# Adsorption of Linear Alkylbenzene Sulfonate (LAS) using Moringa oleifera Seeds

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# Adsorption of Linear Alkylbenzene Sulfonate (LAS) using *Moringa oleifera* Seeds

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**ABSTRACT**

*One of the main components in detergent is Linear Alkylbenzene Sulfonate (LAS), an anionic surfactant. In the aquatic environment, LAS has the potential to cause pollution and cannot be decomposed under anaerobic conditions (no air), so it is necessary to study processing methods that can reduce the concentration of LAS in the waters. In this research, a study of LAS adsorption by Moringa seeds was carried out. The parameters studied were the influence of contact time and solution pH. A study on the isothermic adsorption of LAS on Moringa seeds using the Freundlich and Langmuir approach was also carried out. The concentration of LAS was determined by the Methylene Blue Active Surfactant (MBAS) method using a UV-Vis spectrophotometer. The results showed that adsorption reached equilibrium after 90 minutes. A pH value of 5 is the optimum pH value for the adsorption of LAS by Moringa seeds. Using the Langmuir approach, the LAS adsorption capacity of Moringa seeds was calculated to be 400 mg/g*

Keywords: adsorption, detergents, LAS,Moringa seeds

## 1. INTRODUCTION

Domestic waste mainly comes from household activities, such as water used for washing clothes, wastewater from kitchens and bathrooms and other domestic activities.[1] One of the pollutants that is often found in domestic waste is detergent. Detergents can negatively impact the aquatic environment as the presence of detergents might increase the solubility of several carcinogenic organic compounds, such as 3,4-benzopyrene.[2]

In general, the composition of detergents can be divided into three main groups, namely, surfactants, which are the active substances of detergents, builders (phosphate compounds) and other compounds added as



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additives (such as additional fragrances or bleaching agents).[3] One of the main characteristics of surfactants is their structure, which causes their molecules to be simultaneously hydrophilic and lipophilic. This property enables surfactants to encourage the mixing of oil and water.[3] The surfactants in detergents are generally anionic surfactants such as LAS (Linear Alkylbenzene Sulfonate).[4] In the aquatic environment, LAS has the potential to cause pollution [5], as in a water environment that lacks oxygen (anaerobic), LAS is difficult to degrade biologically. Thus, the presence of LAS in turbid waters, such as in most rivers in Indonesia, can potentially degrade the environmental quality.[3]

A potential method to control environmental pollution caused by detergent waste is the adsorption method. As reported by Al-Sa'adi and Al-Me'ammar [4], the adsorption method using modified bentonite can reduce the LAS concentration in water by up to 81%. In light of adsorption as a method to treat detergent wastewater, a promising material that can be utilized for this purpose is the seed of the Moringa oleifera plant. This plant, commonly found in many Asian countries, including Indonesia, has been widely explored for its potential as an environmentally-friendly adsorbent.[6] For example, Moringa oleifera has been studied as a lead adsorbent, where its adsorption efficiency reaches up to 83.6958%.[5] Its ability to remove pollutants is due to its numerous functional groups. For example, a compound found in Moringa seeds is 4-alpha-4-rhamon-siloxybenzyl isothiocyanate, has isothiocyanate and carboxyl groups and can potentially bind pollutant molecules.[7] Based on the description above, it is interesting to study the potential of Moringa seeds in adsorbing LAS to remove it from water. While Moringa seeds have been studied to remove LAS through coagulation [8], studies on LAS adsorption by Moringa seeds and the factors influencing are still limited. This research examines the potential of Moringa seeds as a LAS adsorbent. This research analyzed several factors that could influence adsorption, i.e., the pH of the solution and the contact time. In addition, the adsorption capacity of Moringa seeds on LAS was also studied using the adsorption isotherm approach.

