Effect of Contact Time Adsorption of Rhodamine B, Methyl Orange and Methylene Blue Colours on Langsat Shell with Batch Methods

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Abstract. This study aims to determine the uptake capacity of langsat (Lansium domesticum) skin on the adsorption of dyes along with the contact time. Textile dyes are dyes which is harmful for the environment and living things. This textile industry waste can cause a decrease in water quality. When this carcinogenic dye enters the human body, it can lead to cancer. The process of these dyes adsorption use langsat skin samples. The components of langsat skin that can adsorb dyes are triterpenoids, saponins and flavonoids. This study uses a batch method by treating the contact time variations of several dyes. The results reveal that the biomass adsorption on rhodamine B, methyl orange, and methylene blue dyes were 11,578 mg/g, 3.8425 mg/g, 36,735 mg/g respectively and with optimum contact time of 60, 90 and 150 minutes, respectively.

1. Introduction
The textile industry is a fairly developed industrial activity in Indonesia. Things that need to be considered in the textile industry are waste that can pollute the environment, especially water pollution. Textile industry waste will flow into the gutter or into the river, so that this liquid waste can reduce the natural cleaning power owned by water, can change the colour of river water, and can even cause the death of aquatic organisms that are important for human life. The amount of dye waste that is non-biodegradable will cause problems for the environment and health. Substance synthetic colours are generally derived from azo compounds and derivatives of benzene groups. The benzene group is very difficult to degrade and requires a long time [1]. Azo compounds are carcinogenic so they can cause cancer if they accumulate too long and enter the body. While benzene compounds are also compounding that are difficult to degrade.

Various techniques have been used to treat industrial wastes containing heavy metals by precipitation, adsorption, ion exchange, membrane technology and electrosynthetic. Some of these methods require relatively high costs. One method that can be used to tackle water pollution due to the presence of textile dyes is through the biosorption method because it does not require high costs and is easy to apply, and the use of environmentally friendly adsorbents derived from natural materials. The biosorption method is based on the interaction of adsorbent functional groups with dyes via ion exchange.
In the biosorption method, the surface of the adsorbent will play a role in adsorbing dyes in the waste. Biosorbent has lacked is a low density, instability and a different particle size can be minimized by activation of the acid [3]. However, recent research shows that several types of dry biomass such as longan skin, banana peel, orange peel and lemon peel [4,5]. The dye waste will enter and be bound into the pores of the adsorbent so that the waste produced with dyes contaminants with levels smaller than before. Some of the adsorbents that have been studied are: corn cobs and pineapple wheat fibre. One of the environmentally friendly adsorbents which is also a waste is langsat (Lansium domesticum) skin. This material was chosen because it is easy to find in Indonesia and the price is cheap. In the skin of langsat there are flavonoid compounds, terpenoids and saponins. In the triterpenoid compound there are lancolic acid and lansiolat acid and functional groups contained in the components of these compounds such as: NH, OH, C = O and COOH [6].

Contact time is one of the factors that influence adsorption. Determination of the optimal contact time is done after the optimum pH and concentration are known. Determination of contact time aims to obtain the best time in the process of adsorption of Rhodamine B dye with Langsat skin. The contact time chosen in the adsorption process is not too long so that the rhodamine B dye which is absorbed in the adsorbent does not experience desorption, which means that the dye bonds are released from the adsorbent [7].

There are two treatment methods in biosorption, namely batch and column. The batch method is mixed with the solution and shaken with an absorbent until equilibrium occurs. The column method is carried out by placing the biosorbent in the column and flowing the sorbate through the column containing the sorbent to saturated biosorption. Good sorbent requirements include has great adsorption, solids with large surface area, insoluble in the substance to be adsorbed, does not react chemically with the mixture to be purified, can be regenerated easily, and non-toxic [8].

