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Isolation and characterization of Humic Acid from organic waste as an adsorbent for Rhodamine B

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ABSTRACT

Humic acid compounds are organic materials distributed across various terrestrial and aquatic ecosystems, playing a crucial role in environmental pollutant absorption. This study aims to isolate and characterize humic acid from organic waste as an adsorbent for rhodamine B. The isolation process of humic acid was conducted using the extraction method with 0.5 N NaOH solution followed by acidification using 3 M HCl solution. Characterization was carried out using a UV-Vis spectrophotometer and Fourier Transform Infrared (FTIR) spectrophotometer. The UV-Vis characterization results showed that the maximum wavelength of humic acid is 286 nm. FTIR analysis of humic acid indicates the presence of functional groups such as hydroxyl, carboxylate, and aromatic groups, consistent with the typical characteristics of humic acid. The adsorption kinetics was determined by interacting rhodamine B with humic acid after determining the optimal pH of 4, optimal time of 30 minutes, and optimal concentration of 20 ppm. The research results indicate that the adsorption kinetics of rhodamine B on humic acid follows pseudo-second-order kinetics with a reaction rate of 0.0566 min^{-1} and follows the Freundlich adsorption isotherm.

Keywords:
Adsorption; Rhodamine B; Humic Acid.

Introduction

The availability of clean water is crucial for the survival of all living beings, including humans. However, the amount of clean water is declining due to the contamination of surface water and groundwater. Rhodamine B dye is a significant contributor to water pollution. Rh-B is widely used in leather, plastics, textiles, paper, dyeing, and printing industries. Rh-B is neurotoxic and carcinogenic and can cause respiratory disorders, gastrointestinal irritation, liver damage, and thyroid dysfunction, thus posing a threat to human survival on Earth (Mousavi et al., 2023). Even at concentrations as low as ≤1 mg/L, it can cause eye irritation (Ajiboye et al., 2021). The Maximum Allowable Concentration - Quality Standard (MAC-QS) sets the maximum permissible concentration of Rh-B in water to prevent acute toxic effects on aquatic organisms at 140 µg/L. Meanwhile, the Annual Average - Quality Standard (AA-QS) establishes a limit of 14 µg/L for Rh-B in water over a specific period to prevent chronic toxic effects. These standards protect aquatic ecosystems from short-term and long-term Rh-B exposure (Oladoye et al., 2024).

Therefore, removing Rh-B from contaminated water is critical before the water is returned to the environment. Various physical and chemical approaches have been employed to address Rh-B pollution, such as adsorption, chemical oxidation, electrochemical oxidation, and photocatalytic oxidation (Postai et al., 2016). Most dyes resist to photodegradation, biodegradation, and oxidative agents (Oyekanmi et al., 2019). Hence, adsorption is considered one of the most efficient and economical methods for removing dyes from wastewater. Moreover, adsorption has proven effective when applied in the liquid phase (Postai et al., 2016). The adsorption process requires adsorbent materials to capture dye pollutants.

Humic acid is a natural organic material widely distributed in soils and aquatic environments (Chen et al., 2017). It forms through the degradation of lignin, carbohydrates, and proteins (Doulia et al., 2009). Humic acid exhibits high reactivity in interacting with organic and inorganic contaminants (Machado et al., 2020). This high reactivity is attributed to reactive functional groups such as carboxylate, phenol, carbonyl, and hydroxyl (Maimunawaro et al., 2021). These functional groups act as electron-pair donors in binding cationic dye molecules (Noorhidayah et al., 2021). Therefore, this study aims to investigate the adsorption characteristics of humic acid on Rhodamine B. The initial steps involve isolating and characterizing humic acid from cattle feed compost. Subsequently, the effects of pH, time, and adsorption capacity of humic acid on Rhodamine B are identified.

Methods

Materials

The materials used in this study consisted of compost soil from grass obtained from natural cattle farms in Lamongan, East Java; chemicals produced by Merck with analytical-grade purity, namely sodium hydroxide, hydrochloric acid, and hydrofluoric acid; rhodamine B; and distilled water.

