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Review Article

Chitosan/Rice Husk-Derived Silica Mixed Matrix Membrane as Potential Separator for Peatwater Purification

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Abstract. Indonesia has the largest distribution of peatlands worldwide and is spread over Sumatra, Kalimantan, and Papua islands. Peatland is one of the land resources with a hydrological function and can store water in the form of peat water. Peat water is brownish-red due to high dissolved organic matter, especially in the form of humic acid and its derivatives, high organic matter content, low pH, and low cation content. Peat water is classified as polluted water, unsuitable for consumption, and cannot be used directly as drinking, bathing, or washing water. The Mixed Matrix Membrane Fabrication method is expected to be used for peat water purification by adding silica filler from rice husk ash. Rice husk has a high silica filler content of >90%. The higher the silica level, the better the material absorbs harmful chemical compounds in peat water, one of which is humic acid.

Keywords: Mixed matrix membrane, Peatwater purification, Silica, Chitosan, Rice husk.

1. Introduction

It is estimated that the area of peatlands in the world covers 420 million hectares, and 30-45 million hectares are types of tropical peat. Indonesia has the widest distribution of tropical peat in the world, which reaches around 14.9 million hectares and is spread over the islands of Sumatra, Kalimantan, and Papua (Ritung & Sukarman, 2016). Peatland is a land resource with a potential hydrological function in storing water as peat water (Widiastuti & Latifah, 2017). So that the surrounding community often uses peat water for their daily needs. A method is needed to purify peat water from the peat water potential. Several methods were reported for peat water purification such as flocculation, coagulation, photocatalytic degradation, and membrane separation. Each method had their own advantages and limitation for peat water purification due to the presence of complex compound. Peat water has the characteristics of being brownish red as a result of the high content of dissolved organic matter in the form of humic acid and its derivatives, high organic matter content, low pH, and low cation content, which is harmful to health if used continuously over a long period (Widiastuti & Latifah, 2017).

Membrane separation was promising and widely used technology for peat water purification. It can be used several types membrane, i.e. polymeric membrane, ceramic or inorganic membrane, and mixed matrix membrane. This Mixed Matrix Membrane fabrication utilizes biopolymer will be used as the main material, then the biopolymer will be filled with inorganic fillers to produce improved mechanical properties and thermal stability. One of the things is prioritized in this mixed matrix membrane is high permeability. Generally, the higher the membrane's permeability, the lower the selectivity. The mixed matrix membrane method is a combination of polymer membranes that have organic fillers with selective properties (Iqbal et al., 2020). The polymer membrane has a weakness such as poor physical properties. However, this weakness can be overcome by adding a filler which will be used to improve the physical properties of the polymer and prevent damage to the membrane. One of the suitable filler used for mixed matrix membranes is silica material (Iqbal et al., 2020). The silica material can be obtained from rice husks with heat treatment..

Rice husk is used as a material because it has a very high silica content.. Silica is also widely used as a basic material for making ceramics, glass, soluble silicate and other silicon-based chemicals. Silica can be isolated from rice husks simply by burning, which will produce ash. Rice husk ash has a silica content of >90% and can be used as an adsorbent, scouring ash, and additive in manufacturing building materials such as concrete and cement. However, suppose the combustion process of the rice husk is inappropriate. In that case, the ash from the rice husk will contain crystalline silica, which will harm and disturb health, due to the presence of inorganic impurity compounds containing potassium and sodium that can reduce the melting point of silica to accelerate the phase change into crystalline (Sapei et al., 2015).

The silica content of the rice husk can also be used as a good filler in the mixed matrix membrane method. A membrane is a thin layer between two fluid phases, namely the feed phase and the permeate phase, which can separate substances of different sizes and limit the transport of various species. The membrane is semipermeable, which means it can withstand specimens larger than its size. The selective nature of this membrane can be used in the separation process (Mutia, 2019). Based on the explanation, it is hoped that the Mixed Matrix Membrane Fabrication method using rice husk material which produces silica which will be used as a filler in making membranes can be used for peat water purification, so that peat water can be used in daily life.