## 2. EXPERIMENTAL

### *2.1. Chemicals, Equipment and Instrumentation*

The equipment used were standard laboratory glassware, dropper pipettes, UV-visible spectrophotometer, FTIR, pH meter, oven, analytical balance, stopwatch, magnetic stirrer, separating funnel, 60 mesh sieve, and cuvette. Meanwhile, the materials used were filter paper, Moringa oleifera seeds, distilled water, hydrochloric acid (HCl), sodium hydroxide (NaOH), sulfuric acid ($H_2SO_4$), phenolphthalein indicator, methylene blue solution, chloroform ($CHCl_3$), sodium dihydrogen phosphate monohydrate ($NaH_2PO_4.H_2O$), and Linear Alkylbenzene Sulfonate (LAS) powder.

### *2.2. Research Procedure*

**Moringa Seed Preparation**

Moringa seeds peeled from their shells were dried in the oven for 5 hours at 105°C. The dried seeds were ground into powder and sieved with a 60-mesh sieve.

**Effect of LAS Adsorption Contact Time on Moringa Seeds**



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Fifty mg of Moringa seed powder was added to 250 mL of LAS solution at a concentration of 5 ppm. The adsorbent was then separated from the solution phase by filtration after various contact times (10, 15, 30, 60, and 90 minutes). The remaining LAS concentration was determined by the Methylene Blue Active Surfactant (MBAS) method using a UV-Vis spectrophotometer.

**Determination of Optimum pH for LAS Adsorption on Moringa Seeds**

The pH of 500 mL LAS solution with a five ppm concentration was adjusted by adding 1 M HCl or 1 M NaOH. The pH variations of 4, 5, 6, 7, and 8 were obtained and used in this study. Two hundred fifty mL of the solution was then taken from each solution, and 50 mg of Moringa seed powder was added. The remaining 250 mL solution was used as a negative control. The mixture was stirred for 120 minutes and then filtered. The remaining LAS concentration in the solution was determined by the MBAS method using a UV-Vis spectrophotometer at the maximum wavelength.

**Determination of LAS Adsorption Capacity on Moringa Seeds**

A series of LAS solutions with different concentrations (1, 3, 10, 20, and 25 ppm) were prepared in 250 mL beakers. The pH of each solution was adjusted to the optimum pH obtained from the previous step. Fifty mg of Moringa seed powder was added to each LAS solution, stirred for 24 hours and filtered. The remaining LAS concentration was determined by the MBAS method using a UV-Vis spectrophotometer, and the adsorption isotherm was determined using both Langmuir and Freundlich adsorption isotherm models.

**Determination of Optimum Wavelength**

To determine the optimum wavelength in determining the LAS concentration using the MBAS method, the adsorption of a 2 ppm LAS solution was measured using a UV-Vis spectrophotometer within the range of 600-700 nm. After the optimum wavelength was determined, a standard curve was created by measuring the adsorption of several LAS solutions with various concentrations at said wavelength.

## 3. RESULTS AND DISCUSSION

### *3.1. Moringa Seed Preparation*

After drying, a ready-to-use adsorbent from the Moringa seed was produced in powder form. This powder has a distinctive odour and a brownish-yellow colour. The Moringa seed powder was then characterized using an FTIR spectrophotometer. The IR spectrum from the Moringa seed is presented in Figure 1. Based on the IR spectrum in Figure 1, the presence of a broadening peak in the 3431.90 $cm^{-1}$ area indicates stretching of the O-H bond. The absorption bands in the wave number region of 2924.39 $cm^{-1}$ and 2853.66 $cm^{-1}$ originate from the presence of symmetric and asymmetric stretching of the C-H bonds of $CH_2$. The presence of the carbonyl group (C=O) from the ester can be seen in the peak at wave number 1745.47 $cm^{-1}$. [9] The vibration of –N=C=S provides absorption at a wave number of 1547.09 $cm^{-1}$, where this functional group can interact with adsorbate molecules. [10] The absorption band in the wave number area of 1461.57 $cm^{-1}$ indicates C-H bond stretching. [11]



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The absorption band in the wave number area of 1237.65 $cm^{-1}$ shows C-O from aromatics, and 1162.80 $cm^{-1}$ is the vibration range that occurs C-O-C from ether. [10] The absorption band in the wave number area of 722.12 $cm^{-1}$ is $CH_2$ vibration. [12] Due to the adsorbed/attached LAS, the vibration intensity of the clusters of Moringa seeds decreases.

