Jurnal Kimia Sains dan Aplikasi 26 (1) (2023): 19–27

# Jurnal Kimia Sains dan Aplikasi Journal of Scientific and Applied Chemistry

Journal homepage: http://ejournal.undip.ac.id/index.php/ksa

# Fabrication of Polystyrene Sulfonate-Chitosan (PSS-Chitosan) Membrane as Dodecyl Benzene Sulfonate (DBS) Adsorbent in Laundry Wastewater

Mandrea Nora<sup>a</sup>, Adyatma Bhagaskara<sup>a</sup>, Virna Agustisari<sup>a</sup>, Alice Lim<sup>a</sup>, Hardian Ridho Alfalah<sup>b</sup>, Dwi Siswanta<sup>a,\*</sup>

(62.4 ± 7.2) %.

<sup>a</sup> Department of Chemistry, Faculty of Mathematics and Natural Sciences, Gadjah Mada University, Indonesia <sup>b</sup> Department of Biology, Faculty of Biology, Gadjah Mada University, Indonesia

\* Corresponding author: dsiswanta@ugm.ac.id

https://doi.org/10.14710/jksa.26.1.19-27

ISSN: 1410-8917

e-ISSN: 2597-9914

Jurnal Kimia – Sains & Aplikasi

#### Article Info

#### Article history:

Received: 25<sup>th</sup> September 2022 Revised: 23<sup>rd</sup> November 2022 Accepted: 20<sup>th</sup> January 2023 Online: 31<sup>st</sup> January 2023 Keywords: DBS; chitosan; laundry wastewater; PSS-chitosan membrane; styrofoam

### 1. Introduction

Styrofoam is a non-biodegradable material frequently utilized for a variety of purposes. Global styrofoam production reached 9.4 million tons in 2018 [1]. Other studies have reported that styrofoam is the most abundant plastic waste in Jakarta Bay by 11–35% [2], and even the quantity exceeds 50% in the Citarum river [3]. Additionally, styrofoam takes approximately 500 years to decompose naturally in the natural environment [4]; it will not completely disintegrate and turn into microplastic. Processing styrofoam physically and chemically can help lessen the harmful effects of its widespread use. One of the frequently employed physical

processing methods is combustion. This process must be controlled for the produced exhaust gas. Burning styrofoam produces harmful gases such as hydrochlorofluorocarbon (HCFC), styrene, polycyclic aromatic hydrocarbons (PAHs), and carbon monoxide [5].

Meanwhile, chemical processing can be performed using polystyrene compounds (90–95%) found therein. Several studies have modified polystyrene by chemically reacting it with chelating agents [6] or through a nitration reaction [7] and sulfonation [8, 9]. This sulfonation reaction can change polystyrene, which is nonpolar, to be polar due to the addition of sulfonate



Abstract

The combination of polystyrene and chitosan can form polyelectrolyte (PE) membranes. Polystyrene sulfonate-chitosan (PSS-chitosan) adsorbent membrane can adsorb dodecyl benzene sulfonate (DBS) in laundry wastewater. This study aimed to synthesize, identify characteristics, and formulate adsorption effectiveness by PSS-chitosan membranes. The research methods included converting polystyrene into PSS, isolating chitosan, optimizing geometry, making PSS-chitosan membranes, studying adsorption, and applying membranes to laundry wastewater. The resulting membrane was characterized using FTIR and SEM. The results of the infrared spectra showed vibrations of -OH and -NH<sub>2</sub> groups at 3418 cm<sup>-1</sup>, while the SEM image showed a homogeneous membrane surface. The quality of chitosan isolation from shrimp shells was indicated by the degree of deacetylation of 61.3%. The results of the geometry optimization showed the change in the structure's total energy after adsorption. The PSS-chitosan membrane is resistant to acids but decomposes under alkaline conditions. Optimum adsorption of PSS-chitosan membrane on DBS occurred at pH 8 for 100 minutes. The adsorption kinetics of the PSS-chitosan membrane follows the first pseudo-order equation. PSS-chitosan membrane adsorption isotherm follows the Langmuir isotherm model with an adsorption capacity and efficiency of 3.97 mg.g<sup>-1</sup> and 76.6%, respectively, at 0.6 ppm. At the application stage, the PSS-chitosan membrane could adsorb DBS in laundry wastewater by groups. The addition of these groups results in more negatively charged surfaces that can subsequently be modified into polyelectrolyte complexes.

In addition to synthetic waste, there are organic waste materials, such as shrimp shells, that have the potential to be utilized. According to the Ministry of Maritime Affairs and Fisheries [10], shrimp production in Indonesia reached 1,217,859 tons in 2021. Shrimp is a commodity with high economic value that is commonly processed but leaves the shell and head underutilized, ranging from 35–50% of their body weight [11]. The deacetylation of chitin into chitosan is an alternative method of handling shrimp waste. Shrimp shells contain 15–25% chitin, which can be transformed into chitosan. This cationic polysaccharide is necessary for forming polyelectrolyte complexes because it can enhance the adsorbent's capacity [8].

