INTRODUCTION

The textile industry is a crucial part of the global economy, providing employment opportunities and contributing to the socio-economic balance (Adane et al., 2021). However, it faces significant environmental challenges that cast doubt on its sustainability. To address these issues and ensure long-term viability, it’s necessary to integrate environmental, economic, and social considerations and develop a sustainable strategy. This requires meeting environmental requirements, as the industry consumes vast amounts of water and generates wastewater with high levels of pollutants, including unfixxed dyes (Periyasamy, 2024). Worldwide, the manufacturing and coloring of fabrics release around 140,000 tonnes of toxic substances annually, most of which evade conventional wastewater treatments (Guezzen et al., 2020).

Synthetic dyes are in most cases carcinogenic and toxic, causing serious harm to human health (Alsukaibi, 2022; Dutta et al., 2024). The discharge of effluents stemming from dyeing processes is frequently channeled into proximal...
water bodies, encompassing agricultural fields, irrigation conduits, and other exterior aquatic reservoirs, subsequently infiltrating larger aqueous expanses such as rivers and seas (Yerima et al., 2024). Industrial effluent release from textile and dye sectors induces alterations in the physical, chemical, and biological attributes of aquatic milieus, instigating perturbations in turbidity, olfactory qualities, temperature gradients, and pH levels (Islam, Mostafa, 2018; Sudiana et al., 2022). These transformations impact community well-being, livestock welfare, wildlife populations, piscine communities, and overall biodiversity indices. The presence of dye residues within surface aquatic domains renders them aesthetically displeasing and serves as a fomite for myriad waterborne ailments (Rao and Rao, 2006; Chhandama et al., 2024). The pollution of aquatic ecosystems poses a substantial menace to public health and exerts deleterious ramifications on the overarching epidemiological and socio-economic fabric.

Rhodamine B (RhB) is one of the synthetic dyes commonly employed across diverse industries, including textiles (Al-Gheethi et al., 2022; Nyakairu et al., 2024). However, its toxicity has raised significant concerns regarding its environmental impact (Shah et al., 2024). Effluents containing RhB can pose aesthetic concerns and may have adverse effects on the environment (Nguyen et al., 2023; Umejuru et al., 2024). Research has shown that RhB can induce toxicity in aquatic organisms, particularly at concentrations exceeding 1 mg/L (Skjolding et al., 2021). To address this issue, various techniques for removing this cationic dye have been proposed and implemented (Peng et al., 2024; Vosough et al., 2024), with adsorption being one prominent method. This approach has been cited in numerous recent studies as a cost-effective, industrially feasible, promising, and efficient means of combating a spectrum of pollutants (Ghibate, Ben Baaziz, Taouil, et al., 2024); Kerrou et al., 2021), inclusive of RhB dye. In recent decades, several investigations have regarded agricultural waste as a viable source of low-cost adsorbents (Bettayeb et al., 2024; Sanad et al., 2024).

Additionally, research has demonstrated that pomegranate fruit and its extracts exhibit preventive and ameliorative properties against numerous disorders and chronic ailments (Doostkam et al., 2020; Moradnia et al., 2024). Owing to its indisputable benefits, there has been a substantial surge in demand for the fruit and its derivative products worldwide. Consequently, global production has escalated to fulfill consumer requirements, leading to a noteworthy upsurge in peel generation globally. It has been estimated that approximately 1.9 million tonnes of pomegranate peel were produced worldwide in 2017 (Ghibate et al., 2020). Thus, there arises a pressing need for its valorization. Furthermore, it is imperative to underscore that this biomass harbors significant quantities of tannins. The abundance of these phenolic compounds, characterized by hydroxyl groups, facilitates the formation of complexes with various chemical species, particularly dyes.

These considerations have prompted the exploration of a pertinent approach to ensure the sustainability of this industry, employing adsorption with pomegranate peel. This endeavor aims to serve dual ecological purposes: the valorization of agricultural waste and the remediation of effluents laden with RhB.

**MATERIALS AND METHODS**

**Rhodamine B dye**

The Rhodamine B (RhB) compound, supplied by Alfa Aesar with a purity of 98% and a molecular formula of C_{28}H_{31}ClN_{2}O_{3}, was used as received to prepare a stock solution. This stock solution (1000 mg/L) was diluted to the desired concentration for the adsorption experiments. Figure 1 depicts the chemical structure of RhB dye.

**Pomegranate peel**

**Powder preparation**

After being separated from the pomegranate, the peel undergoes a washing procedure with distilled water, followed by three weeks of exposure to sunlight for drying. The fragments are then crushed into a powder and subjected to several washes with distilled water until they achieve a solution devoid of coloration (Bettayeb et al., 2024; Sanad et al., 2024).

