Fig 2. Reaction mechanism for the formation of sodium silicate [40]

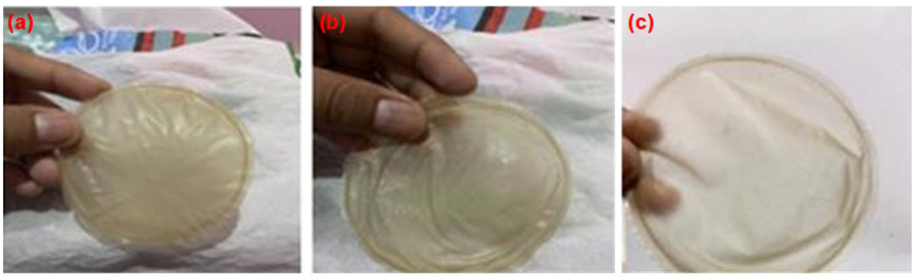


Fig 3. SCM variation (a) A, (b) B, and (c) C

The interaction between chitosan and silica as illustrated in Fig. 4, is from hydrogen bonds between the OH, NH, or carbonyl groups (C=O) in chitosan and the OH groups in silica [41-42]. Chitosan combined with inorganic oxides such as silica can potentially concentrate molecules with different properties: extended specific surface, functional group accessibility, and thermal stability. Another silica-chitosan interaction comes from the electrostatic interaction between the negatively charged silica particles and the positively charged chitosan molecules [43-45]. Chitosan and silica are combined through weak interactions, such as hydrogen bonds between the amine, acetamide, or hydroxyl groups of the biopolymer and the silanol groups of silica. or the electrostatic force between the protonated amino group and the dissociated hydroxyl group.

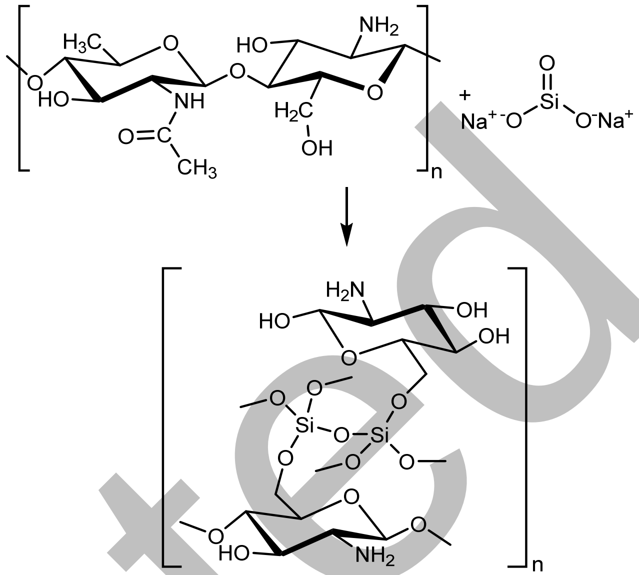


Fig 4. Illustration of cross-linking between chitosan and sodium silicate

SCM Adsorption Power of Petung Leaves (*D. asper*)

The three variations of SCM (A, B, and C) of petung bamboo (*D. asper*) leaves produced were tested for their adsorption capacity using Pb(II) metal solution. The concentration of the permeate produced after the adsorption process was measured using AAS. The adsorption results of SCM can be seen in Table 2. Adsorption power data of the three variations of SCM leaves of petung bamboo (*D. asper*) has increased, and the one that produces the highest adsorption power is the membrane variation C with a percentage of 99.63% for an initial concentration of 10 ppm and 96.67% for an initial concentration of 25 ppm. The increase in adsorption power is due to the increased amount of silica used so that the O^{2-} group on the membrane increases, where the O^{2-} group is negatively charged and will bind Pb(II) [36]. According to the HSAB theory that Pb(II) is a borderline acid group (between hard acids and soft acids) that can bind to hard bases and soft bases, while the O^{2-} the group is a hard base group so that Pb(II) can bind to the O^{2-} [46-47]. The pores formed in the membrane occur due to intermolecular bonds between silica and oxygen, thus forming long chains of SiO_2 and bonds between silica and oxygen in the –OH group. The addition of silica can also increase the affinity of the membrane for heavy metals [11-12].