The combination of polystyrene and chitosan can be synthesized into an adsorbent polyelectrolyte complex. Generally, this adsorbent membrane is applied to overcome cationic pollutants such as dyes (methylene blue and malachite green) [12] and heavy metals (Cu(II), Ni(II), Cd(II), and Pb(II)) [8, 13]. The membrane has the potential as an adsorbent for anionic pollutants because the chitosan amine groups in the membrane contain positive sites, which are further enhanced by the presence of polystyrene sulfonate as the matrix. Research that applies this application has not been widely reported. The polystyrene sulfonate-chitosan (PSS-chitosan) adsorbent membrane is expected to be a solution for handling laundry waste.

The anionic surfactant component of linear alkyl sulfonate (LAS) in laundry waste is difficult to degrade, making it an environmental issue [14]. Surfactants are challenging to decompose due to their complex branched chain structure [15], thus destroying beneficial bacteria in aquatic environments such as rivers [16]. Metal photocatalysts are a different strategy for solving anionic surfactant pollutants in laundry waste. However, this method has its drawbacks, including the inability to provide data on pollutant degradation as metal photocatalysts require exposure to UV light and the potential risk of metal bioaccumulation in the bodies of aquatic organisms [17]. Another method being developed is the adsorption of anionic surfactants using silica [18] and graphene [19] as adsorbents. Due to the weak bond between the adsorbent and anionic surfactants and the silica adsorption methods can reduce the selectivity for these substances [20]. Meanwhile, the weakness lies in the high cost of the raw materials used to manufacture graphene [21].

Another method to lessen the harmful effects of laundry waste is using a PSS-chitosan membrane-type material as an adsorbent before the anionic surfactants are discharged into the environment. This anionic surfactant can bind to the active site of the PSS-chitosan adsorbent. Previous studies have used chitosan from shrimp shells and polystyrene sulfonate as adsorbents for metal waste and dyes [8]. However, applying the two combinations as adsorbents in laundry waste has never been done. It is necessary to perform this research to produce polystyrene sulfonate-chitosan adsorbent as an environmentally friendly method for dealing with laundry waste. This research aims to examine the manufacturing process and characterization of PSSchitosan membranes, determine the optimum conditions for the adsorption process, study models of adsorption kinetics and isotherms, and formulate the effectiveness of PSS-chitosan membranes in the adsorption of anionic surfactants in laundry waste.

# 2. Experimental

# 2.1. Materials

Shrimp shell waste was obtained from the Kulonprogo area and Kranggan Market, styrofoam waste, detergent waste from the laundry business around Jalan Pogung Baru, distilled water, Whatman filter paper no. 42, sulfuric acid  $(H_2SO_4)$  (95–98%, Merck), ethanol (C<sub>2</sub>H<sub>5</sub>OH) 96%, acetic acid (CH<sub>3</sub>COOH) (1%, Merck), acetone, chloroform (Merck), solid sodium hydroxide (NaOH) (Merck), solution 1.5 M hydrochloric acid (HCl), dichloromethane (Merck), methanol, DBS standard solution was purchased from PT. Brataco, methylene blue solid (Merck), anhydrous sodium sulfate  $(Na_2SO_4)$ , and sodium dihydrogen phosphate monohydrate (NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O) solid.

# 2.2. Synthesis of Polystyrene Sulfonate from Styrofoam Waste

A total of 10 g of styrofoam waste was mashed after being washed with double distilled water and then dried in an oven at 100°C for 30 minutes. Styrofoam waste was dissolved in 250 mL of chloroform, reacted with 150 mL of 95–97% sulfuric acid, and stirred for 3 hours [8]. After 3 hours, the mixture was put into hot water (T = 90°C) slowly until a white precipitate formed and then washed with double distilled water until the pH was neutral. The precipitate was dried at 50°C for 10 hours and characterized using FTIR (Shimadzu FT-IR 8201PC).

#### 2.3. Isolation of Chitosan from Shrimp Shells

Chitosan was isolated from shrimp shells using the methods described by Agustina *et al.* [22] and Sukma *et al.* [23]. Shrimp waste was washed and sun-dried afterward. The dried shrimp waste was sieved through a 100-mesh sieve. As much as 200 g of shrimp shell powder was demineralized using 1.5 M HCl solution with a ratio of 1:15 (w/v) for 4 hours at  $60-70^{\circ}$ C, washed with distilled water, and then dried at 80°C for 24 hours. After that, the deproteination process was performed using 3.5% NaOH with a ratio of 1:10 (w/v) for 4 hours at  $60-70^{\circ}$ C. The mixture was washed with distilled water and oven-dried at 80°C for 24 hours.

The following process was depigmentation using 96% ethanol with a ratio of 1:10 (w/v) for 30 minutes at  $25-27^{\circ}$ C. After 30 minutes, the depigmentation results were washed using a mixture of hot double distilled water and acetone (1:1). The last process was deacetylation using 60% NaOH with a ratio of 1:20 (w/v) for 4 hours at 100-110°C, then washed with double distilled water. The final stage of the depigmentation

and deacetylation process was also performed by drying at 80°C for 24 hours. The chitosan obtained was characterized by FTIR, and its degree of deacetylation (DD) was calculated.