2. Peatwater

Peatland is a land resource with a hydrological function and can store water in the form of peat water. Peat water is brownish-red due to high dissolved organic matter, especially in the form of humic acids and their derivatives, high organic matter content, low pH and low cation content. Humic acids are formed from the decomposition of organic materials such as trees, wood and leaves (Widiastuti & Latifah, 2017). Peat water has a high iron content, which can be seen from the brownish-red color of peat water (A'idah et al., 2018). The concentration of peat water can be seen from the color—the more intense the color, the higher the organic matter content (Suherman & Sumawijaya, 2013). Figure 1 shows the relationship between the color and the chemical properties of humic substances.

The main compounds in peat water are humic, humin, and fulvic acid. These three compounds result from the dissolution of humus found in peatlands. Humic substances are complex organic molecules in soil, water, and sediments. They are formed through the decomposition of organic matter by microorganisms and other natural processes. Humic substances are characterized by their high molecular weight and structural complexity. They are crucial in soil fertility, nutrient cycling, and environmental processes. Humic substances are typically divided into three major components based on their solubility (Jarukas et al., 2021). Humic acid is alkali-soluble and has a high molecular weight with a brown to black color (Figure 2). Fulvic acid is part of the humic substance with water-soluble properties and has a golden-yellow to yellow-brown color (Figure 3). At the same time, humin is an insoluble residue with a black color characteristic (Suherman & Sumawijaya, 2013).

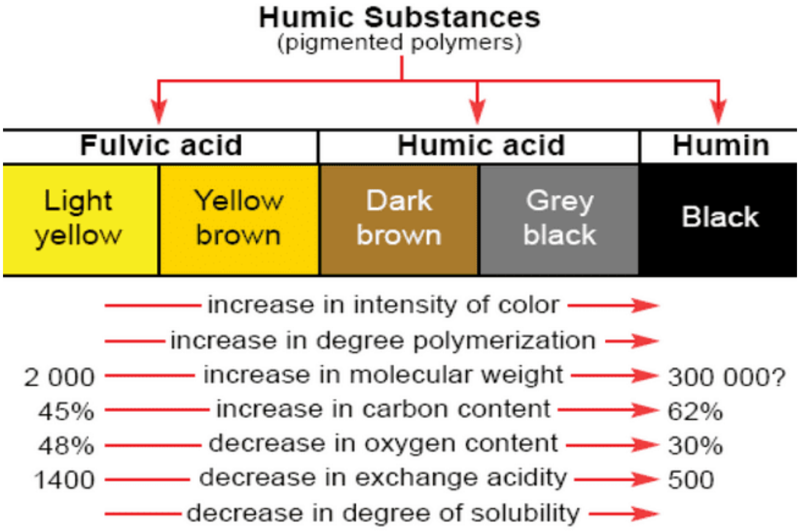

Figure 1. Relationship between the color and the chemical properties of humic substances (Suherman & Sumawijaya, 2013)

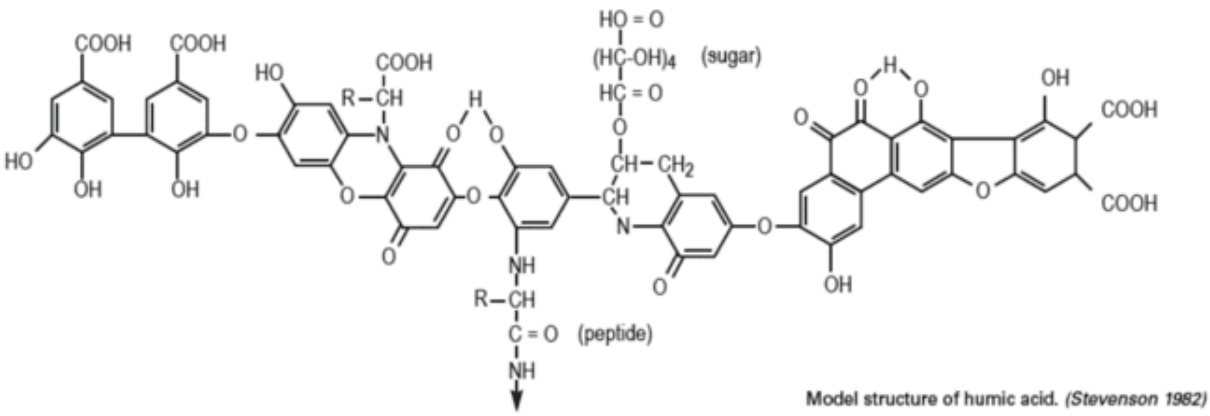

Figure 2. Structure model of humic acid (Suherman & Sumawijaya, 2013)