When studied using the HSAB theory of bonds involving strong acids or bases, the resulting bonds have the character of ionic bonds. The petung bamboo leaf ash chitosan-silica membrane variation 3 at a concentration of 10 ppm produced the highest adsorption percentage reaching 99.63%. This could mean that the active groups on the surface of the membrane have bound the Pb(II) ion with a maximum so that the opportunity for a bond to occur between the Pb(II) ion and the active group is small [48]. The proportion of adsorption will be high if there are more active groups than metal ions, until there are the same number of active sites as metal ions [49]. Besides that, the addition of silica to the membrane can form pores in the membrane [50]. The pores that form in the membrane occur due to the bonding of silica with intermolecular oxygen, thus creating long chains of SiO_2 and bonds between silica and oxygen in the OH group. The addition of silica can also increase the membrane's affinity for heavy metals [51].

Based on Table 2, it can be said that the increase in the concentration of metal Pb(II) from 10 to 25 ppm decreased the percentage of adsorption. This is due to higher concentrations, the amount of metal ions in solution is not proportional to the number of adsorbent

Table 2. Adsorption data using SCM

SCM Variation	Concentration initial (ppm)	Concentration end of average (ppm)	Concentration adsorption Pb (ppm)	Percentage adsorption (%)
Variation A	10	0.1899	9.8101	98.10
2%:5.73%	25	2.6579	22.3421	89.36
Variation B	10	0.1190	9.8870	98.87
2%:11.47%	25	1.4194	23.5806	94.32
Variation C	10	0.0361	9.9639	99.63
2%:22.95%	25	0.8145	24.1855	96.67

particles available so the surface of the adsorbent will reach a saturation point and there is a possibility that a desorption process or re-release between the adsorbent and metal ions will occur [52-53].

SCM Morphological Analysis of Petung Bamboo Leaves (*D. asper*)

SEM testing to see the surface morphology of the membrane pores that have the highest adsorption capacity, namely the C variation membrane before and after adsorption. Based on Fig. 5, before and after adsorption, it can be seen that there is a non-uniformity of the membrane surface where in the picture before adsorption, there are many clumps indicating the presence of silica or chitosan that does not dissolve completely. In contrast, in the picture after adsorption, the surface of the membrane is smoother, this indicates the dissolution of silica or chitosan is more maximal. Therefore, producing a uniform surface of the two membranes requires uniform steps and uniform conditions of the materials used during membrane synthesis so that the resulting membrane surface is more

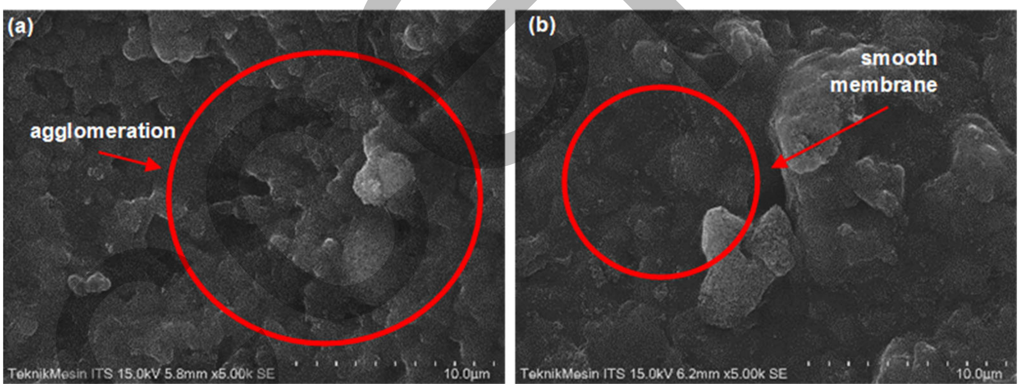
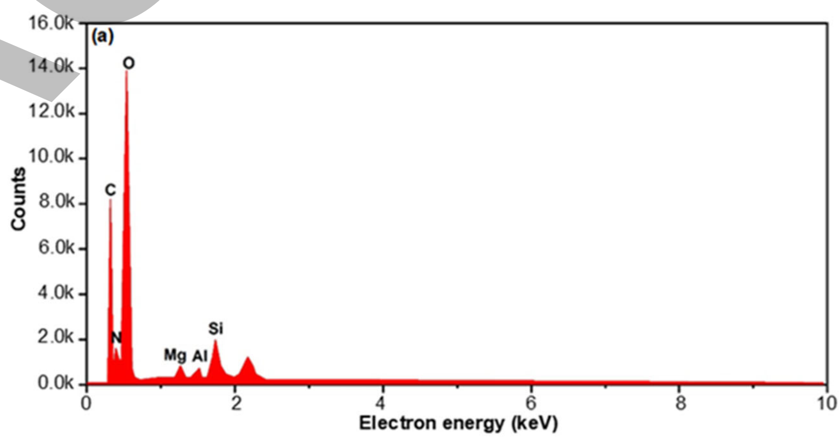