Equipment

The equipment used in this study included glassware, spatula, magnetic stirrer, 80-mesh sieve, blender, oven, analytical balance, porcelain crucible, pestle and mortar, centrifuge; characterization tools UV-Visible spectrophotometer (Thermo Scientific Orion Aquamate 8000) and Fourier Transform Infrared (FTIR) spectrometer (Bruker Alpha II).

Procedures

Extraction and Purification of Humic Acid

The process begins by drying compost soil samples at 40°C for 36 hours. The samples are then cooled, ground, and sieved to achieve a particle size of 80 mesh. Next, 100 grams of the sample are placed in a 1-liter beaker, mixed with 0.5 N NaOH, and stirred at 50 rpm for 24 hours. The mixture is then filtered with Whatman No. 40 filter paper and acidified with 3M HCl until the pH approaches 2. The resulting precipitate is separated via centrifugation at 3500 rpm for 20 minutes, yielding crude humic acid. This crude humic acid is then purified using 6 M HCl until the pH reaches approximately 1, and the humic acid precipitate is separated through centrifugation. The resulting precipitate is mixed with 0.1 N HCl and 0.3 N HF in a beaker at a volume ratio of 3:2, then stirred for 24 hours. The resulting product is washed with deionized water until reaching a constant pH. Finally, the purified samples are dried in an oven at 70°C for 8 hours. The samples are characterized using FTIR and UV-Vis.

Determination of Rhodamine B Maximum Wavelength

Test samples with a concentration of 20 ppm and blanks using deionized water are prepared for the rhodamine B adsorption process. The absorbance of these samples is measured using a UV-Vis spectrophotometer in the wavelength range of 500-600 nm.

Determination of Optimal pH for Dye Adsorption on Humic Acid

Pure humic acid is weighed at 20 mg and dissolved in 20 mL of rhodamine B solution with a concentration of 20 ppm. This is done at varying pH levels of the rhodamine B solution, namely pH 1, 2, 3, 4, 5, and 6. The mixture is stirred with a magnetic stirrer at 450 rpm for 20 minutes. Subsequently, it is filtered, and the filtrate is analyzed with UV-Vis.

Determination of Optimal Adsorption Time for Dye on Humic Acid

20 mg of humic acid is added to 20 mL of rhodamine B solution with a concentration of 20 ppm. It is then stirred with a magnetic stirrer at 450 rpm for various contact times of 5, 10, 20, 30, 50, and 75 minutes. Afterward, it is filtered, and the filtrate is analyzed with UV-Vis.

Determination of Optimal Concentration for Dye Adsorption on Humic Acid

Humic acid as the adsorbent is added at 20 mg to 20 mL of rhodamine B solution with varying initial concentrations of 5, 10, 20, 30, 50, and 75 mg/L, where the solution pH is adjusted to the optimum pH. It is then stirred with a magnetic stirrer at 450 rpm for 20 minutes. After filtration, the filtrate is analyzed with UV-Vis. Percentage of rhodamine B adsorbed can be calculated using the formula provided in Equation 1 (Safrianti et al., 2012):

$$\%\,Adsorption = \left(\frac{[C_o - C_e]}{W \times V}\right) \times 100\% \qquad (1)$$

where Co is the initial concentration of Rhodamine B (mg/L), Ce is the final concentration of Rhodamine B (mg/L), W is the mass of adsorbent humic acid (g), and V is volume of Rhodamine B solution (L).

Results and Discussions

FTIR Characterization Result of Humic Acid

The characterization results of humic acid after purification showed sharper absorption compared to before purification (Figure1). At the absorption of 3368 cm^{-1}, O-H bond vibrations were observed, indicating the presence of hydroxyl groups. The absorption peak of purified humic acid exhibited symmetric and asymmetric stretching of C-H bonds at a wavenumber of 2921 cm^{-1}. Meanwhile, the symmetric and asymmetric stretching of C-H bonds in humic acid before purification appeared at a higher wavenumber, 2924 cm^{-1}, suggesting interactions between impurities and the C-H groups that shortened the bonds (Natsir & Shimazu, 2020).