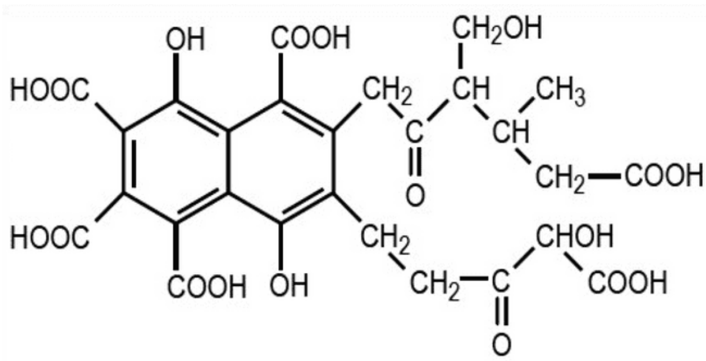

Figure 3. Structure model of fulvic acid (Suherman & Sumawijaya, 2013)

Humic substances have a wide range of functions in the environment. They can improve soil structure, enhance water retention, chelate with metals, facilitate nutrient uptake by plants, and influence the bioavailability of organic and inorganic compounds. Their intricate molecular structure and versatile properties make them a subject of ongoing research in various fields, including agriculture, environmental science, and medicine (Jarukas et al., 2021).

3. Chitosan Mixed Matrix Membrane Fabrication

Membranes are thin, highly selective barriers between two phases that regulate the transport of the substance. One of the constituent components of the membrane is a polymer developed using chitosan (Novi et al., 2016). Mixed Matrix Membrane is a combination of polymer membranes with inorganic fillers that are selective for separation process. However, polymer membranes have poor physical properties, so it is necessary to add fillers. The addition of filler is used to improve the polymer's physical properties, prevent the chemical attack and degradation, then it enhanced the mechanical properties, This Mixed Matrix Membrane fabrication also utilizes biopolymers which will be used as the main material, filled with inorganic fillers to produce good thermal stability. The Mixed Matrix Membrane method uses biopolymers, one of which is chitosan, which can be isolated by burning rice husks to produce silica filler (Iqbal et al., 2020).

Chitosan is a white amorphous solid and insoluble in alkali and mineral acids. Chitosan can also be interpreted as a multi-functional polymer because it contains three types of groups, namely primary and secondary hydroxyl groups and amino acids, which cause chitosan to have high reactivity. Chitosan is poly-(2-amino-2-deoxy-β(1-4)-D-glucopyranose) and has the molecular formula $(C_6H_{11}NO_4)_n$. Chitosan can be obtained from chitin deacylation and found in organisms such as shrimp and crabs that contain chitosan in their shell (Iriana et al., 2018; Wiyarsi & Priyambodo, 2008). Chitin is the main component that functions as a support and protector. Chitin is a polysaccharide polymer composed of beta 2-acetamido-2-deoxy-D-glucose or poly(1,4-N-acetylglucosamine) units. Through this chitin deastylation process, chitosan will be obtained. Another name for chitin compounds is 2-acetamide-2-deoxy-D-glucopyranose (Pratiwi, 2014). Figure 4 shows the structure of chitin and chitosan. Chitosan is a biological product that is cationic, biocompatible, nontoxic, and biodegradable. Chitosan can be utilized as a biopolymer with alternative resources to be used as much as possible. In addition, chitosan can also be utilized as an adsorbent/metal chelator (Wiyarsi & Priyambodo, 2018).