## 2.4. Fabrication of Polystyrene Sulfonate-Chitosan Membrane

PSS-chitosan membrane 0.6% (w/v) was prepared with a weight ratio of PSS: chitosan of 30:70, 50:50, and 70:30. PSS powder was dissolved in dichloromethane: methanol 30:70 until homogeneous, then mixed with a chitosan solution in 1% acetic acid [8]. The mixture was stirred with a magnetic stirrer for 3 hours, poured into a petri dish, and dried at room temperature for 48 hours. The membranes formed were characterized using FTIR and SEM (Phenom Pro X), studied the optimization of the geometry of the membrane structure, and tested for stability in acids and bases. Adjusting the pH of the solution was done with a solution of 0.1 M NaOH and 0.1 M HCl.

#### 2.5. Study of Adsorption of Anionic Surfactants on PSS-Chitosan Membranes

The solution used in this adsorption study was a linear dodecyl benzene sulfonate (DBS) solution. DBS levels were measured using the MBAS (Methylene Blue Active Substance) method using a UV-Vis spectrophotometer (Hanna Iris HI801 and Orion Aquamate 8100) at a wavelength of 654 nm (SNI 06-6989.51-2005). This wavelength was obtained from UV- Vis spectra at various concentrations of standard DBS solutions (0, 0.2, 0.4, 0.6, and 0.8 ppm).

#### 2.5.1. Optimization of pH

A 120 mg of PSS-chitosan membrane was put into 120 mL of 0.4 mg.L<sup>-1</sup> DBS standard solution, the pH of which had been adjusted to pH 6, 7, 8, 9, and 10. The adsorption process was conducted at room temperature for 60 minutes. After the adsorption process, the solid filtrate were separated. The and the filtrate concentration was measured with а UV-Vis spectrophotometer at the maximum wavelength.

#### 2.5.2. Adsorption Kinetics Study

Adsorption kinetics studies were conducted at contact times of 10, 15, 30, 45, 60, 100, and 120 minutes. The adsorption process was performed at room temperature and optimum pH conditions. DBS adsorption kinetics were studied using two kinetic models: pseudo-first-order kinetics (Lagergren) and pseudo-second-order kinetics (McKay and Ho).

## 2.5.3. Adsorption Isotherm Models

Adsorption isotherm model studies were determined at various DBS concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 mg.L<sup>-1</sup>. The adsorption process was conducted at room temperature with optimum pH and contact time conditions. The DBS adsorption isotherm was determined using Langmuir and Freundlich isotherms.

#### 2.6. Application of PSS-Chitosan Membrane in Laundry Waste

The adsorption process was performed in triplicate using the best membrane variation at optimum solution pH and contact time. The absorbances of the solution before and after the adsorption process were measured using a UV-Vis spectrophotometer, and the percent reduction in anionic surfactant content was calculated.

#### 2.7. Analysis Method

The data analyzed included several components. Firstly, the computational optimization of the membrane's structural geometry was examined. Secondly, FTIR characterization of chitosan and polystyrene sulfonate, isolated results, FTIR spectra, and SEM images of the membrane were analyzed. Lastly, the stability of the polystyrene sulfonate-chitosan membranes was tested under both acidic and alkaline conditions, and adsorption studies were conducted to determine the kinetics and adsorption isotherm models based on regression equation results.

### 3. Results and Discussion

# 3.1. Functional Group Identification of PSS, Chitosan, and PSS-Chitosan Membrane

The functional groups on the PSS-chitosan membrane were identified by characterizing the membrane using an FTIR spectrophotometer. The functional groups present in the PSS-chitosan membrane were then demonstrated by comparing PSS and chitosan spectra. FTIR spectra of the PSS-chitosan membrane are presented in Figure 1.



Figure 1. FTIR spectra of PSS, chitosan, and PSSchitosan membranes

The absorptions that appear in the FTIR spectra of PSS and chitosan are also found in the PSS-chitosan spectra. The absorption characteristics of PSS and chitosan that appeared on the PSS-chitosan membrane spectra are 1111 cm<sup>-1</sup>, 1604 cm<sup>-1</sup>, and 3417 cm<sup>-1</sup>. The absorption occurs with relatively high intensity, where the wavenumber of 1111 cm<sup>-1</sup> is indicated as a symmetric  $-SO_3$  stretching vibration and C–O stretching vibration. The aromatic  $-CH_2$  vibration and C=O stretching vibration of the amide group (RHN–C=O) are evidenced by the absorption of the wavenumber of 1605 cm<sup>-1</sup>. The

band at 3418  $\rm cm^{-1}$  corresponds to an –OH stretching vibration of the sulfonate group, –OH group, and –NH<sub>2</sub> group.

Other absorptions have also been found at 1420 cm<sup>-1</sup>, 2854 cm<sup>-1</sup>, and 2924 cm<sup>-1</sup>, which are asymmetric C-H sp<sup>2</sup> stretching vibration, C-H sp<sup>3</sup> vibration, and -CH<sub>2</sub> bending vibration, respectively [8, 24, 25, 26]. Even though certain absorptions exhibited a slight shift, these absorptions are sufficient to demonstrate that the produced PSS-chitosan membrane had PSS and chitosan characteristics.