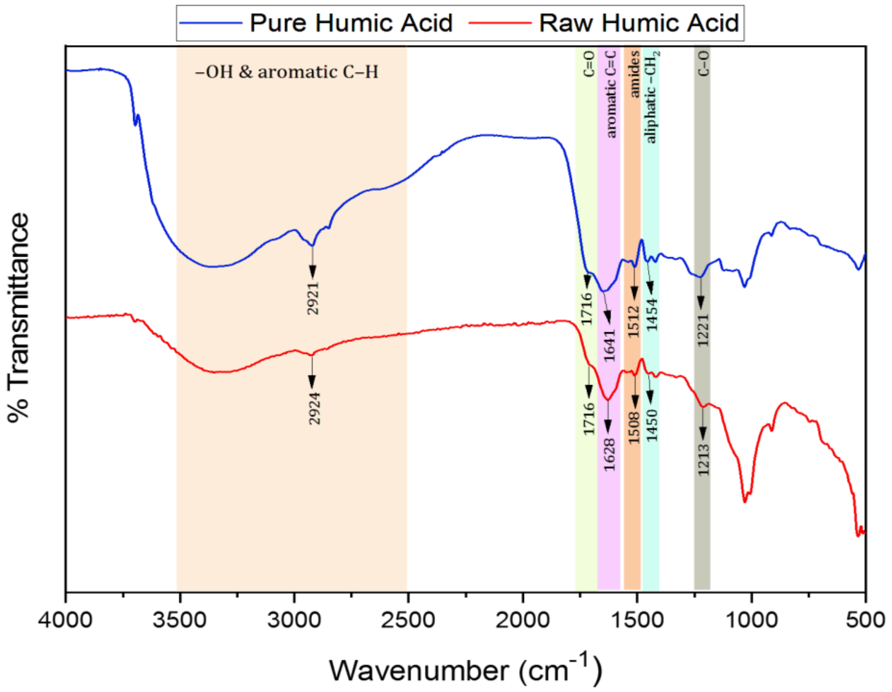

Figure 1. FTIR Spectrum of Humic Acid from Compost Before and After Purification

The presence of carbonyl groups from the C=O stretching of COOH showed no difference in absorption peaks before and after purification, both detectable at 1716 cm^{-1}. The aromatic C=C group conjugated with C=O or COO^- in humic acid after purification was observed at a wavenumber of 1641 cm^{-1}, while for humic acid before purification, it was found at 1628 cm^{-1}. Furthermore, at 1512 cm^{-1}, there was an amide group vibration in humic acid after purification, whereas for humic acid before purification, it occurred at 1508 cm^{-1}. This shift to a lower wavenumber could indicate the presence of impurities binding to the amide group, resulting in bond elongation.

The aliphatic -CH_2 stretching in humic acid before and after purification was observed at wavenumbers of 1450 cm^{-1} and 1454 cm^{-1}, respectively. The difference in absorption was caused by the interaction of impurities with humic acid before purification, which altered the bond length of the aliphatic -CH_2. The C-O stretching of humic acid before and after purification was observed at wavenumbers of 1221 cm^{-1} and 1213 cm^{-1}, respectively. It indicates the presence of aryl ether or phenol groups. The differences in absorption were due to impurities interacting with humic acid before purification, causing changes in the bond length of the C-O group.

UV-Vis Characterization Result of Humic Acid

Characterization of UV-Vis spectra is used to determine the maximum wavelength characterized by the highest absorbance. UV-Vis spectrum analysis of humic acid is performed by examining the interaction of electrons with UV-Vis light (Pavia et al., 2009). Figure 2 shows the results of testing humic acid samples in the 200-700 nm wavelength range. The results show that the maximum wavelength of humic acid originating from compost is 286 nm.