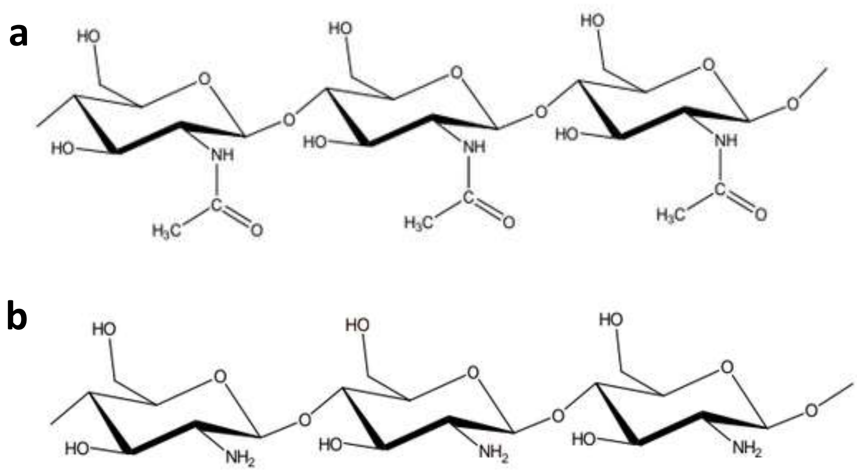

Figure 4. The Structure of (a) Chitin and (b) Chitosan (Wiyarsi & Priyambodo, 2018)

4. Rice Husk

Rice husk or grain skin is the outermost part of the rice grain, which has the highest silica content compared to other rice processing (Fernandes et al., 2017). Rice husk is widely used for fertilizer because it has low NPK content. But adding husk ash will have a positive effect, especially in silica absorption. In this mixed matrix membrane method, rice husk is used as filler to prevent damage to the membrane. The type of filler used is silica content in rice husk. Silica can be obtained from rice husks using a simple method: direct combustion. In this direct combustion process, the right way is needed. If the combustion is not right, it will produce ash that has transformed into crystalline silica due to the presence of inorganic impurity compounds such as potassium and sodium, which can reduce the melting point of silica so that it can accelerate the change of amorphous phase to crystalline (Fernandes et al., 2017; Prasad & Pandey, 2012).

Silica can be obtained from rice husk ash, resulting from the decarbonization of the husk. In burning rice husks, cellulose, hemicellulose and other compounds will be converted into CO_2 and H_2O under atmosphere condition. The rice husk ash will produce a whitish color as much as 13.1-29.04% of dry weight. Based on Table 1, it can be seen that SiO_2 content in rice husk ash is very high compared to other chemical compounds, so rice husk ash is used as filler for the mixed matrix membrane method with high silica content and prevents damage to the membrane (Liu et al., 2016; Prasad & Pandey, 2012; Putranto et al., 2021).

Table 1. Chemical Composition of Rice Husk Ash (Husain et al., 2016)

Compounds	% of Dry Weight
SiO_2	86.9-97.8
K_2O	0.58-2.50
Na_2O	0.0-1.75
CaO	0.20-1.50
MgO	0.12-1.96
Fe_2O_3	0.0-0.54
P_2O_5	0.20-2.84
SO_3	0.10-1.13
Cl_2	0.0-0.41

5. Silica

Silica is a mineral found naturally in free form or as part of mixtures with other minerals that form silicates. Silica can be divided into two main types, namely (Liu et al., 2016):

1. Amorphous silica has variations in the degree of hydration. It is a form of silica that does not have a regular crystalline arrangement. Examples include silica gel or silica gel. The degree of hydration in amorphous silica can differ, affecting the material's properties and structure.
2. Crystalline Silica: Crystalline silica is a form of silica with a regular crystal structure. It consists of different types, such as quartz, cristobalite, and tridymite. This form can be formed through temperature modification from low to high temperature, which causes crystal symmetry and density changes.

Due to their easy availability and good absorption capabilities, silica membranes are often utilized in mixed matrix membrane methods. In general, silica possesses chemically and physically appealing properties for various applications. It can interact with multiple chemicals and has a good absorption capacity for various molecules (Novi et al., 2016).

Silica exhibits stability towards hydrogen, except for fluorine, and remains inert with all acids except hydrofluoric acid (HF), forming silicon hexafluoride (Reaction 1). When silica reacts with concentrated bases, such as NaOH, under elevated temperatures, it can transform silica into water-soluble silicates (Reaction 2). The reaction shown below.

$$SiO_{2(s)} + 6\ HF_{(aq)} \rightarrow H_2(SiF_6)_{(aq)} + 2\ H_2O_{(l)} \quad \text{(Reaction 1)}$$
$$SiO_{2(s)} + 2\ NaOH_{(aq)} \rightarrow Na_2SiO_{3(aq)} + H_2O_{(l)} \quad \text{(Reaction 2)}$$

Silica possesses physical properties characterized by the molecular formula SiO_2. It appears as a white substance with a melting point of 1610°C and a boiling point of 2320°C. Additionally, silica exhibits the property of insolubility in cold and hot water, as well as in alcohol. However, it can dissolve in HF.