#### 3.2. Deacetylation Degree of Chitosan

The degree of deacetylation (DD) measures the number of acetyl groups missing from the acetamide groups in chitin. The high DD value indicates that more chitosan is formed compared to chitin. This is a determining factor for the quality of chitosan isolation results. The results of chitosan isolation can be calculated using various equations; however, the Domszy and Robert baseline equations were employed in this study. This equation uses the IR spectra as a reference for calculations by considering the absorbance of the amide group ( $A_{1655}$ ) and the primary amine group ( $A_{3450}$ ). In addition, the Domszy and Robert equations use a perfect absorbance value of 1.33 in their calculations [27, 28].

$$DD = 100 - \left[ \left( \frac{A_{1655}}{A_{3450}} \right) \times \frac{100}{1.33} \right]$$
(1)

Based on the IR spectra of chitosan, the absorbance value at 1655 nm was 0.296, and the absorbance value at 3450 nm was 0.575. The data was processed using this equation, which yielded a result of 61.3% for the degree of deacetylation of the isolated chitosan. This result shows that the chitosan produced from shrimp shell waste is relatively high.

#### 3.3. Surface Morphology of Polystyrene Sulfonate-Chitosan Membrane

The membrane surface morphology was analyzed using a scanning electron microscope (SEM) at 5000× and 2500× magnification. This magnification variation aims to observe the surface morphology of the PSSchitosan membrane visually.



Figure 2. SEM images of (a) PSS-chitosan membrane (30:70) at 5000× magnification, (b) the membrane cross-section at 2500× magnification

Figure 2 shows the morphological characteristics of the surface of the PSS-chitosan 30:70 membrane, which support the adsorption process of anionic surfactants. In Figure 2(a), it can be seen that this membrane has a homogeneous surface. This shows that the adsorption sites for anionic surfactants are evenly distributed on the

membrane surface to accommodate a sufficient amount of DBS molecules. Meanwhile, Figure 2(b) reveals the pattern of fibers in the membrane cross-section. The fiber structure becomes a pathway for surfactant molecules on the PSS-chitosan membrane, facilitating adsorption.

DBS molecules can bind to the surface of the membrane through a diffusion mechanism [29]. This diffusion occurs when more DBS molecules on the surface of the PSS-chitosan membrane have not been adsorbed than those that have. This phenomenon helps in the migration of DBS molecules on the membrane surface.

#### 3.4. Geometry Optimization of PSS-chitosan Membrane Structure

The molecular mechanic method using the Avogadro software (MMFF94 force field) was employed to optimize the geometry since it is more in line with the characteristics of organic molecules. Geometry optimization aims to determine the stability and potential for forming PSS-chitosan membrane structures. In addition, this method can demonstrate the possibility of successful synthesis of PSS-chitosan membranes before laboratory testing to maximize the yield through the appropriate comparison of raw material composition. The results of this geometry optimization will support the explanation of the adsorption potential of anionic surfactants in laundry waste. Moreover, the geometry optimization data reveals the type of bond produced between PSS and chitosan and between the PSS-chitosan membrane and DBS anionic surfactant.



Figure 3. The interaction of PSS-chitosan membrane and DBS

**Table 1.** The result of the computational calculation ofthe total energy of the structure

Structure	Total energy (kJ mol <sup>-1</sup> )
Chitosan (monomer)	439.5
Hydrogen bonds in the –OH groups	384.0
Hydrogen bonds in the $-NH_2$ group	347.0
Adsorption of DBS by PSS-chitosan membrane	344.8

From Table 1, the geometry optimization results show that the structural energy of the chitosan monomer is around 439.5 kJ mol<sup>-1</sup>. The energy decreased after binding to the PSS monomer, indicating that the stability of the chitosan structure increased. The stability of a material can be seen from the interactions between molecules, such as hydrogen bonds between chitosan molecules and PSS [30]. Figure 3 shows the energy difference between the PSS-chitosan membrane structures with hydrogen bonds in the amine groups  $(-NH_2)$  and hydroxyl groups (-OH) of chitosan. The structure of the PSS-chitosan membrane with hydrogen bonding through the amine group is more stable than that through the hydroxyl group. This is because the negative charge of oxygen on the hydroxyl group repels oxygen on the sulfonate group, increasing the energy of the structure. The effect of this charge can be distributed evenly on the surface of the adsorbent, influencing the adsorption of anionic surfactants [31]. The total energy decreases once the amine group of the PSS-chitosan membrane forms a bond with dodecyl benzene sulfonate (DBS), indicating the stability of the structure [32]. This shows that the adsorption procedure was successful since the DBS molecule could bond tightly enough to prevent its release back into the environment.

### 3.5. Stability Test in Acidic and Alkaline Conditions

The stability test of the PSS-chitosan membrane aims to obtain an optimal membrane to serve as an adsorbent in the anionic surfactant adsorption process. Stability testing was done at pH 4 (acidic), 7 (neutral), and 10 (alkaline), the results of which are presented in Table 2.

 
 Table 2. PSS-chitosan membrane stability test results in acidic and alkaline conditions

Membrane Variation	Acidic	Neutral	Alkaline
PSS: Chitosan (30:70)	Stable	Stable	Decomposed
PSS: Chitosan (50:50)	Stable	Stable	Decomposed
PSS: Chitosan (70:30)	Stable	Stable	Decomposed

Based on the observations made, it can be seen that all variations of the PSS: chitosan membrane are relatively stable at a pH of around 3-8 (acidic and neutral) but become unstable until they decompose at a pH  $\ge$  10 (alkaline). Membrane instability at pH  $\ge$  10 is caused by the ability of -OH molecules to form hydrogen bonds with the amine groups in chitosan, thereby weakening the connection between PSS and chitosan and causing membrane instability.