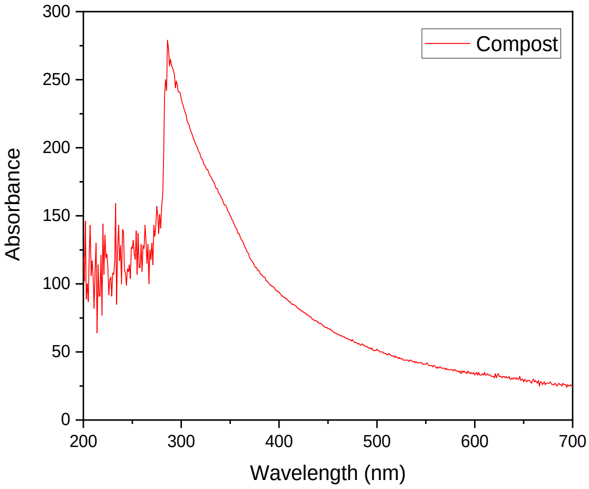

Figure 2. The UV-Vis spectrum of Humic Acid

Specific wavelengths can be used to identify functional groups in organic compounds due to the presence of chromophores that cause electron transitions in specific orbitals (Pavia et al., 2009b). Peaks observed at wavelengths around 205 nm indicate electronic transitions from n to π^* orbitals, suggesting the presence of groups such as R-COOH and R-COOR' in the structure of humic acid. Additionally, absorption at the maximum wavelength of 286 nm indicates the possibility of R-CHO and R-CO-R bonds as electron transitions occur from n to π^* orbitals triggered by the chromophore (Uyguner & Bekbolet, 2005). These results are consistent with the functional groups present in the structure of humic acid in Figure 2. However, other groups such as R-OH and R-O-R are not observed because electron transitions at wavelengths less than 200 nm, thus, cannot be observed in this study.

pH Test Results

One of the factors influencing an adsorbent's adsorption process is the solution's pH. This factor affects the binding process of the dye to the adsorption sites and the ionization process of Rhodamine B dye. The initial adsorption process of Rhodamine B was carried out to determine the optimal pH, with pH variations ranging from 1, 2, 3, 4, 5, to 6. Adsorption was conducted at room temperature with an initial adsorbate concentration of 20 ppm and an adsorbent mass of 20 mg.

As shown in Figure 3, the adsorption of Rhodamine B increased from pH 1 to pH 4. At pH 4, adsorption reached its optimum point with an adsorption capacity of 19.78 mg/L, followed by a decrease at pH > 4. The low adsorption of Rhodamine B at pH < 4 was due to excess H^+ ions competing with the cations of the dye. Significant adsorption of Rhodamine B occurred at pH 4 because Rhodamine B exists in a cationic form at this pH, allowing it to bind with hydroxyl or carbonyl groups. The adsorption capacity reached 19.78 mg/g with an efficiency of 98.93%.

At pH levels above 4, the zwitterionic form of Rhodamine B predominates and tends to aggregate in water due to electrostatic interactions between the carboxylate and xanthene groups of the monomer. Zwitterionic Rhodamine B molecules aggregate to form larger molecular structures (dimers), which hinder the adsorption of dye molecules (Wang et al., 2017).

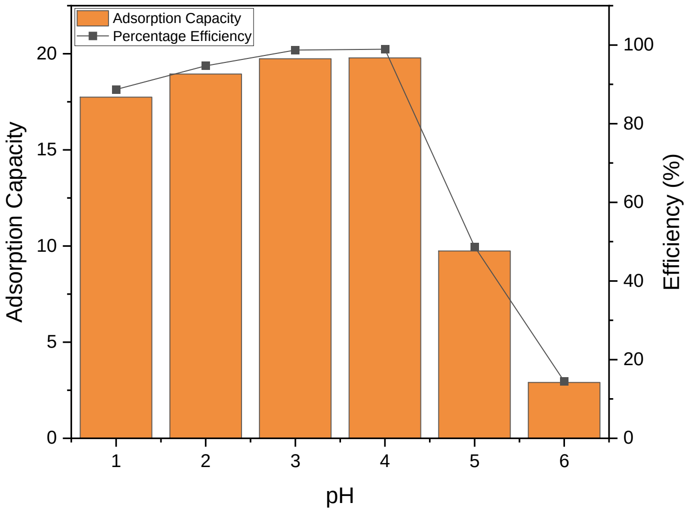

Figure 3. Graph of pH variation against adsorption capacity and percentage efficiency