2. Experimental

2.1. Reagents and chemicals
Glassware, shaker (model: VRN-480), pH meter (HI2211), analytical balance (ABS 220-4), filter paper, magnetic stirrer (MR Hei Standard), oven, spray bottle, sifter (BS410 ). The instrument used was FTIR (Fourier Transform Infra-Red) Perkin Elmer universal type ATL Sampling Accessor 735 B and Spectronic 21. The ingredients used in this study were langsat shell, Distillate water, 1000 mg/L Rhodamin B, Methyl Orange and Methylene Blue Solution, NaOH 0,1 M, HNO$_3$ 0,01 M, HNO$_3$ 0,1 M, HNO$_3$ 1 M, HNO$_3$ 0,5 M, HNO$_3$ 5 M.

2.2. Sample preparation
Langsat shell from the main market in the city of Padang. Langsat cleaned and destroyed using a grinding machine, mashed with mortar and pestle, and then sifted to a size of 150 (Kurniawati et al.; 6).

2.3. Activation of Langsat Shell Biosorbent
A total of 20 grams of langsat peel was activated with HNO$_3$ 0,01 M. For 2 hours, then washed with distilled water until neutral, then dried and dried [9].

2.4. Dyestuff Biosorption Experiments
Biosorption of dyes on the skin of langsat was applied in a flask containing 25 mL and biosorbent was stirred at 150 rpm, a massa of 0,2 g and a particle size of 150 μm. We studied the effects of pH (4) and initial metal ion concentration (100 mg/L) with variations of contact time 30, 60, 90, 120 and 180 minutes. The filtrate is measured by Spektronic. The amount of dyes adsorbed per unit mass of the adsorbent was evaluated by using the following equation [9]:
\[ q = \frac{(C_o - C_f)}{M} x V \]  \hspace{1cm} (1)

Where,
- \( q \) = the amount of dyes adsorbed per unit mass of the adsorbent (mg/g)
- \( C_o \) = initial metal concentration (mg/L)
- \( C_f \) = final concentration of metal ions (mg/L)
- \( M \) = mass of adsorbent (g)
- \( V \) = volume of solution (L)

3. Results and Discussion

3.1. FTIR analysis

FT-IR (Fourier Transform Infra Red) spectroscopy is one of the measurement methods to detect the molecular structure of compounds through identification of compound functional groups. Functional groups have an important role in the process of adsorption of dyes that are influenced by the number of functional groups, types of functional groups, interaction processes, chemical structures and affinity for biosorbents [10]. The infrared spectrum obtained is then plotted as the intensity of the energy function, wavelength (\( \mu \)m) or number of waves (cm\(^{-1}\)).

FTIR characterization was carried out on pure langsat shell, activated langsat shell and activated langsat shell after contact with rhodamine B dye solution. The results of the FTIR test can be seen in the Figure.1:

![Figure 1. FTIR langsat shell. (a)before activation, (b)after activation](image)

The results of infrared spectroscopic analysis showed that the langsat shell samples contained O-H functional group uptake, C = C group vibrations, C-N amines and C-O bonds. And the results of the FTIR test after activation with HNO\(_3\) contained the -NO\(_2\) functional group and the addition of the O-H functional group.

FTIR test results on langsat skin samples (Lansium domesticum) before activation showed absorption at wide and strong wavelengths observed at 3330.46 cm\(^{-1}\) there were NH, CH stretching bonds at 1381.37 cm\(^{-1}\), aromatic C = C rings at wave peak 1625.90 cm\(^{-1}\) and CO stretching at 1256.16 cm\(^{-1}\).

FTIR test results after activation there was a shift in the N-H group from 3330.46 cm\(^{-1}\) to 3329.21 cm\(^{-1}\). And there was also a shift in the O-H group from 2157.57 cm\(^{-1}\) to 2221.65 cm\(^{-1}\). And the addition of O-H functional groups at 2080.75 cm\(^{-1}\) and -NO\(_2\) at 1379.51 cm\(^{-1}\) due to the influence of
HNO3 solution at the time of activation. And in the C-H group there was also a shift from 1381.37 cm\(^{-1}\) to 1430.96 cm\(^{-1}\).