#### 3.6. Anionic Surfactant Adsorption Study

#### 3.6.1. Optimization of pH

To identify the optimal pH, we first examined the effect of membrane composition variations on the adsorption efficiency of DBS anionic surfactants. This examination allowed us to identify the membrane composition variations that produced the highest adsorption efficiency. We then used these optimal membrane compositions to study the kinetics and adsorption isotherm models. The effect of the best membrane composition variation can be seen in Figure 4(a).

Based on tests carried out on all variations of the PSS-chitosan membrane composition, it can be seen that the membrane with the PSS: chitosan variation (30:70) gave the highest adsorption efficiency results compared to the other variations. Chitosan has a natural charge in the form of a positive charge which allows ionic interactions to occur with DBS [33]. Therefore, the greater the composition of chitosan (polycation), the more positive sites are contained in the membrane, so more DBS (anionic surfactant) is adsorbed. However, if the number of chitosan components exceeds the amount of PSS in the PSS-chitosan membrane, in that case, the membrane structure becomes less stable. As a result, it can easily decompose.



**Figure 4.** (a) Effect of variations in membrane composition, (b) Optimization of pH solution on the adsorption process of DBS by PSS-chitosan membranes

The optimal pH was determined using a membrane with the best composition variation, as seen in Figure 4(b). Optimization results show that the adsorption process of DBS anionic surfactant occurs optimally at pH 8. Under these conditions, DBS is in its anionic speciation form [34], allowing the interaction of adsorbent and adsorbate occurs optimally. Increasing the pH towards alkaline will reduce the adsorption capacity of DBS by the membrane. This is because the – OH molecule can weaken the bond between PSS and chitosan by closing the amine group  $(-NH_2)$ , causing the adsorption efficiency to decrease. The pH of the solution is a crucial parameter that affects the adsorption capacity of the membrane by influencing the protonation and deprotonation mechanism at the active site of the adsorbent [13].

At pH 10, there was nonlinearity in the results of DBS adsorption using PSS-chitosan 30:70 and PSSchitosan 50:50. The membrane with a 50:50 composition showed a higher percentage of adsorption compared to the 30:70 composition. This was due to a more stable membrane structure resulting from an equal amount of PSS, and chitosan added, even under alkaline conditions (pH 10). Meanwhile, the decrease in adsorption percentage by the 30:70 composition was caused by the small amount of PSS added, which decreased the membrane's stability. The decrease in adsorption percentage can be attributed to the closure of active sites by hydroxyl ions. The primary factor controlling the adsorption mechanism at pH 10 is no longer the number of active chitosan sites but rather the result of compromising the strength of the membrane derived from polystyrene sulfonate (PSS) with active chitosan sites.

#### 3.6.2. Adsorption Kinetics Study

Adsorption kinetics studies were conducted to determine the optimum contact time and the adsorption kinetics equation. This research was conducted on membranes with a composition of 30:70 because it has the highest adsorption efficiency and an optimal pH of 8. The effect of the contact time on the adsorption of DBS on the PSS-chitosan membrane is shown in Figure 5.



Figure 5. Determination of the optimum contact time for DBS adsorption on PSS-chitosan membrane

According to the data in Figure 5, the highest adsorption efficiency of 89.55% is achieved within 100 minutes. Adsorption efficiency values tended to increase with increasing contact time but decreased at 120 minutes as the membrane became saturated in adsorbing adsorbate. Table 3 shows the results of the kinetic parameters of DBS adsorption on the PSSchitosan membrane.

**Table 3.** Kinetic parameters of DBS on PSS-chitosanmembrane

	Pseudo-first-order			Pseudo-second-order		
Sample	k <sub>1</sub> (min <sup>-1</sup> )	qe (mg.g⁻ ¹)	R <sup>2</sup>	k <sub>2</sub> (mg.g <sup>-1</sup> .min <sup>-1</sup> )	qe (mg.g <sup>-1</sup> )	R <sup>2</sup>
DBS	0.0396	9.84	0.9541	-0.002	51.4	0.7989

The adsorption process of DBS on the PSS-chitosan membrane followed a pseudo-first-order adsorption

kinetics model (Lagergren model) with a linear regression value of 0.9541 (Table 3). The pseudo-firstorder kinetic model shows that the adsorption kinetics is influenced by one active site, the amine group  $(-NH_2)$ . This result follows the geometric optimization results, which show that the interaction between anionic surfactants and the membrane is more stable in -NH2 groups than in -OH groups. As confirmed through geometry optimization, the system's stability results from hydrogen bonding between the amine group hydrogen atoms and the DBS oxygen atoms. Moreover, the amine group in the solution has a partial positive charge. This charge will cause electrostatic interactions with the DBS molecule [35]. The rate constant value obtained for DBS adsorption was 0.0396 min<sup>-1</sup>, and the adsorption capacity was 9.84 mg g<sup>-1</sup>.

