Adsorption of Rhodamine B from Aqueous Solution Using Langsat (Lansium domesticum) Shell Powder

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ABSTRACT
The potential of langsat (Lansium domesticum) shell powder to adsorb rhodamine B from aqueous solution has been investigated through bath experiments. The rhodamine B adsorption was found to be dependent on pH, initial rhodamine B concentration. The equilibrium data were described by Freundlich and Langmuir with the maximum adsorption capacity was 2.1531 mg/g in a pH 5. While the optimum concentration at 100 ppm with a capacity of 12.3743 mg/g. In order to know the biosorption mechanism FT-IR analyses were performed for langsat shell before and after uptake of rhodamine B. The result showed different functional groups on the biomass surface and the ability of these groups bind with rhodamine B in aqueous solution.

Keywords: Biosorption, Rhodamine B, Bath Method, Langsat (Lansium domesticum).

1. INTRODUCTION
Dyes have been declared as environmental pollutants so they do not meet the requirements for living needs. Dyestuff reduction can be done by adsorption. To prevent problems with textile waste, to eliminate harmful dyes. Liquid waste as a by-product of industrial activities which often causes problems for the surrounding environment. Liquid waste has materials that are not good for health or are dangerous. One of the most common hazardous substances found in wastewater is a dye. Dyes are color compositions that are widely used in the textile, plastic, paper and many other industries. One of them is a textile dye which is widely used as rhodamine B (C28H31ClN2O3).

Rhodamine B is one of the dangerous dyes that is often used in small industries. Rhodamine B is dangerous for health because it contains heavy metals in it, containing chlorine (Cl) compounds. Chlorine compounds are dangerous and reactive halogen compounds that will cause toxic and carcinogenic properties.

Various techniques have been used for the treatment of industrial wastes containing hazardous textile dyes by precipitation, adsorption, ion transfer, membrane technology and electrochemistry. Traditional biosorption methods as an alternative source for removing harmful dyes.

Rhodamine B is widely used by the textile industry. This compound contains an alkaline group and a benzene nucleus, so rhodamine B is a compound that is difficult to be degraded naturally by microorganisms. The inclusion of rhodamine B in water is a serious environmental problem. Rhodamine B molecule is very dangerous if it enters the human body because it can cause various diseases, especially liver cancer.

Some biosorbents are used to absorb dyes because they have functional groups such as hydroxyl, carboxyl, carbonyl and amines. However, recent research shows several types of dry biomass such as orange peel, banana peel can be used as inexpensive adsorbents. The reason is because the skin contains functional groups such as -CO2H, -OH, N-H, C-H, C = O, C = C, which can form ligands when the dye ions remain on the surface. Langsat skin contains chemical compounds such as triterpenoids, flavonoids and saponins.

2. MATERIALS AND METHODS
2.1. Materials
Materials needed are erlemeyer, spray bottle, mortar and pestle, sieve (BS410), analytical balance (ABS 220-4), pH meter (HI2211), magnetic stirrer (MR Hei standard), shaker (model: VRN-480). The equipment used for characterization is Spectronic 21 and FTIR. The material used is 0.01 M HNO3, NaOH 1 N, Rhodamine B standard solution.
2.2. Procedure
-Sample preparation and production of langsat skin biomass
Langsat shell is crushed by using a grinding machine and mashed with mortar and pestle, then sifted to a certain size.

-Activation of langsat skin biosorbent
The shell of langsat in a 0.01 M HNO₃ solution was activated for 2 hours with 20 g of biomass over 80 mL of 0.01 M HNO₃, followed by thorough washing with deionized water and then dried with air (Kurniawati et al.; 2016).

-Effect of pH
0.2 g of langsat shell contacts 25 mL of 50 ppm rhodamine B solution with stirring for 30 minutes at 200 rpm at pH 2, 3, 4, 5, 6 and 7. Then use filtered and absorbance from the filtrate to be used with Spektronics 21.

-Effect of concentration
0.2 g of langsat shell contacted 25 mL of rhodamine B solution and optimal pH with stirring for 30 minutes at a speed of 200 rpm at concentrations of 50, 100, 150, 200 and 250 ppm. Then the benefits are filtered and absorbance from the filtrate value with Spektronics 21.

3. RESULT AND DISCUSSION

3.1. Rhodamine B standard curves
Making a calibration curve for rhodamine B solution begins with diluting 1000 mg/L rhodamine B solution which is put into a 100 mL volumetric flask, and diluted to the mark limit. Then made a standard solution of 2, 4, 6, 8, 10 and 12 ppm. Furthermore, the solution was measured using 21 spanners. The maximum wavelength of rhodamine B obtained is 550 nm, which is used as measure the absorbance of the prepared solution. So that the absorbance obtained is made a calibration curve and linear regression equation, illustrated on the graph with absorbance as the y axis and wavelength as the x axis. Based on the curve obtained R² value of 0.998, this value shows a linear relationship between absorbance and the concentration of the measured solution. The regression equation obtained is 

\[ y = 0.222x + 0.043 \]

Can be seen in the graph below:

3.2. Effect of pH
pH is a parameter involved in the biosorption process. Determination of the optimal pH at the absorption capacity is needed to get the pH of rhodamine B during this absorption process is maximum. The treatment of variations changes the concentration of H⁺ and OH⁻ ions in solution and determines changes in adsorbents that have carboxylates (Kurniawati et al.; 2015). One factor that affects the ability of adsorbents to bind is reliability, the concentration of the adsorbent solution on the chemical binding of metal ions on the surface. Measurement of initial test variations ranging from 2, 3, 4, 5, 6 and 7.