Sapei et al. (2015) characterized rice husk silica using XRD and FTIR (Figure 5). The XRD characterization results show that the silica produced from the study is amorphous because it has a wide peak at 2θ = 22° (Figure 5a). The amorphous nature of the silica ash can be seen from the FTIR spectra at wave numbers 460-487, 808-823, and 1064 cm^{-1}, which are fingerprints of amorphous silica (Figure 5b) (Sapei et al., 2015).

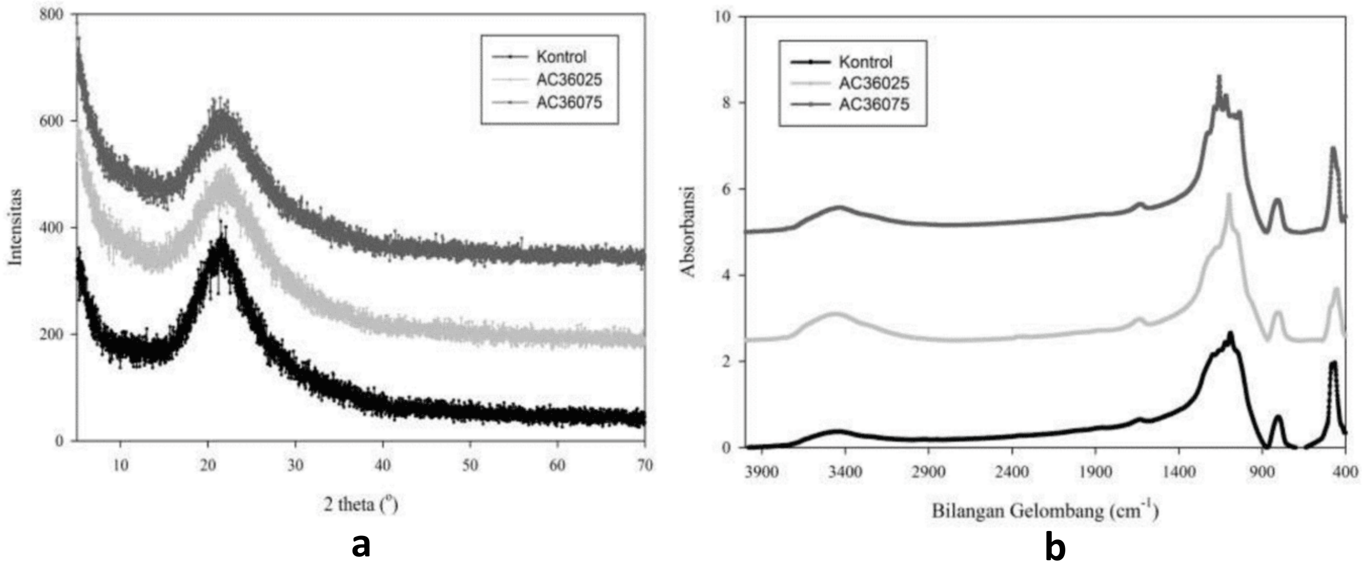

Figure 5. The results of rice husk ash characterization using (a) XRD and (b) FTIR (Sapei et al., 2015)

6. Synthesis of Rice Husk Ash-Based Silica

The synthesis of silica from rice husks begins with calculating the yield of synthesized rice husks. This yield represents the amount of silica obtained from the rice husks. Consequently, data is obtained as presented on Table 2 (Shintia Bokau et al., 2014). The data represents the yield results used to determine the rice husks' ash content through three different manufacturing processes. The table illustrates the reduction in rice husk mass to rice husk ash. This phenomenon occurs due to high-temperature combustion, causing the organic compounds to vanish and transform into CO_2 and H_2O.

Producing silica from rice husks begins with washing them using distilled water, followed by sun-drying and drying using an open stove to turn the rice husk into charcoal, changing its color to black. Then, the charcoal is heated in a furnace at a temperature of 600°C for 3 hours, resulting in rice husk ash. The ash is then purified using hydrochloric acid (HCl). The next step involves heating the purified ash at temperatures gradually increasing from 300°C to 600°C, resulting in white rice husk ash silica. Subsequently, the process continues by producing a 2% chitosan solution. The formed chitosan is dissolved in a 1% acetic acid solution and stirred using a magnetic stirrer until homogenous. Silica powder is then added, stirring the mixture for 2 hours to form a dope solution. This solution is then cast onto a glass plate, dried, and immersed in sodium hydroxide (NaOH) solution. This process yields chitosan/rice husk MMMs (Mixed Matrix Membranes) (Qian et al., 2018; Shintia Bokau et al., 2014).