#### 3.6.3. Adsorption Isotherm Models

The effect of adsorbate concentration on adsorption capacity is utilized to optimize the adsorption process, which aims to determine the optimum adsorbate concentration. The initial DBS concentration was varied to 0, 0.2, 0.4, 0.6, 0.8, 1, and 1.2 ppm. The adsorption process was performed at pH 8, 100 minutes of contact time, and different initial concentrations of 0, 0.2, 0.4, 0.6, 0.8, 1, and 1.2 ppm. The effect of the initial adsorbate concentration on the adsorption of DBS on the PSSchitosan membrane is shown in Figure 6.



**Figure 6.** Determination of initial concentration variation on adsorption capacity (q) and adsorption efficiency of DBS by PSS-chitosan membrane

Based on the data shown in Figure 6, it can be seen that the initial concentration of the adsorbate affects the adsorption capacity of DBS on the membrane. The value of DBS adsorption capacity increased with increasing initial concentration and reached a maximum when the concentration was 0.6 ppm. The increase in adsorption capacity indicates that the DBS adsorption process follows the Langmuir isotherm model, where the pattern of increase will be sloping or saturated at the adsorption capacity value. Table 4 shows the results of calculating the adsorption isotherm model parameters of DBS molecules on the surface of the PSS-chitosan membrane.

 
 Table 4. Adsorption isotherm parameters for DBS adsorption on PSS-chitosan membranes

	Langmuir			Froundlich		
	Langinun			Fleundhein		
Sample	$q_m$ (mg.g <sup>-1</sup> )	$K_L (L mg^{-1})$	R <sup>2</sup>	$K_{f}$ (L g <sup>-1</sup> )	n	R <sup>2</sup>
DBS	3.97	37.0	0.8667	4.32	5.12	0.5493
220	5.71	5,10	0.0007	4.72	J.12	0.7472

The DBS adsorption isotherm follows the Langmuir isotherm mechanism with the assumption that the active group of the adsorbent in adsorbing DBS is homogeneous and forms a monolayer. From Table 4, the large  $q_m$  and  $K_L$  values were obtained at 3.97 mg.g<sup>-1</sup> and 37.0 L.mg<sup>-1</sup>. The higher  $q_m$  value indicates more solute adsorbed when the adsorbent mass is saturated. Meanwhile, the higher  $K_L$  value indicates that the bond between the adsorbent and the adsorbate is getting stronger.

#### 3.7. Application of PSS-Chitosan Membrane in Laundry Waste

The PSS-chitosan membrane was applied to laundry waste in triplicate to determine the efficiency of surfactant adsorption before being applied directly to the environment. Laundry waste was prepared beforehand using physical filtration to remove macro impurities, such as sand. Based on the measurement results in Table 5, the average adsorption efficiency of anionic surfactants from laundry waste on PSS-chitosan membrane was  $(62.4 \pm 7.2)\%$ .

 
 Table 5.Results of PSS-chitosan membrane application on laundry waste

Treatment	C <sub>initial</sub> (ppm)	Absorbance	C <sub>final</sub> (ppm)	Efficiency (%)	SD
1	1.3	0.346	0.394	68.7	7 2
2	1.3	0.352	0.573	54.5	1.2
3	1.3	0.348	0.454	64.0	

The PSS-chitosan membrane's ability to adsorb anionic surfactants was less effective than the standard DBS solution. This result is due to impurities, such as phosphate ions, being adsorbed on the active site of the membrane. The phosphate ion has a negative charge almost the same as anionic surfactants so that the amine groups can adsorb it on the surface of the PSS-chitosan membrane.

#### 4. Conclusion

The PSS-chitosan membrane was successfully synthesized with the best ratio between PSS: chitosan of 30:70. This membrane has a homogeneous surface, and this characteristic is proven by the SEM Figure and the amine group  $(-NH_2)$ , which serves as the active adsorption site. The optimum adsorption process of anionic surfactants on the PSS-chitosan membrane was at pH 8 with a contact time of 100 minutes. The adsorption kinetics of this anionic surfactant followed the Lagergren model. At an initial DBS concentration of 0.6 ppm, the adsorption model, which followed the Langmuir isotherm, had an adsorption capacity of 3.97 mg.g<sup>-1</sup>. The adsorption efficiency of DBS anionic surfactant in laundry waste on PSS-chitosan membrane is  $(62.4 \pm 7.2)\%$ .

#### Acknowledgment

We thank the Directorate of Learning and Student Affairs of the Indonesian Ministry of Education, Culture, Research and Technology, Gadjah Mada University, PKM Center UGM, and the Laboratory of Analytical Chemistry for their support in providing funds, facilities, guidance, and laboratory facilities during this research.

## References

- [1] HDIN Research, Polystyrene Market Global Review and Outlook, 2019
- [2] Muhammad Reza Cordova, Intan Suci Nurhati, Major sources and monthly variations in the release of land-derived marine debris from the Greater Jakarta area, Indonesia, *Scientific Reports*, 9, 18730, (2019), 18730 https://doi.org/10.1038/s41598-019-55065-2