Contact Time Test Results

This study aims to determine the optimal time for the adsorption process of humic acid with rhodamine B. The faster an adsorbent can adsorb, the better it performs. The optimal time is determined after knowing the optimal pH. This is because pH can influence other test parameters. pH can affect the structure of the adsorbent, thereby affecting the activity of adsorption sites on the adsorbent surface. pH affects the surface charge of the adsorbent. This surface charge influences the electrostatic attraction between the adsorbent and the adsorbate. Additionally, the pH of the solution affects the solubility of the adsorbate. Adsorbates that become ions will affect the electrostatic interactions between the adsorbent and the adsorbate (Oyetade et al., 2018).

The variation of time used in this study ranged from 5, 10, 20, 30, 50, to 75 minutes. In Figure 4, the effect of contact time on the adsorption of rhodamine B dye can be observed. The absorption of rhodamine B increases from a contact time of 5 minutes to 30 minutes. This is because there are still active surfaces on the adsorbent that have not adsorbed. However, with a contact time exceeding 30 minutes, the adsorption capacity reaches a maximum condition because all active adsorbent sites have been fully occupied, thus no longer able to react with the dye. The adsorption capacity reached at 30 minutes is 19.16 mg/g with an efficiency of 95.82%.

This is related to the equilibrium phenomenon. Therefore, the optimum adsorption time for rhodamine B dye by humic acid is at a contact time of 30 minutes.

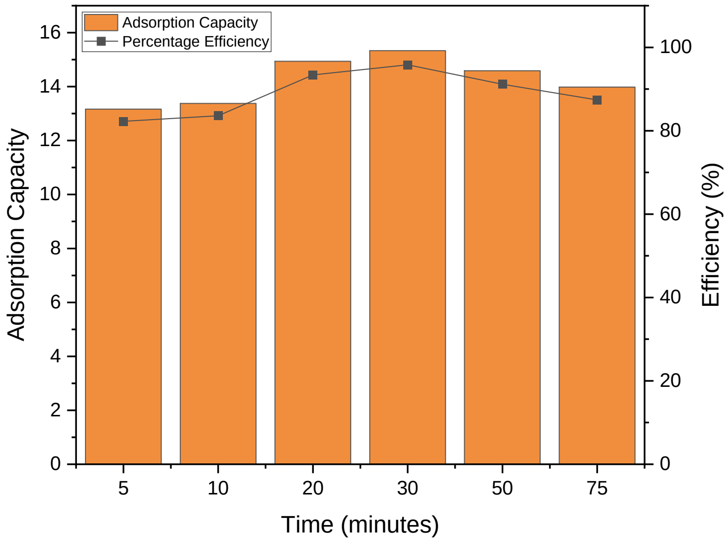

Figure 4. Graph of time variation against adsorption capacity and percentage efficiency

Rhodamine B Adsorption Kinetics

Determining the rate constants is crucial in understanding adsorption kinetics. In this study, the rate constants for the adsorption of humic acid on rhodamine B was calculated using first-order (Figure 5) and second-order kinetics (Figure 6). The results from the first-order kinetics showed an R^2 value of 0.0774, while the second-order kinetics resulted in an R^2 value of 0.9976. Determining the rate constants for the adsorption process of humic acid on rhodamine B indicates that the adsorption process follows second-order kinetics. This suggests that adsorption is not only influenced by the properties of the adsorbent but also by the properties of the rhodamine B ion, indicating that this adsorption process exhibits chemical characteristics.

