



## Development of Chitosan/Glutaraldehyde Cross-Linked Film with Silica Addition as Membrane Material for SLS Rejection in Detergent Wastewater

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**Abstract** – The pollution resulting from domestic waste has increased with the growing population density, and one of the potential contributors to groundwater contamination is detergent waste. Sodium Lauryl Sulphate (SLS) serves as a common active ingredient in detergent formulations. By leveraging membrane technology, SLS can be processed to reduce its concentration in water to environmentally safe levels. Chitosan, a promising material for membrane composition, is considered as the base material. Exploiting the hydrophilic characteristics of chitosan, silica is introduced to enhance membrane selectivity by reducing pore size through cross-linking between chitosan and silica molecules. The performance of the silica-modified membrane is then evaluated through tests measuring the rejection coefficient against SLS, membrane swelling degree, morphological profiling of functional groups using FTIR, and tensile strength measured with a Universal Testing Machine. The result found that membrane modification affect its rejection coefficient in Sodium Lauryl Sulphate (SLS) solution, resulting in 53.97%. Incorporating silica into the membrane improves its surface morphology.

**Keywords:** chitosan, detergent, membrane, silica, SLS

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### INTRODUCTION

In 2010, the Jakarta Public Works Department, in partnership with the Japan International Cooperation Agency (JICA) team, provided statistics showing that 75% of water contamination in Jakarta was caused by residential garbage, totaling 1,038,205 cubic meters per day. Multiple sources of household trash, particularly detergents, make a substantial contribution to this problem. Surfactants and builders are the primary components found in detergents (Watkins, 2001). Surfactants, which are vital constituents of detergents, are found in every formulation. The interaction of these detergent constituents may increase the concentration of phosphates in water, resulting in unregulated

proliferation of algae (eutrophication). Consequently, this may lead to a reduction in the level of oxygen dissolved in water, which has the potential to have detrimental effects on aquatic life (Boricha & Murthy, 2010).

Therefore, it is crucial to adopt a diligent approach to wastewater treatment in order to mitigate the pollution caused by the waste produced. A range of wastewater treatment approaches, including physical, chemical, and biological procedures, or their mixtures, may be used to tackle this issue. The anaerobic degradation approach has shown a degradation efficiency of 79%, however it requires a lengthy duration of 165 days (Puji, et al., 2012). During a 40-hour incubation period, the use of

*Comamonas testosteroni* bacteria for aerobic degradation resulted in bacterial growth and a detergent degradation rate of 87.5%. Nevertheless, the disadvantage stems from the extended period it takes for deterioration to occur (Puji, et al., 2012). The use of activated carbon for treating detergent waste resulted in an 80% degradation rate. However, this method required a longer period and presented difficulties in controlling pH and temperature (Puji, et al., 2012).

Given the limitations of conventional wastewater treatment technologies, which need large amounts of land, chemicals, and significant time and expenses, there is a demand for a more sophisticated approach. Membrane technology arises as a promising option, with the ability to surpass the constraints of prior approaches. Membrane technology may be used for separation, purification, and concentration processes, providing benefits over traditional separation techniques. These advantages encompass uninterrupted operation without the requirement of extra chemicals, minimal energy usage at low temperatures, applicability for separating compounds that cannot tolerate high temperatures, insensitivity to extreme conditions such as pH and temperature, and flexibility in the choice of membrane material for easy adjustment and integration with other separation methods (Eriviana & Mariyamah, 2019).

Based on the aforementioned factors, it is proposed to create membrane technology for treating surfactant waste utilizing chitosan as a raw material. Chitosan, extensively used in membrane applications, exhibits properties such as biodegradability, bioactivity, and non-toxicity, making it a versatile polymer with a multitude of uses (Eriviana & Mariyamah, 2019). Nevertheless, since chitosan membranes have inadequate physical durability throughout their manufacturing process, it is essential to include supplementary substances, such as silica, to achieve membranes with favorable properties. Adding silica to chitosan membranes may improve their selectivity, increase the permeability of oxygen, and strengthen their resilience to heat (Eriviana & Mariyamah, 2019). Thus, the objective of this study is to create hydrophilic chitosan membranes that have been modified with silica for the purpose of filtering surfactant wastewater.