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**Adsorbent characterization**

The chemical characterization of pomegranate peel was conducted using a Bruker Alpha II Fourier Transform Infrared spectrometer, in conjunction with a diamond crystal attenuated total
Batch adsorption

The experimental procedure involved the removal of RhB at its initial pH through batch adsorption. The suspension, consisting of 0.2 g of powdered pomegranate peel and 100 mL of the dye solution, was maintained under magnetic agitation at 300 rpm. The adsorption kinetic experiments were carried out over reaction times ranging from 5 to 300 minutes at 25 °C and a RhB concentration of 50 mg/L. To conduct the isotherm study, 0.2 g of pomegranate peel was immersed in 100 mL of RhB solutions with initial concentrations ranging from 50 to 650 mg/L. These suspensions were agitated for 120 minutes at 25 °C. After the experiments, the separation of the suspensions was ensured using 5 minutes of centrifugation at 3800 rpm. The residual concentrations of the supernatants were analyzed using a double-beam UV-Vis spectrophotometer at 554 nm, a characteristic wavelength of RhB dye. The quantity adsorbed per unit mass of adsorbent at time t \( (q_t) \) can be determined using the following Equation:

\[
q_t = \frac{(C_0 - C_\ell)}{m_{ads}} \cdot V_{RhB}
\]

where: \( C_0 \) – initial RhB concentration (mg/L), \( C_\ell \) – residual RhB concentration after time t of adsorption (mg/L), \( V_{RhB} \) – volume of RhB solution (L), \( m_{ads} \) – mass of adsorbent (g).

Kinetic study

The RhB adsorption kinetics data were analyzed using pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Below are the linear expressions of each model in the order mentioned in the text.

\[
\ln(q_e - q_t) = \ln q_e - K_1t \quad (2)
\]

\[
\frac{1}{q_t} = \frac{1}{K_2q_e^2} + \frac{1}{q_e} \quad (3)
\]

\[
q_t = K_{id}t^{1/2} + c \quad (4)
\]

where: \( q_e \) and \( q_t \) – amounts of RhB adsorbed per gram of adsorbent at time t and at equilibrium, respectively (mg/g), t – contact time (min), \( K_1 \) – rate constant of the pseudo-first-order model (min\(^{-1}\)), \( K_2 \) – rate constant of the pseudo-second-order model (g/mg min), \( K_{id} \) – intraparticle diffusion rate constant (mg/g·min\(^{1/2}\)), c – boundary layer thickness constant.

Isotherm study

The adsorption isotherm was studied using Langmuir and Freundlich models. The Langmuir isotherm model assumes structural homogeneity among all adsorption sites on the adsorbent, with adsorption limited to a monolayer. It also suggests that molecules adsorbed on adjacent sites do not interact. Consequently, further adsorption ceases at equilibrium, indicating a finite adsorption capacity. The Langmuir isotherm can be expressed as follows:

\[
q_e = \frac{q_{max}K_LC_e}{1+K_LC_e} \quad (5)
\]
The subsequent equation provides the linearized form of the Langmuir model:

\[
\frac{c_e}{q_e} = \frac{1}{K_L q_{\text{max}}} + \frac{c_e}{q_{\text{max}}}
\]

(6)

where: \( q_{\text{max}} \) – adsorption capacity at its maximum (mg/g), \( K_L \) – Langmuir constant (L/mg).

The Freundlich isotherm is applied to multilayer adsorption scenarios, considering non-uniform distributions of adsorption heat and affinities across heterogeneous surfaces. The Freundlich isotherm has the following mathematical expression:

\[
q_e = K_F c_e^{1/n}
\]

(7)

The linearized expression for the Freundlich model is as follows:

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln c_e
\]

(8)

where: \( K_F \) – Freundlich coefficient linked to the adsorption capacity (mg/g)(L/g)\(^n\), \( n \) – Freundlich’s affinity coefficient (n).

**Models error analysis**

Error functions provide a robust way of assessing a model’s suitability and underlying assumptions. Four statistical metrics were utilized (Eq. 9–Eq. 12): \( R^2 \) (coefficient of determination), \( \text{ARE} \) (average relative error), \( \text{RMSE} \) (root mean square error), and \( \chi^2 \) (chi-square). A preferred model should demonstrate a coefficient of determination nearing unity while minimizing the values of ARE, RMSE, and \( \chi^2 \) for enhanced accuracy and reliability.

\[
R^2 = \frac{\sum_{i=1}^{N}[(q_{\text{cal}}-q_{\text{exp}})^2]}{\sqrt{\sum_{i=1}^{N}[(q_{\text{cal}}-q_{\text{exp}})^2]_i} + \sum_{i=1}^{N}[(q_{\text{cal}}-q_{\text{exp}})^2]_i}
\]