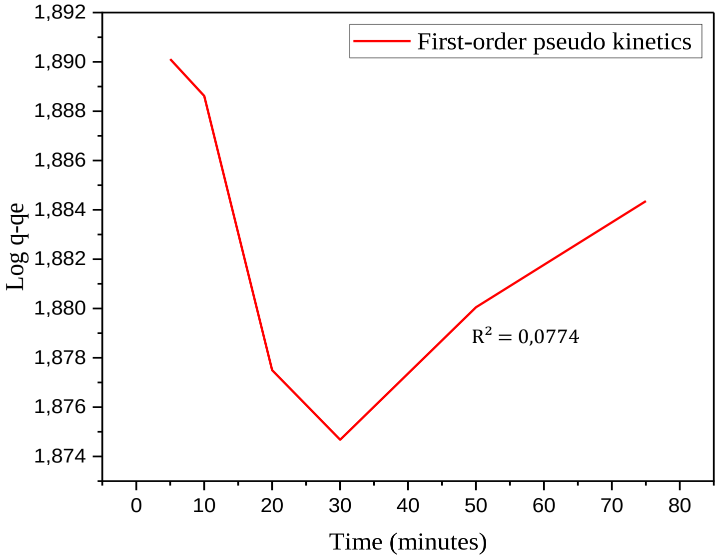

Figure 5. First-order pseudo kinetics curve

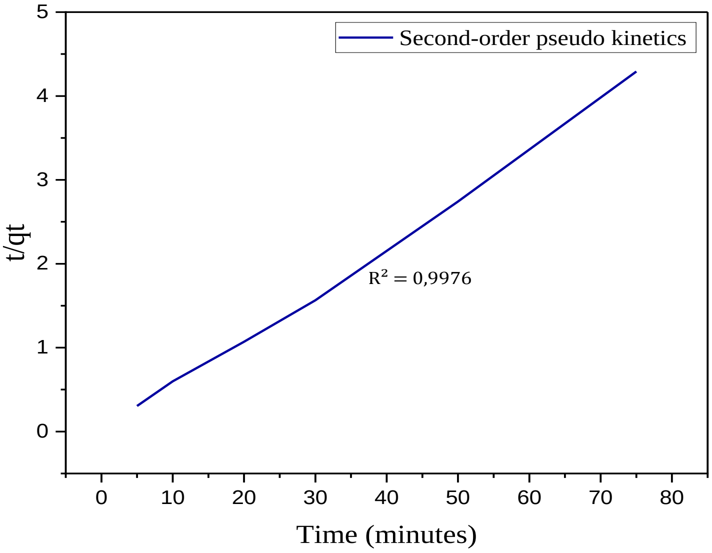

Figure 6. Second-order pseudo kinetics curve

Test Results of Concentration Variance

The variations of rhodamine B used were 5 ppm, 10 ppm, 20 ppm, 30 ppm, 50 ppm, and 75 ppm. To understand the influence of concentration on the adsorption capacity of rhodamine B, 20 mg of adsorbent mass was used, with the optimal pH set at 4 and the best contact time being 30 minutes (Figure 7). Based on the data from the graph (Figure 8) regarding concentration variation and adsorption capacity, it can be observed that the optimal point of rhodamine B absorption by the adsorbent occurs at a concentration of 20 ppm, where the adsorption capacity reaches 19.56 mg/g with an efficiency of 97.82%. In the concentration range from 5 ppm to 20 ppm, there is a significant increase in the adsorbent's ability to absorb rhodamine B. However, after reaching this optimal point, there is a decrease in the absorption capacity.