3.2. **Effect of contact time for rhodamin B dyes on langsat skin**

Contact time is crucial in the adsorption process, because contact time allows the diffusion and adhesion of adsorbate molecules to take place. To determine the optimum contact time in this study carried out in 5 time variations namely 30, 60, 90, 120 and 180 minutes with pH 4, concentration of 100 mg/L, volume of dye solution 25 mL and mass of adsorbent 0.2 grams.

![Figure 2](image)

**Figure 2.** Effect of contact time on the uptake capacity of rhodamine B dyes is by using the skin with batch method (0.2 grams of biosorbent, 25 mL rhodamine B dye solution 100 mg/L pH 4, size 150 μm, speed 200 rpm).

In Fig 2 it can be seen that the optimum contact time occurs at 60 minutes with an uptake capacity of 11.578 mg/g. This condition decreases after the contact time of 60 minutes, this is due to polysorbents that have been saturated by the dyes ions little by little the active sites that bind begin to release the dye ions back into the solution, so that the addition of time no longer increases the adsorption of Rhodamine B dyes. The results obtained are the same as those produced by using Chorrella Sp biomass which is immobilized in silica gel as the adsorption of rhodamine B dyes.

3.3. **Effect of contact time for methyl orange dyes on langsat skin**

Effect of contact time is closely related to the process of biosorption, the longer contacting the adsorption power will be even better [11]. However, prolonged contact can result in decreased adsorption because the active site which binds to the dye has been saturated so that it cannot bind anymore [9]. The variation of contact time is done at 30, 60, 90, 120 and 180 minutes. The effect of contact time variations on the adsorption of methyl orange can be seen in Fig.3.
In Fig.3. The optimum contact time appears to occur at 90 minutes after contact with an uptake capacity of 3.8425 mg/g. The optimum time is the time of equilibrium between the adsorption and desorption rates [12]. Furthermore, after contact for more than 90 minutes the adsorption will decrease because the active site of the methyl orange binder is saturated so that it cannot bind anymore [13].

3.4. **Effect of contact time for methylene blue dyes on langsat skin**

Determination of the optimum contact time is intended to determine how long the methylene blue is adsorbed maximally by langsat shell. The effect of contact time on the uptake capacity of methylene blue by Langsat skin can be seen in Fig.4.

![Uptake capacity of Methyl Orange using activated langsat skin](image1)

**Figure 3.** Effect of contact time on the uptake capacity of Methyl Orange using activated langsat skin (0.2 grams of biosorbent, 25 mL of 150 mg/L Methyl Orange solution, pH 4, 150 µm biosorbent particle size, 200 rpm).

**Figure 4.** Effect of contact time on the uptake capacity of methylene blue using activated Langsat skin (0.2 gram biosorbent, 25 mL of methylene blue solution 350 mg/L, pH 6, 150 µm biosorbent particle size, 200 rpm).

Fig.4 shows that the optimum contact time of adsorption of methylene blue by langsat skin is shown at 150 minutes where the adsorption capacity is mg/g. At 30 minutes to 150 minutes an increase in uptake capacity, but at 180 minutes a decrease in the uptake capacity of langsat skin adsorbents. From the results of this experiment it can be said that adsorption occurs in two stages, namely the initial adsorption that occurs quickly and then the stage of releasing adsorbed substances.
slowly this is because the amount of adsorbed substances has exceeded the maximum number of compounds that can be adsorbed by adsorbents in other words adsorbents has experienced saturation. If the active site on the surface of the adsorbent has been saturated by a number of adsorbates, the addition of the adsorption time can no longer increase the adsorption and even tends to decrease. In this condition, it shows that the optimum time of adsorption by methylene blue is 150 minutes and because the process takes longer to make the bond between the adsorbate and the adsorbent that has been formed will be released again so that the capacity and percentage of adsorption decreases.

4. Conclusion

Langsat shell (*Lansium domesticum*) which is agricultural waste can be used as an adsorbent to adsorb various dyes. The optimum uptake for rhodamine B, methyl orange, and methylene blue dyes were 11,578 mg/g, 3,8425 mg/g, 36,735 mg/g respectively by batch method and with optimum contact time were 60, 90 and 150 minutes, respectively.

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