(9)

\[
\text{ARE} = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{q_{\text{exp}}-q_{\text{cal}}}{q_{\text{exp}}} \right|
\]

(10)

\[
\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{N}[(q_{\text{cal}}-q_{\text{exp}})^2]}{N}}
\]

(11)

\[
\chi^2 = \sum_{i=1}^{N} \left[ \frac{(q_{\text{exp}}-q_{\text{cal}})^2}{q_{\text{cal}}} \right]_i
\]

(12)

where: \( q_{\text{exp}} \) – experimental adsorbed amount (mg/g), \( q_{\text{cal}} \) – model-predicted adsorbed amount (mg/g), \( N \) – number of data points acquired through experimentation.

**RESULTS AND DISCUSSION**

**Adsorbent characterization**

Figure 2 illustrates the infrared spectrum of pomegranate peel powder. The analysis of this spectrum depicted that the studied adsorbent possesses many oxygenated groups, including hydroxyl, carbonyl, and carboxyl. These groups facilitate the adsorption process by enabling interactions with RhB dye via hydrogen bonding, electrostatic attractions, and van der Waals forces. The frequencies corresponding to various functional groups of this biomass are displayed in Table 1.

The SEM images in Figure 3 depict pomegranate peel powder at various scales. As evident from these figures, the adsorbent surface exhibits
heterogeneity. A heterogeneous surface provides more available active sites, which are conducive to the adsorption process. Furthermore, the pomegranate peel surface showcases hollow cavities and a porous structure (Figure 3b), both of which are significant in facilitating RhB adsorption.

**Parameters effects**

**Effect of adsorption time**

The RhB/pomegranate peel contact time can help ascertain the optimum time for adsorbing the dye. Additionally, the time of contact is an essential factor that governs the reaction process’s kinetics and influences the adsorption’s economic efficiency. As depicted in Figure 4, the quantity of RhB adsorbed initially experiences rapid growth attributable to the availability of unoccupied active sites of adsorption. Subsequently, the adsorption process decelerates due to a reduction in active adsorption sites until equilibrium is attained at 120 min. This aligns with data published by other authors (Chrachmy et al., 2024; Kooh et al., 2016). Furthermore, the equilibrium adsorption capacity for an initial RhB concentration of 50 mg/L equaled 19.41 mg/g.

**Effect of initial dye concentration**

The behavior of the pomegranate peel towards RhB was examined by varying its initial concentration from 50 to 650 mg/L (Figure 5). The results demonstrate that elevating the initial RhB concentration from 50 to 650 mg/L leads to a rise in adsorption capacity from 19.41 to 44.28 mg/g. Specifically, a higher RhB concentration induces a greater entrainment force attributed to the concentration gradient. Consequently, this facilitates the diffusion of RhB molecules at the interface of the pomegranate peel. Ding et al., 2014, demonstrate a
similar behavior in their study for RhB adsorption using activated carbon derived from rice husk.

**Kinetic modeling**

Table 2 presents the kinetic parameters and statistical metrics for the pseudo-first-order and pseudo-second-order models. Upon reviewing Figure 6 and Table 2, it can be inferred that the pseudo-second-order model is the most appropriate for describing the adsorption of RhB onto pomegranate peel. Notably, this model has the lowest values of ARE, RMSE, and $\chi^2$, as well as the closest coefficient of determination to one.

Figure 6c depicts the amount of RhB adsorbed over time, represented by the square root of time. The plot exhibits multilinearity, suggesting a multi-step adsorption process (Ghibate, Ben Baaiz, Amechrouq, et al., 2024; Ouallal et al., 2024). The initial sharp rise indicates the first step, likely allocated to the diffusion of RhB from the solution to the external surface of the pomegranate peel or boundary layer diffusion. Subsequently, the gradual increase represents the second stage, indicating the adsorption process’s

<table>
<thead>
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<th>Model</th>
<th>Parameters at 25 °C</th>
<th>Statistical metrics</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$q_{e,cal}$ (mg/g)</td>
<td>$K_1$ (min$^{-1}$)</td>
</tr>
<tr>
<td>Pseudo-first-order</td>
<td>7.53</td>
<td>0.0219</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>19.93</td>
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Figure 6. Analysis of RhB adsorption through pseudo-first-order (a), pseudo-second-order (b), and intraparticle diffusion (c) kinetic models
gradual progression. This stage may involve intraparticle diffusion as the limiting factor. Finally, the third stage involves further diffusion of RhB to adsorption sites. This pattern is consistent with findings of an earlier investigation (Ghibate et al., 2021), which also demonstrate similar behaviors in the adsorption of RhB by this biomass at a different concentration. The rate constant for intraparticle diffusion and the boundary layer thickness (estimated based on the slope of the second segment in Figure 6c) are reported in Table 3.