The results are shown in Figure 3. showing that the maximum absorption of rhodamine B occurs at pH 5 with an absorption capacity of 2.1531 mg/g. Acidity affects the competition between the rhodamine B dye ion and hydrogen ions to be able to bind to the active site on the surface of the adsorbent. Variation of pH 1 is not carried out because in high acidic conditions there is a repulsive force which rejects electrostatically on rhodamine B dyes so that absorption occurs very little. At low pH, there are many H⁺ ions in solution, so H⁺ ions will compete with the rhodamine B dye ion to bind the negative charge to the active group on the biosorber surface, thus the absorption at the pH is low.

At pH 7 there is a decrease, this is because too many OH⁻ ions in the solution are not able to be captured by the dye, so there are still many OH⁻ ions that are free in the solution. The carboxyl group contained in the adsorbent is an active group with a partially positive charge, so that at the time of base addition, the color tends to be negatively partially charged. This causes competition between the dye and the OH⁻ free ion to occupy the surface of the adsorbent which will reduce the adsorption power of the dye with the adsorbent.

3.3. Effect of Concentration
The concentration of the solution is a parameter that affects the biosorption process. Determination of the optimum concentration aims to find out the optimum concentration in the biosorption process of rhodamine B, the effect of concentration on the absorption of rhodamine B dyes was used variations in the concentration of 50, 100, 150, 200 and 250 ppm.

![Fig 2. Rhodamine B calibration curve](image)
![Fig 3. effect of pH on rhodamine B biosorption with langsat skin (lansium domesticum), 25 mL of rhodamine B solution 50 ppm, for 0.2 grams of langsat skin, speed of 200 rpm for 30 minutes.](image)
Fig 4. effect of concentration on rhodamine B biosorption with langsat shell (lansium domesticum), 25 mL of rhodamine B solution 50,100,150,200 and 250 ppm, for 0.2 grams of langsat shell, speed of 200 rpm for 30 minutes.

The concentration of absorbed metal ions will continue to increase until at a time when the addition of the concentration no longer affects the adsorption. This is because the dye ion concentration is proportional to the number of active sites found on the biosorbent surface, causing the active site to saturate or have reached equilibrium (Chergui et al.; 2007). The effect of variations in solution concentration can be seen in Figure 4. The greater the concentration of the solution interacted with the amount of biosorbent, the greater the number of ions absorbed by the biosorbent. As long as the active site is not saturated or is in a state of equilibrium, the increase in concentration will increase the absorption of the dye. Based on Langmuir adsorption theory states that on the surface of biosorbents there are a number of active sites that are proportional to the surface area of biosorbents.

The isotherm model contained in the graph obtained R2 value of 0.918. y= 0.080x + 2.099. Based on the images obtained from each isotherm equation, the Langmuir isotherm can be approved to be more suitable for the dye adsorption process by activated langsat shell.

3.4. FTIR Analysis

FT-IR (Fourier Transform Infrared) 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 absorption of dyes that are influenced by the number of functional groups, types of functional groups, interaction processes, chemical structures and affinity for biosorbents (Bhernama, 2017). The infrared spectrum obtained is then plotted as the intensity of the energy function, wavelength (μm) 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:

Fig 5. Isoterm Langmuir

Fig 6. Isoterm Freundlich

Langmuir isotherm model contained in the graph obtained R2 value of 0.918. y= 0.080x + 2.099. Based on the images obtained from each isotherm equation, the Langmuir isotherm can be approved to be more suitable for the dye adsorption process by activated langsat shell.

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 HNO3 contained the -NO2 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 3292.21 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 -NO2 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}.

The active spectrum is contacted with rhodamine B dye solution, absorption of the visible wave number is 3350.83 cm^{-1} which is an O-H vibration. Absorption at wave number 1637.17 cm^{-1} shows vibrations of C = O. The peak shift indicates the interaction between rhodamine B dye
ions and the biosorbent surface. interaction can not only be seen at the peak shift, but also seen from the intensity of each peak (Chaidir, et al., 2015).

4. CONCLUSION
The optimal absorption conditions in the langsat shell occur at pH 5 with a size of 150 μm and an absorption capacity of 2.1531 mg/g. The maximum absorption capacity obtained from the absorption of rhodamine B dyes using langsat shell activated as biosorbents is equal to 2.099 mg/g with a value of R² = 0.918 using the isotherm Langmuir.

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