Fig 5. Membrane (a) before and (b) after adsorption, at 5000× magnification



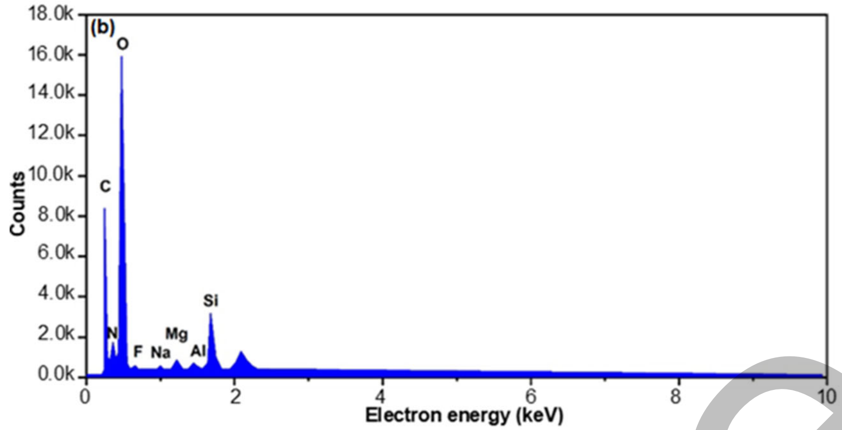


Fig 6. EDX results of membranes (a) before and (b) after adsorption

uniform. The calculation results show that the pore diameter of the membrane before adsorption is around 13 µm, and the pore diameter of the membrane after adsorption is around 9.7 µm. Energy Dispersion X-Ray (EDX) spectroscopy analysis showed the presence of elements C, N, and O, constituent elements of chitosan, and Si, which are constituent elements of silica. The results of the EDX analysis can be seen in Fig. 6.

■ CONCLUSION

The characteristic of the membrane in this research delved more into the diameter size of the membrane pore. The pore diameter of the membrane before adsorption is around 13 µm and the pore diameter after adsorption is around 9.7 µm. The SEM results show that the membrane surface is non-uniform. Based on the physical appearance of the membrane, it can be described as a thin colorless (transparent) sheet, stiff in the dry state, and elastic in the wet state. The highest adsorption capacity was membrane variation 3, with an average percentage of 99.63% for an initial concentration of 10 ppm of Pb(II) and 96.67% for an initial concentration of 25 ppm of Pb(II).

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■ AUTHOR CONTRIBUTIONS

Hasri, a corresponding writer, acted as an investigator, carried out calculations, and wrote the manuscript. Diana Eka Pratiwi, Isriyanti Safitri, and Satria Putra Jaya Negara wrote, revised, and finalized the data and report. All authors agreed to the final version of this manuscript.

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