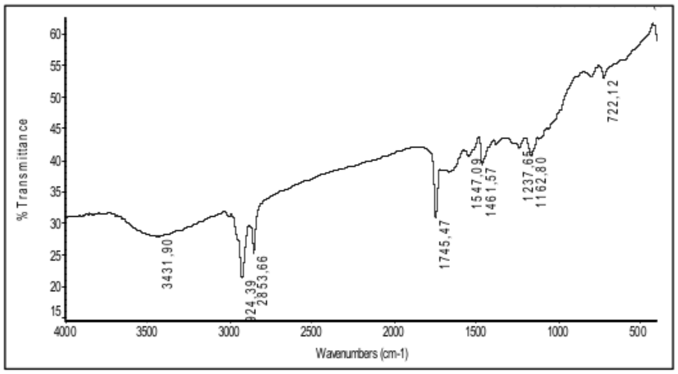


**Figure 1.** IR Spectrum of Moringa seeds

Figure 2 provides information about the IR spectrum of Moringa seed powder that has been in contact with LAS. Most functional groups contained in Moringa seed powder before and after contact with LAS are the same. However, the absorption of Moringa seed powder that had been contacted with LAS experienced a shift, and some was also lost. For example, the absorption loss in the wave number area 1547.09 $cm^{-1}$ is the active group of Moringa seed powder, namely alkyl isothiocyanate (N=C=S). This indicates that the active site in Moringa seed powder forms a bond with LAS. The formation of this bond is what causes LAS to be adsorbed on Moringa seeds.

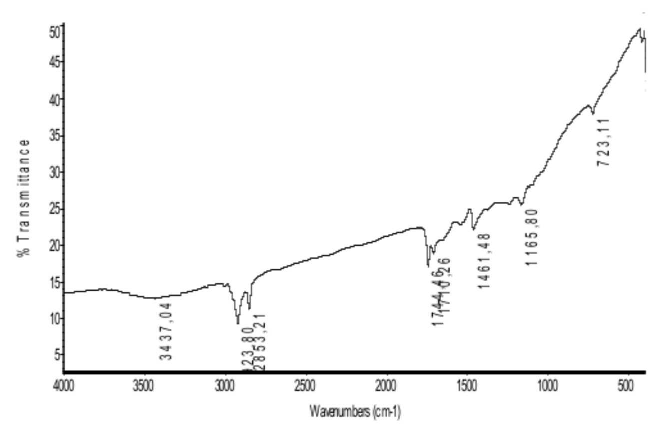


**Figure 2.** IR Spectrum of Moringa seeds after contact with LAS solution



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### *3.2 Effect of Contact Time on LAS Adsorption on Moringa Seeds*

The interaction between LAS molecules and Moringa seeds will need enough time to form a strong bond to keep the LAS from being released into the solution phase. In this study, the contact time between the Moringa seeds and the solution samples was varied to investigate the effect of contact time towards the removal efficiency of LAS using Moringa seeds as the adsorbent. The result is presented in Figure 3.