**Isotherm modeling**

The adsorption equilibrium of RhB on the pomegranate peel surface was investigated using Langmuir and Freundlich models at 25 °C (Figure 7). The corresponding parameters were determined and compiled in Table 4 through statistical analysis.

Figure 7 shows the graphical representations of the Langmuir and Freundlich models’ linear fitting. The Langmuir model performed better than the Freundlich model in terms of fitting performance. This is supported by the $R^2$ value closest to one and the values of ARE, RMSE, and $\chi^2$, which are the lowest (Table 4). These results indicate that RhB tends to form a monolayer on the pomegranate peel surface. The validation of the Langmuir model is strengthened by Figure 8. Upon a quick examination of this figure, it becomes evident that the Langmuir model is highly accurate in its predictions. Notably, the Langmuir maximum adsorption capacity (47.17 mg/g) closely aligns with the maximum experimental adsorption capacity (44.28 mg/g).

Furthermore, the dimensionless constant $R_L$ can explain the Langmuir isotherm fundamental characteristics. This parameter is derived from the Langmuir constant ($K_L$) and the initial concentration ($C_0$), as expressed by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (13)$$

The process of adsorption can be classified based on the value of the $R_L$ criteria. When the value of $R_L$ exceeds 1, adsorption is regarded as unfavorable. On the other hand, a value equal to 1 indicates linear adsorption behavior. An $R_L$ value

<table>
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<tr>
<th>Parameter</th>
<th>$K_{id}$,1 (mg/g·min$^{-1/2}$)</th>
<th>$c_1$</th>
<th>$R^2$</th>
<th>$K_{id}$,2 (mg/g·min$^{-1/2}$)</th>
<th>$c_2$</th>
<th>$R^2$</th>
<th>$K_{id}$,3 (mg/g·min$^{-1/2}$)</th>
<th>$c_3$</th>
<th>$R^2$</th>
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<tr>
<td>50 mg/L</td>
<td>1.3484</td>
<td>8.50</td>
<td>0.9790</td>
<td>0.7824</td>
<td>10.75</td>
<td>0.9812</td>
<td>0.0321</td>
<td>18.86</td>
<td>0.9528</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters at 25 °C</th>
<th>Statistical metrics</th>
</tr>
</thead>
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<tr>
<td>Langmuir</td>
<td>$q_{max}$ (mg/g)</td>
<td>$K_L$ (L/g)</td>
</tr>
<tr>
<td></td>
<td>47.17</td>
<td>0.03</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$n$</td>
<td>$K_y$ (mg/g)/(L/g)$^n$</td>
</tr>
<tr>
<td></td>
<td>3.79</td>
<td>9.44</td>
</tr>
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</table>

Figure 7. Modeling RhB adsorption with Langmuir (a) and Freundlich (b) linear isotherm plots
of zero indicates irreversible adsorption. An $R_L$ value ranging between 0 and 1 suggests a favorable adsorption process. It can be observed from Figure 9 that the $R_L$ values range from 0 to 1 for the entire concentration range considered. This indicates the favorability of the RhB adsorption process onto pomegranate peel.

CONCLUSIONS

Using pomegranate peel as an adsorbent for RhB has yielded promising results. The adsorption time and the initial dye concentration significantly influence RhB adsorption onto pomegranate peel. The adsorbent’s chemical characterization elucidates the significant presence of oxygenated groups. These oxygenated groups likely contribute to the adsorption capacity of the pomegranate peel. The morphological characterization sheds light on the adsorbent surface’s heterogeneity, providing more available active sites conducive to the adsorption process. Furthermore, the surface of the pomegranate peel showcases hollow cavities and a porous structure, both of which are significant in facilitating RhB adsorption. Statistical metrics, including $R^2$, ARE, RMSE, and $\chi^2$ were utilized to assess the performance of different kinetic and isotherm models. The kinetic analysis revealed that the pseudo-second-order model outperforms the pseudo-first-order model in describing RhB adsorption. Moreover, it was observed that intra-particle diffusion does not act as the limiting step in the adsorption process. The adsorption process appears to adhere more closely to the Langmuir model, suggesting a monolayer adsorption behavior. This inference is supported by the nearly identical values of the Langmuir maximum adsorption capacity (47.17 mg/g) and the experimental maximum adsorption capacity (44.28 mg/g). Importantly, the study suggests that pomegranate peel waste can be regenerated and reused effectively as an adsorbent for removing dyes from industrial effluents, highlighting its potential for sustainable wastewater treatment solutions.

REFERENCES


undergraduates. Journal of Chemical Education, 101(2), 559–566. https://doi.org/10.1021/acs.jchemed.3c00685