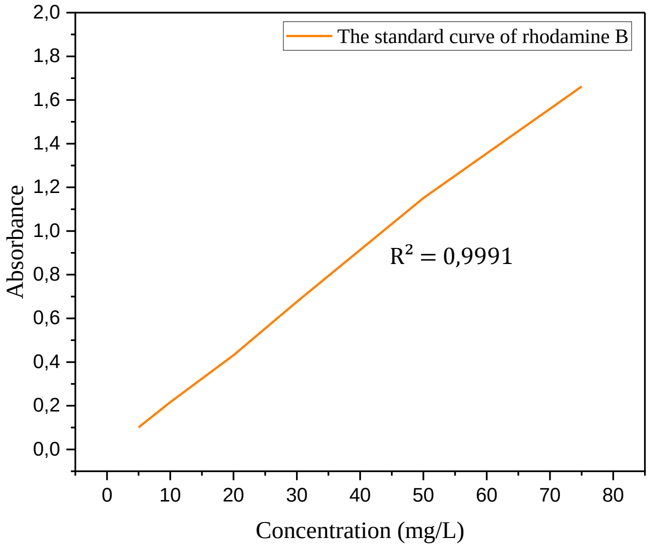

Figure 7. The standard curve of rhodamine B.

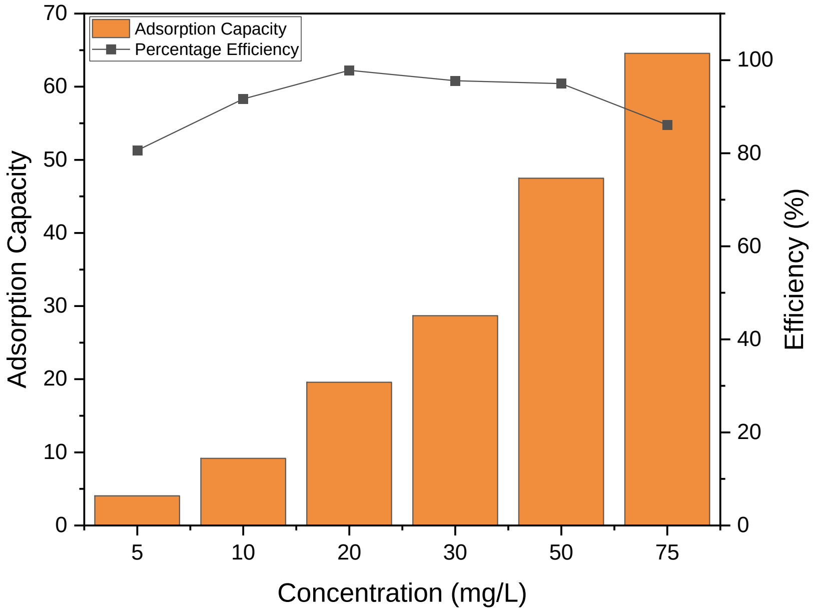

Figure 8. Graph of concentration variation against adsorption capacity and percentage efficiency

The higher the dye concentration in the solution, the more dye molecules are available to interact with the adsorbent. It can increase the amount of dye that a specific mass of adsorbent can adsorb until saturation is reached. The adsorbent will reach saturation as the active adsorption sites become filled with dye molecules. With increasing concentration, the time required to reach saturation may be faster (Rohmatullaili, 2020).

Although the amount of rhodamine B continues to increase, its effect on absorption efficiency is limited by the maximum adsorption capacity reached. Therefore, even though the concentration of rhodamine B is increased, the absorption efficiency does not increase proportionally. It illustrates how the interaction between the amount of rhodamine B and the adsorbent's adsorption capacity can reach saturation, where increasing concentration no longer positively impacts absorption efficiency.

Adsorption Isotherm

The commonly used adsorption isotherms are the Langmuir (Figure 9) and Freundlich (Figure 10) isotherms. Analysis of adsorption isotherms is typically conducted through a common approach of plotting graphs on the x-axis and y-axis to obtain linear regression equations that can assist in determining the most suitable isotherm model. Determination of the isotherm model involves comparing the correlation coefficients (R^2).