## METHODOLOGY

### Materials and Equipment

The equipment used in this study comprises a vacuum filtration device, a spectrophotometer, a magnetic stirrer, an oven, and a Universal Testing Machine (StrengthLab). The components used include chitosan, sodium silicate, 50% glutaraldehyde, 99% glycerol, and acetic acid, all of which were obtained from Sigma-Aldrich (Jakarta, Indonesia). All

chemicals used in this investigation were of analytical grade.

### Membrane Preparation

The following membrane used in this research were made using the formulation in this table below.

Table 1. Membrane formulation

Variance	Chitosan (gr)	Sodium silica (gr)
K1R1	2	3.33
K1R2	2	10.00
K1R3	2	16.60
K2R1	3	3.33
K2R2	3	10.00
K2R3	3	16.60
K3R1	4	3.33
K3R2	4	10.00
K3R3	4	16.60

Referring to previous research conducted by Eriviana & Mariyamah (2019), the preparation of the chitosan solution involves using the specified variables along with the addition of glutaraldehyde, 1% acetic acid, and 2.5% glycerol. The mixture is then homogenized in an Erlenmeyer flask and stirred using a magnetic stirrer until it dissolves completely. Subsequently, the solution is cast and dried using an oven at temperature of 60°C.

### Determination of Membrane Rejection to SLS

The determination of the rejection coefficient was conducted using a vacuum filtration instrument and a spectrophotometer to ascertain the absorbance values in the sodium lauryl sulfate solution. This process was carried out in accordance with the methodology established in prior research conducted by Hidayat (2015). Coefficient rejection ( $R_c$ ) was calculated using Eq. 1.

$$R_c = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (1)$$

where  $R_c$  was coefficient rejection of membrane;  $C_p$  was SLS concentration in the permeate; and  $C_f$  was SLS concentration in the feed.

### Determination of Membrane Functional Group using FTIR

The determination of functional groups in the chitosan-silica membrane was observed using FTIR instrumentation, following the methodology outlined in previous research conducted by Hidayat (2015). The wavelength range examined was  $1/\lambda$  400 – 4000  $\text{cm}^{-1}$ .

### Determination of Membrane Hydrophilicity

The determination of membrane hydrophilicity was conducted in accordance with the methodology outlined in the study conducted by Bokau (2013). This involved cutting membranes of

equal weight, followed by weighing them before and after immersion in distilled water.

### Determination of Membrane Tensile Strength and Elongation

The determination of the mechanical strength of the membrane was tested using a Universal Testing Machine. The tensile strength testing procedure followed the methodology established in previous research conducted by Hidayat (2015).

### Determination of Membrane Surface Characteristic

The surface topography of the membrane was examined using a Scanning Electron Microscope (SEM) with a magnification of 10,000x, following the methodology outlined in the previous study conducted by Liu et al. (2019).

## RESULTS AND DISCUSSION

### SLS Rejection Result

The rejection coefficient was determined by comparing the content of Sodium Lauryl Sulfate (SLS) in the feed to the concentration of SLS in the permeate. Therefore, the data that is obtained is as follows:

Table 2. Results of SLS rejection determination

Variance	SLS feed conc. (ppm)	Permeate conc. (ppm)	SLS rejection (%)
K1R1	30	25.71	14.29
K1R2	30	25.00	16.67
K1R3	30	24.29	19.05
K2R1	30	19.52	34.92
K2R2	30	20.95	30.16
K2R3	30	20.24	32.54
K3R1	30	17.38	42.06
K3R2	30	15.00	50.00
K3R3	30	13.81	53.97

Sample K1R1 had the lowest rejection coefficient, which was 14.29%. Sample K3R3 had the greatest rejection coefficient, reaching 53.97%. Research done by Yunarsih et al. (2013) found that the chitosan membrane had a rejection coefficient of 66% for phosphate in detergent wastewater. In comparison to the current research, the rejection value is lower. However, it is important to highlight that the components that were rejected are distinct from one another. Both phosphate and Sodium Lauryl Sulfate (SLS) are found in detergent effluent. Hence, another investigation is necessary to examine the rejection coefficient of this study in relation to phosphate in detergent wastewater.

The rejection of SLS was facilitated by the adsorptive capabilities of the chitosan membrane,

whereby the SLS molecules were absorbed by the porous structure of the membrane (Spoială, et al., 2021). In addition, the researchers discovered that the interaction between SLS and chitosan is facilitated by ionic bonding. SLS is an anionic surfactant, whereas chitosan is a cationic biomolecule owing to the presence of an amine (-NH<sub>2</sub>) group (Thongngam & McClements, 2004).