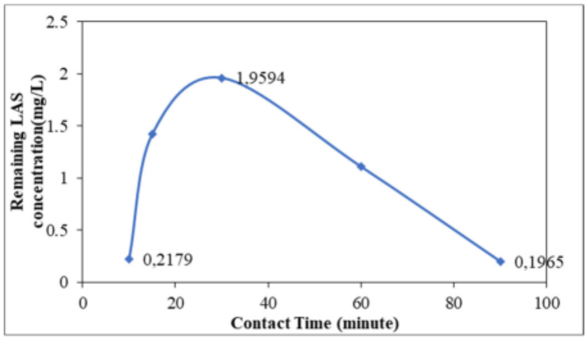


**Figure 3.** Graph Effect of Contact Time Variations

The graph in Figure 3 shows a reduction in LAS concentration as the contact time between the LAS solution and the Moringa seeds adsorbent increased. While in the first 10 minutes, the LAS concentration in the solution decreased quite significantly, the surfactant concentration increased again by 30 minutes. This situation is caused by the LAS molecules that initially had interacted with the active site and was released back into the solution, because the bond formed between the adsorbate and the adsorbent was not strong enough. However, as the contact time increases, the surfactant concentration decreases again at 60 and 90 minutes. This is because the longer contact time allows the active sites on the adsorbent to form stronger bonds with the adsorbent. In addition, the longer contact time between the adsorbate and the adsorbent allows collisions between Moringa seed powder and LAS to occur more frequently so that more LAS can be adsorbed.

### ***3.3 Determination** of Optimum pH for LAS Adsorption on Moringa Seeds*

In many cases, the system's pH is an important factor in adsorption. This is because the pH of the system will determine the compound speciation involved through ionization, and thus, it will affect the way the adsorbent interacts with the targeted adsorbates. In this research, observations were made on the effect of pH on LAS adsorption by Moringa seeds within a pH range of 4-9. Figure 4 shows the remaining LAS concentration in the solution after being treated with Moringa seeds for each pH being studied. Based on Figure 4, at pH 4, the LAS concentration remaining in the solution was still relatively high. This is most likely because at a too low pH, most of the active groups on the surface of the Moringa seed powder adsorbent are still protonated. Figure 4 also shows that Moringa seed powder provides optimal results at pH 5 in reducing the concentration of LAS. A possible explanation for such a result is that as the pH of the solution begins to be increased, the active sites in the Moringa seed powder begin to deprotonate, enabling these sites to bind LAS.


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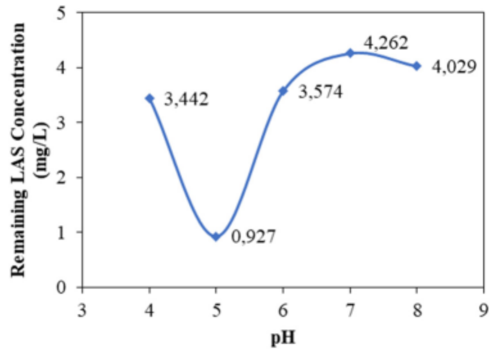
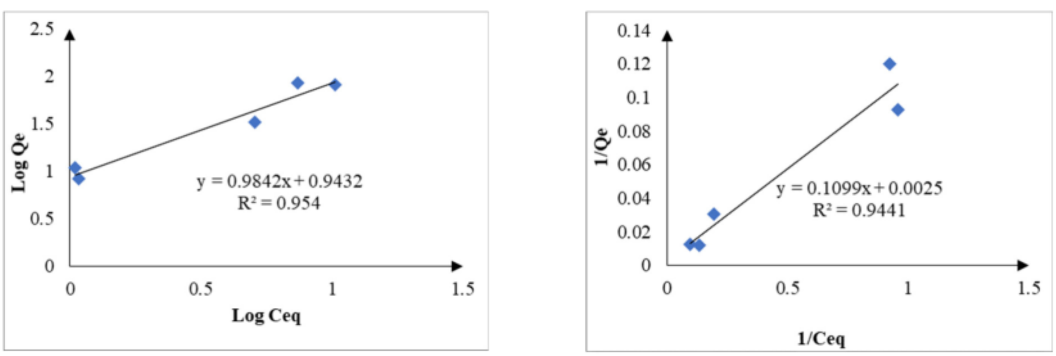



**Figure 4.** Graph of Effect of pH Variations

This probably happens because when the pH is increased, some of the active sites on the adsorbent become negatively charged, increasing the total concentration of negative charge in the solution system. In that case, LAS will try to compensate by releasing $Na^+$ so that LAS becomes negatively charged, which comes from the hydrophilic group of LAS, namely $SO^{3-}$. The similarity of charge between the active site of the Moringa seed powder adsorbent and LAS leads to repulsion between them, and the adsorption process becomes ineffective.