The Langmuir adsorption isotherm describes the adsorption process involving the formation of a single layer on the surface of the adsorbent. Meanwhile, the Freundlich isotherm allows for forming more than one surface layer. The results from the curve fitting of the adsorption isotherm equations for rhodamin B yielded a Langmuir isotherm equation with R^2=0.0529 and a Freundlich isotherm equation with R^2=0.3437. These results indicate that both isotherms demonstrate adsorption interactions, either chemically or physically. However, the tendency leans towards the Freundlich isotherm model due to its higher R^2 value than the Langmuir isotherm. It suggests that the adsorbate particles approach the adsorbent surface through van der Waals forces or hydrogen bonding (Fajar, 2019).

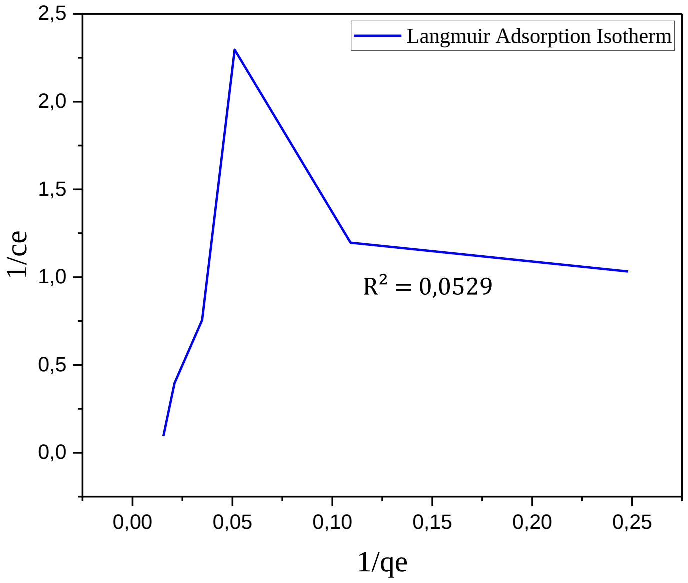

Figure 9. Langmuir Adsorption Isotherm Graph

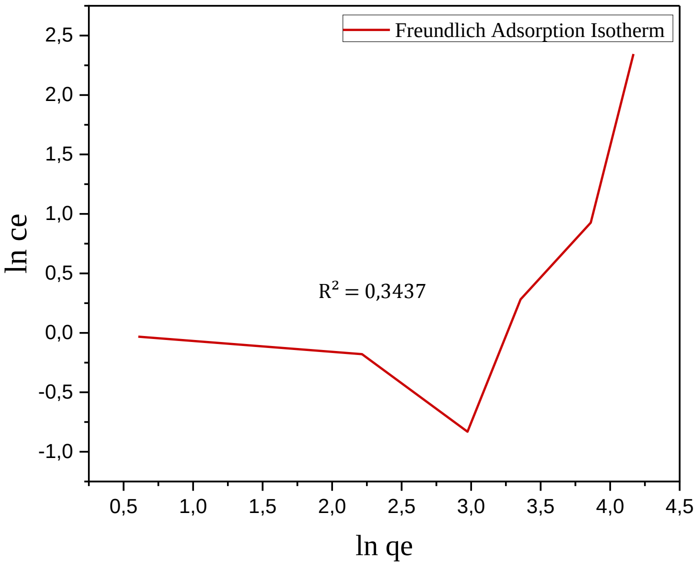

Figure 10. Freundlich Adsorption Isotherm Graph

Conclusion

FTIR characterization results indicate that pure humic acid from compost contains -OH and -COOH groups. Meanwhile, the UV-Vis characterization results show that the maximum wavelength of humic acid from compost is 286 nm. The optimal pH for rhodamine B adsorption using humic acid was pH 4, with an adsorption capacity of 19.78 mg/g. Subsequently, the optimal adsorption time was determined to be 30 minutes, with an adsorption capacity of 19.16 mg/g. Lastly, the optimal concentration for rhodamine B adsorption was 20 ppm, with an adsorption capacity of 19.56 mg/g. The kinetic analysis of rhodamine B adsorption with humic acid as the adsorbent indicates that the adsorption process follows second-order kinetics and obeys the Freundlich adsorption isotherm.

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Conflicts of interest

The authors declare that there are no conflicts of interest.

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