Table 2 Data of rice husk ash yield (Shintia Bokau et al., 2014)

Mass of Rice Husk Charcoal (gram)	Mass of Rice Husk Ash (gram)	Yield of Mass of Rice Husk Ash (%)
180.012	90.6482	49.6432
250.009	122.016	51.1954
250.016	119.308	52.2798
Average Yield of Rice Husk Ash		51.0395

The results of XRD and FTIR characterization indicated the successful synthesis of rice husk ash silica, as shown in Figure 6. The presence of sharp peaks in the XRD pattern signifies the formation of silica from rice husk ash. The broadening of the peak suggests that the formed silica is in an amorphous and hydrated phase. The FTIR analysis revealed functional groups related to the membrane, which were influenced by adding rice husk. The described method aims to generate accurate and accountable data, making it suitable for application in peat water purification (Shintia Bokau et al., 2014).

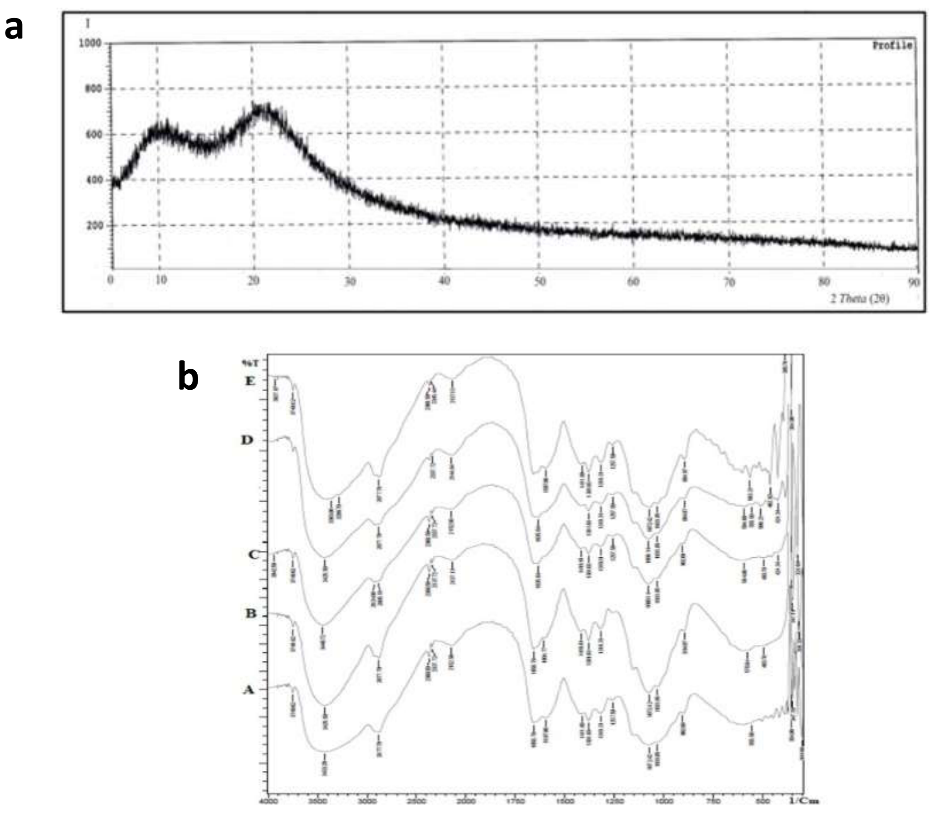

Figure 6. The results of (a) XRD and (b) FTIR characterization (Shintia Bokau et al., 2014)

7. Conclusion

The manufacturing process of the Mixed Matrix Membrane includes introducing a filler, specifically silica obtained from rice husk. This selection is based on the significant silica concentration in rice husk, surpassing 90%. The greater the silica content, the more beneficial the material becomes as it acts as a filler, effectively safeguarding the membrane from damage. Consequently, this membrane can find application in the purification of peat water, ensuring its usability without posing any health-related risks.

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