10093//001.016/10.1030/341390 019 33003 2

- [3] Bayu Pamungkas, Rahmat Kurnia, Etty Riani, Potential Plastic Waste Input from Citarum River, Indonesia, Aquaculture, Aquarium, Conservation & Legislation Bioflux, 14, 1, (2021), 103–110
- [4] Joseph A. Davis, Styrofoam Facts Why You May Want To Bring Your Own Cup, 2019
- [5] Elanda Fikri, Aprilia Veronica, Efektivitas Penurunan Konsentrasi Karbon Monoksida (CO) dengan Sistem Kontak Media Karbon Aktif Menggunakan Variasi Ukuran Partikel Pada Proses Pembakaran Sampah Polistirena Foam, Jurnal Kesehatan Lingkungan Indonesia, 17, 1, (2018), 32-38 http://dx.doi.org/10.14710/jkli.17.1.32-38
- [6] Ali N. Siyal, Saima Q. Memon, Latif Elçi, Aydan Elçi, Extraction of Polystyrene from Styrofoam Waste: Synthesis of Novel Chelating Resin for the Enrichment and Speciation of Cr (III)/Cr (VI) Ions in Industrial Effluents, International Journal of Environmental and Ecological Engineering, 8, 3, (2014), 212-215
- [7] Mohamed E. Mahmoud, Azza E. H. Abdou, Somia B. Ahmed, Conversion of waste styrofoam into engineered adsorbents for efficient removal of cadmium, lead and mercury from water, ACS Sustainable Chemistry & Engineering, 4, 3, (2016), 819-827

https://doi.org/10.1021/acssuschemeng.5b01149

- [8] Nurillahi Febria Leswana, Dwi Siswanta, Adhitasari Suratman, Sintesis Membran Polielektrolit Komplek Polistirena Sulfonat-Kitosan dari Limbah Styrofoam Sebagai Adsorben Logam Cu(II) dan Ni(II), Jurnal Farmasi Etam, 1, 1, (2021), 10–25
- [9] Shu-Hui Liu, Chun-Cheng Lu, Chi-Wen Lin, Shih-Hsien Chang, Rapid modification of waste expanded polystyrene with H<sub>2</sub>SO<sub>4</sub>/trace persulfate in one pot for effective adsorption of fluoroquinolone antibiotic and its regeneration, *Chemosphere*, 271, 129529, (2021), https://doi.org/10.1016/j.chemosphere.2020.129529
- [10] Ministry of Maritime Affairs and Fisheries, *Produksi Perikanan*, 2020
- [11] Beni Setha, Fitriani Rumata, Characteristics of Chitosan from White Leg Shrimp Shells Extracted Using Different Temperature and Time of the Deasetilation Process, Jurnal Pengolahan Hasil Perikanan Indonesia, 22, 3, (2019), 498-507 https://doi.org/10.17844/jphpi.v22i3.29317

- [12] Rikha Yolanda, Pembuatan Kompleks Polielektrolit Polistirena Sulfonat-Kitosan dari Limbah Styrofoam sebagai Adsorben Zat Warna Biru Metilen dan Hijau Malakhit, Master Thesis, Magister Kimia, Universitas Gadjah Mada, Yogyakarta, 2018
- [13] R. D. A. Opier, D. Siswanta, Synthesis of polyelectrolyte complex (PEC) membrane chitosanpolystyrene sulfonate (PSS) from styrofoam waste as adsorbents of Cd (II) and Pb (II) ions, IOP Conference Series: Earth and Environmental Science, 2020

https://doi.org/10.1088/1755-1315/483/1/012028

- [14] Setijo Bismo, Pengolahan Air yang Mengandung Linear Alkyl Benzene Sulfonate (LAS) dan Amonia dengan Kombinasi Proses Ozonasi Gelembung Mikro dan Filtrasi Membran, Jurnal Purifikasi, 12, 2, (2011), 9-20
- [15] Yusmidiarti Yusmidiarti, Analisis Pengelolaan Limbah Cair Usaha Laundry, Jurnal Media Kesehatan, 9, 1, (2016), 30-34
- [16] Hendra Hendra, Eri Barlian, Abdul Razak, Hary Sanjaya, Photo-degradation of surfactant compounds using UV rays with addition of TiO<sub>2</sub> catalysts in laundry waste, Sainstek: Jurnal Sains dan Teknologi, 7, 1, (2016), 59-68 http://dx.doi.org/10.31958/js.v7i1.126
- [17] Aldila Maretta, Qomarudin Helmy, Degradasi Surfaktan Sodium Lauryl Sulfat dengan Proses Fotokatalisis Menggunakan Nano Partikel ZnO, Jurnal Teknik Lingkungan, 21, 1, (2015), 1-8 https://doi.org/10.5614/jtl.2015.21.1.1
- [18] Julie Wolanin, Loïc Barré, Christine Dalmazzone, Daniela Bauer, Investigation of the adsorption of a mixture of two anionic surfactants, AOT and SDBS, on silica at ambient temperature, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 613, 126098, (2021), https://doi.org/10.1016/j.colsurfa.2020.126098
- [19] Rayane R. B. Corona, Cristina M. S. Sad, Mayara da Silva, Diulliany L. Lopes, Juliéte S. D. Leite, Glória M. de F. Viegas, Gustavo R. Gonçalves, Paulo R. Filgueiras, Eustáquio V. R. de Castro, Adsorption of anionic surfactant in graphite oxide: A study for treatment of laundry wastewater, Journal of Environmental Chemical Engineering, 9, 6, (2021), 106858 https://doi.org/10.1016/j.jece.2021.106858
- [20] Marco Masulli, Zi-Long Liu, Feng-Zhi Guo, Xue Li, Ernst J. R. Sudhölter, Naveen Kumar, Temperature effect on the dynamic adsorption of anionic surfactants and alkalis to silica surfaces, Petroleum Science, 19, 4, (2022), 1866-1876 https://doi.org/10.1016/j.petsci.2021.11.008
- [21] Achmad Syarifudin Anwar, Analisis Sifat Mekanik Komposit Rami Epoxy dengan Penambahan Silikon Karbida (SiC) sebagai Bahan Plate Rompi Anti Peluru, Bachelor of Physics, Universitas Islam Negeri Maulana Malik Ibrahim, Malang, 2022
- [22] Sry Agustina, I Made Dira Swantara, I Nyoman Suartha, Isolasi kitin, karakterisasi, dan sintesis kitosan dari kulit udang, Jurnal Kimia, 9, 2, (2015), 271-278