*3.4 Determination of LAS Adsorption Capacity on Moringa Seeds*

Adsorption isotherm is an approach commonly used to study the interaction between adsorbent and adsorbate molecules. In this study, two models, Freundlich and Langmuir isotherm models, were used to study LAS adsorption on Moringa seeds. The figures representing how the data fit both models are presented in Figure 5(a) for the Freundlich model and Figure 5(b) for the Langmuir model.




(a) (b)

**Figure 5.** (a) Freundlich isotherm model; (b) Langmuir isotherm model



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Figure 5(a) shows the Freundlich isotherm adsorption model using the data from this study, where the logarithm value of the amount of adsorbate adsorbed by the adsorbent (log Qe) is described as a linear function of the logarithm value of the concentration of adsorbate remaining in solution (log Ce) obtained from the plot results between Log Ceq and Log Qe. The Freundlich adsorption isotherm model assumes that the interaction between adsorbent and adsorbate occurs on a multilayer surface.[13] The Freundlich isotherm plotted using the data gave a straight-line equation of $y = 0.9842x + 0.9432$, with a regression value ($R^2$) = 0.954.

Figure 5(b) shows the Langmuir isotherm model plotted using the data from this study. In the Langmuir adsorption isotherm, the Qe-1 value (where Qe indicates the amount of adsorbate adsorbed per gram of adsorbent) is described as a linear function of Ceq-1, where Ceq is the concentration of adsorbate remaining in the solution obtained from the plot between 1/Ceq and 1/Qe. The Langmuir isotherm adsorption model is based on the assumption that adsorption process occurs in a monolayer manner, which means that only one layer of adsorbate is formed on the surface of the adsorbent. [13] The Langmuir isotherm plot of the data gave a line equation of $y = 0.1099x + 0.0025$ with a regression value ($R^2$) = 0.944.

The more appropriate adsorption isotherm pattern can be determined based on the regression value obtained from the linear line. As shown in both Figure 5a and 5b, LAS adsorption on Moringa seeds can be explained by using both the Freundlich and Langmuir isotherm models. Using the Langmuir approach, it can be estimated that the LAS adsorption capacity on Moringa seeds is 400 mg/g. Meanwhile, an adsorption affinity of 1.016 was obtained using the Freundlich approach. This adsorption affinity value is large enough that LAS tends to bind to Moringa seeds. Several other studies have been carried out to study LAS adsorption on various other materials. The results of determining adsorption capacity obtained from these studies are shown in Table 1.

**Table 1.** Adsorption Capacity of LAS on Different Types of Adsorbents

| Adsorbent | Adsorption Capacity |
|---|---|
| Moringa oliefera seeds* | 400 mg/g |
| Bentonite-chitosan[14] | 1.7 mg/g |
| Natural bentonite[14] | 3.265 mg/g |
| Activated carbon from Cassava peel[15] | 0.128 mg/g |
| Natural zeolite[16] | 0.201 mg/g |
| Abu sekam padi[3] | 3.894 mg/g |

*this study

Based on the data presented in Table 1, The adsorption capacity of Moringa seeds on LAS is relatively high compared to other adsorbents made from other materials. Therefore, using Moringa seed powder adsorbent shows excellent potential for application in treating waste-containing surfactants.

## 4. CONCLUSION

This research concludes that contact time influences the adsorption ability of LAS on Moringa seeds. LAS adsorption requires sufficient contact time to achieve equilibrium. LAS adsorption by Moringa seeds reaches equilibrium at a minimum contact time of 90 minutes, and the optimum pH condition for LAS adsorption on Moringa seeds is pH 5. The value of LAS adsorption capacity on Moringa seeds is 400 mg/g.



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