The molecular contact between chitosan and the rejected molecule is enhanced at larger concentrations of chitosan, leading to an increased rejection coefficient (Alshahrani, 2019). This is due to a greater number of chitosan molecules interacting with SLS during the rejection process. This idea is consistent with the SLS rejection outcome, where the K3R3 sample with a chitosan content of 4% exhibited the greatest rejection result.

The inclusion of silica also contributed to the increased level of molecular rejection. The previous study conducted by Zulti et al. (2013) found that adding silica to chitosan-based membranes affected the surface morphology. The addition of silica resulted in a higher level of porosity on the surface, which could potentially enhance the rejection process of SLS in this research. This is due to the adsorption process that takes place on the porous surface.

### Functional Group Analysis Result

The effectiveness of the modification process between chitosan and silica was assessed by conducting functional group identification using Fourier Transform Infrared (FTIR) spectroscopy. This included identifying the functional groups present in the membrane. The FTIR observations were conducted at the Integrated Laboratory of Diponegoro University and are shown in the accompanying figure:

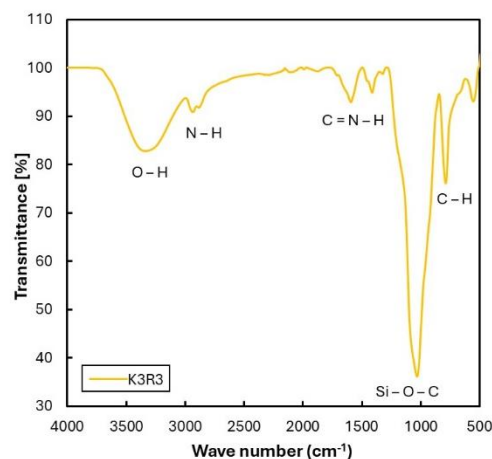


Figure 1. The Fourier Transform Infrared (FTIR) spectra of a membrane containing 4 grams of silica and 16.6 grams of sodium silica

Figure 1 depicts the membrane's functional groups, which consist of O-H, N-H, C=N-H, Si-O-C,

and C-H. The FTIR spectrum exhibits an absorption peak at the wavenumber of 3339.27 cm<sup>-1</sup>, which corresponds to the presence of O-H bonds in chitosan molecules, mostly composed of hydroxyl groups. Additionally, at a wavelength of 2934.42 cm<sup>-1</sup>, there is a distinct absorption peak corresponding to the N-H bond, which suggests the existence of chitosan, a molecule that contains amine groups. An absorption peak at 1879.07 cm<sup>-1</sup> indicates the presence of the C=N-H group, which suggests that glutaraldehyde has been added to the chitosan molecule. At a wavenumber of 1033.21 cm<sup>-1</sup>, the presence of an absorption peak for Si-O-C suggests that silica has been incorporated (Bokau, et al., 2014). An absorption peak for C-H is detected at 789.75 cm<sup>-1</sup>, arising from the chitosan molecule (Ramachandran, et al. 2011).

**Hydrophilicity Result of The Membranes**

The determination of the hydrophilicity of the membrane was conducted by performing the swelling test as described by Hidayat (2015). The hydrophilicity of the material utilized is one of the elements that affects the degree of swelling. The data acquired from the swelling test is shown in the following table:

Table 3. Swelling degrees result of the membranes

Time (min)	Variations	Wd (polymer)	Ws (swollen)	Swelling degrees (%)
60	K1R1	0.1967	0.4704	139.15
60	K1R2	0.2133	0.5162	142.01
60	K1R3	0.2254	0.5497	143.88
60	K2R1	0.2595	0.5294	104.01
60	K2R2	0.2694	0.5946	120.71
60	K2R3	0.2738	0.6259	128.60
60	K3R1	0.2874	0.5275	83.54
60	K3R2	0.3587	0.6894	92.19
60	K3R3	0.3626	0.7287	100.97

The table displays data showing that sample K1R3 had the largest swelling percentage, which may be linked to the addition of silica that increases the hydrophilicity of the membrane. On the other hand, a higher concentration of chitosan in the membrane causes a decrease in the membrane's ability to attract and interact with water molecules. Sample K3R1 had the lowest swelling percentage, suggesting that sample K1R3 has the highest level of hydrophilicity. A research done by Hidayat (2015) demonstrated a comparable correlation between the amounts of chitosan and silica and the extent of swelling. The study found a maximum swelling degree of 134.99%, indicating that the membrane utilized in the research had reduced hydrophilicity.