https://doi.org/10.24843/JCHEM.2015.v09.i02.p19

[23] Dian Harjuna Sukma, Etty Riani, Edward Nixon Pakpahan, Pemanfaatan Kitosan sebagai Adsorben Sianida pada Limbah Pengolahan Bijih Emas, Jurnal Pengolahan dan Hasil Perikanan Indonesia, 21, 3, (2018), 460-470

- [24] Ahmed A. Moosa, Ali Mousa Ridha, Noor Ali Kadhim, Use of Biocomposite Adsorbents for the Removal of Methylene Blue Dye from Aqueous Solution, American Journal of Materials Science, 6, 5, (2016), 135-146
- [25] Hamza El Fargani, Rajae Lakhmiri, Nezha Ait Oukharaz, Abdallah Albourine, Mohamed Safi, Omar Cherkaoui, Removal of Reactive Yellow 135 from Wastewaterof Textile Industry onto Chitosan Extracted by Hydrothermo-Chemical Method, Chemistry and Materials Research, 9, 10, (2017), 21-29
- [26] Emil Salim, Afrizal Afrizal, Zilfadli Zilfadli, Synthesis of Polystyrene Sulfonate and Its Characterization as a Polymer Electrolyte Membrane, Akta Kimia Indonesia, 6, 1, (2021), 153-161

http://dx.doi.org/10.12962/j25493736.v6i2.10916

- [27] Indri Hermiyati, Swatika Juhana, Synthesis of chitosan from the scales of starry trigger fish (Abalistes Stelaris), Oriental Journal of Chemistry, 35, 1, (2019), 377-383 http://dx.doi.org/10.13005/ojc/350147
- [28] Robby Gus Mahardika, Muhammad Jumnahdi, Yekti Widyaningrum, Deasetilasi Kitin Cangkang Rajungan (Portunus pelagicus) Menjadi Kitosan Menggunakan Iradiasi Microwave, Al-Kimia, 8, 2, (2020), 149-158
- [29] I. G. Wenten, K. Khoiruddin, A. N. Hakim, P. T. P. Aryanti, Teori perpindahan dalam membran, Teknik Kimia, Institut Teknologi Bandung, Bandung, 2012
- [30] Kun Ma, Peixun Li, Zi Wang, Yao Chen, Mario Campana, James Doutch, Robert Dalgliesh, Armando Maestro, Robert K. Thomas, Jeff Penfold, Strong synergistic interactions in zwitterionicanionic surfactant mixtures at the air-water interface and in micelles: The role of steric and electrostatic interactions, Journal of Colloid and Interface Science, 613, (2022), 297-310 https://doi.org/10.1016/j.jcis.2022.01.045
- [31] Kuntari Kuntari, Nurul Hidayat Aprilita, Suherman Suherman, Utilization of Coal Bottom Ash a Low-Cost Adsorbent for the Removal Acid Red 114 Dye, EKSAKTA: Journal of Sciences and Data Analysis, 17, 1, (2017), 11-19https://doi.org/10.20885/eksakta.vol17.iss1.art2

- [32] Andrio Suhadi, Rizarullah Rizarullah, Feriyani Feriyani, Simulasi docking senyawa aktif daun binahong sebagai inhibitor enzyme aldose reductase, SEL Jurnal Penelitian Kesehatan, 6, 2, (2019), 55-65 https://doi.org/10.22435/sel.v6i2.1651
- [33] Suhas Gotla, Christopher Tong, Silvina Matysiak, Load-Bearing Nanostructures in Composites of Chitosan with Anionic Surfactants: Implications for Programmable Mechanomaterials, ACS Applied Nano Materials, 5, 5, (2022), 6463-6473 https://doi.org/10.1021/acsanm.2c00560
- [34] Rika Wulandari, Dwi Siswanta, Adsorption of sodium dodecylbenzene sulfonate (DBS) by C-3, 4di-methoxyphenylcalix [4] resorcinarene triphenylphosphonium chloride, Jurnal Riset Teknologi Pencegahan Pencemaran Industri, 9, 1, (2018), 1-8

https://doi.org/10.21771/jrtppi.2018.v9.no1.p1-8

[35] Westriani Prambaningrum, Khabibi Khabibi, Muhammad Cholid Djunaidi, Adsorpsi Ion Besi (III) dan Kadmium (II) Menggunakan Gel Kitosan, Jurnal Kimia Sains dan Aplikasi, 12, 2, (2009), 47-51 https://doi.org/10.14710/jksa.12.2.47-51