Regarding the previous research conducted by Fathanah et al. (2020) it was discovered that greater

concentrations of chitosan led to increased flow in chitosan-based membranes. This increased flux was attributed to the membrane's hydrophilic characteristic. The previous finding was consistent with the hydrophilicity outcome of this study, where the chitosan concentration of 4% (K3R1) yielded the maximum level of hydrophilicity.

**Tensile Strength and Elongation of The Membrane**

The membrane underwent tensile strength testing to assess its elasticity and capacity to endure a certain amount of force. The mechanical characteristics were measured using a Universal Testing Machine, resulting in the following results:

Table 4. Tensile strength result of the membrane

Variasi	Force (N)	Tensile Strength (MPa)	Elongation at Break (%)
K3R3	7.05	4.14	26.8

The data obtained show a tensile strength of 4.14 megapascals (MPa) and an elongation at break of 26.8. The tensile strength observed in this work surpasses the findings of Kusumastuti et al. (2021), who reported a tensile strength of 4.70 MPa. Nevertheless, the elongation value obtained in this research is superior, measuring 26.8%, in contrast to the elongation value of 6.07% reported by Kusumastuti et al. (2021). The variation in results may be ascribed to the disparity in the chitosan and silica ratio used. Specifically, our work utilized a ratio of 1:4, while Kusumastuti et al. (2021) employed a ratio of 1:1. Within this particular framework, silica serves as a fundamental component connecting chitosan molecules, hence enhancing the tensile strength of the chitosan-based membrane (Liu, et al. 2019).

**Membrane Surface Analysis**

The surface of the chitosan membrane modified with silica was analyzed using Scanning Electron Microscopy (SEM) equipment. The testing was conducted on the membrane that exhibited the highest rejection rates for detergent wastewater. The scanning electron microscopy (SEM) findings for the treated membrane are shown in Figure 2 below.

The picture above clearly shows that the membrane surface contains dispersed particles with distinct and well-defined forms. These particles are a result of the inclusion of silica, which contributes to the crystalline properties of the membrane (Zhang et al., 2023). Furthermore, there are vacant areas or gaps that arise from the inadequate dissolving of the solution during the manufacturing process.

Based on the measurement findings, 1.2175 nm is the average size of the particles scattered over the membrane surface. Sugiyo et al. (2011) discovered, in contrast, that the surface of the silica additions tended to be more rounded. The crystallinity

characteristics of the chitosan and silica used in this investigation, however, are responsible for the additional silica's inclination to be more pointed in this research (Liu, et al. 2019).

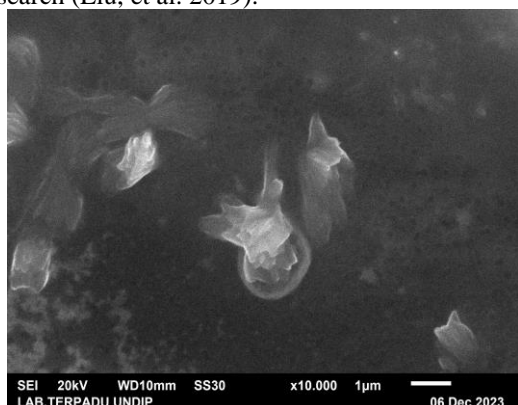


Figure 2. Result of surface analysis obtained from SEM

Table 5. Particle size result

No.	Particle Size (nm)
1	1.303
2	1.132
<b>Average</b>	<b>1.2175</b>

## CONCLUSION

Chitosan-based modified membrane could be obtained in several ways. The C=N-H bond is formed by the functional groups of C-NH<sub>2</sub> in chitosan, which are altered by the addition of glutaraldehyde as a crosslinking agent in chitosan-based membranes. The functional groups that compose the Si-O-C bond have been impacted by the inclusion of silica for membrane development. The results indicated that the modification made have an impact on the membrane's rejection coefficient in a solution of sodium lauryl sulphate (SLS), with a rejection coefficient of 53.97% consequently. Furthermore, the addition of silica to the membrane's formation improves the membrane's surface shape.

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