Separation of Rhodamine B Dye from Aqueous Media Using Natural Pomegranate Peels

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Abstract: Natural pomegranate peels (PPs) ground powder was proved as effective natural biomass for the separation of RhB from different aqueous media by batch adsorption experiments. Several parameters that affect the maximum adsorption capacity toward RhB dye, e.g., the pH solution, initial dye concentration, adsorbent dosage, shaking time, and solution temperature in the sorption behavior, were studied. Adsorption of RhB dye from aqueous media of pH ≈ 5 reached equilibrium in 10 min and was independent of the initial concentration of RhB. RhB dye sorption followed pseudo-second order kinetic with an overall rate constant (k2) of 0.04 g mg⁻¹ min⁻¹. Furthermore, the sorption isotherm was found 31.95 ± 0.02 mg g⁻¹ for the sorption capacity of RhB onto PPs. The thermodynamic parameters (ΔH, ΔS, and ΔG) of RhB retention by the sorbent were calculated. The positive value of ΔH confirms the endothermic behavior of the adsorption of RhB by PPs from aqueous solution. The positive value of entropy (ΔS = 42.17 J mol⁻¹ K⁻¹) of the sorption of RhB onto the sorbent surface may be attributed to the increase in the degree of freedom of the RhB molecules is more restricted in the PPs structure than in solution.

Keywords: adsorption; rhodamine B; natural pomegranate peels; kinetic; thermodynamic

INTRODUCTION

In recent years, water pollution is increasing tremendously, so accessing clean water and safe drinking water is important to protect the ecosystem and the health of its organisms. However, one sixth of the world’s population needs access to pure water that is free of toxic organic and inorganic substances [1-2]. This situation is threatening the whole ecosystem on earth [3-5]. Furthermore, food additives such as food dyes are toxic, stable, and non-biodegradable [6]. Thus, the elimination of these dyes became a real concern because of their difficulties in the treatment processes, such as the treatment of wastewater by chemical and biological conventional methods [7]. These methods include: layer double oxides and hydroxides [8], sonochemical processes [9], coagulation [10], and adsorption [1,11-13]. However, adsorption process proved to be an effective technique for the separation of these dyes from different matrices.

In general, various porous materials are often used to adsorb harmful chemicals and sequentially remove dyes from aqueous environments [14]. There are many examples, including nickel oxide nanoplates [11,15], clays [16], activated carbons [6,17], composites of hydroxyapatite with organic substrates, and graphene oxides [18]. Moreover, non-toxic and completely biodegradable natural fruits, flowers, roots, and leaves are used for removing inorganic dyes and toxic heavy metals [19-20]. The removal of RhB (Table 1), methylene blue, and acidic dye was carried by natural coal, orange peel, and coir pitch [21-22].

Pomegranate peels (PPs) were used as a cheap sorbent for separation of phenols [23], phenolic compounds [24], chromium(VI), nickel, and crude oil
Table 1. Selected properties of RhB dye

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common name</td>
<td>Rhodamine B</td>
</tr>
<tr>
<td>Chemical name</td>
<td>[9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride.</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C_{28}H_{31}ClN_{2}O_{3}</td>
</tr>
<tr>
<td>Maximum wavelength</td>
<td>553 nm</td>
</tr>
<tr>
<td>Appearance</td>
<td>Red to violet powder</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>479.02 g/mol</td>
</tr>
</tbody>
</table>

The goal of this quest is the removal of Rhodamine B, RhB, using natural pomegranate peels (PPs), which is the most widely used in various textile-processing industries. This can be achieved by studying several parameters that affect the maximum adsorption capacity toward RhB dye, such as the pH solution, initial dye concentration, adsorbent dosage, shaking time, and solution temperature in the sorption behavior toward RhB dye. Moreover, the proposed method of adsorption using natural pomegranate peels (PPs) was performed and applied to real environmental samples in order to investigate its capacity for RhB uptake.

EXPERIMENTAL SECTION

Materials

All chemical solutions and organic solvents used were of analytical reagent grade quality. Deionizer distilled water (DDW) was used throughout the experiment. Pomegranate peels (PPs) were used as bio-sorbent purchased from the local store in Jeddah, KSA. An accurate concentration, equal to 0.1 M, of sodium hydroxide from (NaOH) Merkland, Germany, and 0.1 M Hydrochloric acid (HCl) from fisher scientific were used to adjust the pH of the RhB solution. RhB is a positive charge dye, purchased from Merck Millipore Corporation, Germany (% purity of RhB is 95%). The stock solution of 1000 mg L^{-1} RhB (0.1 %w/v) was prepared by dissolving 0.1 g in 100 mL of DDW, then 10 mL of the previous solution was diluted with 100 mL.
DDW to produce 100 mg L\(^{-1}\) RhB stock solution. The standard solutions (0.5–80 mg L\(^{-1}\)) of the RhB stock solution were prepared with DDW.

**Instrumentation**

A Perkin Elmer (Lambda EZ-210) double beam spectrophotometer (190–1100 nm) with 1 cm (path width) quartz cell was used for recording the electronic spectrum of RhB and the absorbance measurements. A Corporation Precision Scientific mechanical shaker (Chicago, CH, USA) in which it’s shaking rate is in the range 10–300 remand a thermostatically controlled shaker (GFL1083 model, Germany) were used in batch extraction experiments of RhB using PPs as sorbent. The sorbent was crushed with high speed cyclone mill (cT 193 cyclotec TM). DDW was gotten from Milli-Q Waters Plus system (Milford, MA, USA). A Thermo Fisher Scientific Orion model 720 pH Meter (Milford, MA, USA) was–in addition–used to prepare the stock and more diluted solutions of RhB and pH measurements, respectively.

**Procedure**

**Preparation of pomegranate peels powder**

The PPs (see Fig. 2) were used as a solid-phase extraction to adsorb RhB dye from water. The PPs were washed thoroughly with running tap water for several times to remove any external dust particles or impurities, then washed with DDW to remove adhering dirt particles from the surface and dried overnight in a static air oven at 80 °C. Once it was completely dry, an electric grinder (ELEKTA-EFBG-1586 model) was used to crush and to grind the PPs into powder. The sorbent powder was sieved through a 53-µm electric sieve (Nicomp Z380-USA). The PPs powder was stored for later uses in the experiments.

**Recommended batch experiments**

The adsorption study performed using 53 µm particle size of the PPs to determine the effect of different parameters for the removal of RhB from aqueous solution. The experimental procedure was obtained by shaking a known weight (0.1 ± 0.001 g) of PPS with 50.0 mL of (5.0 mg/L) RhB solution for 60 min on a mechanical shaker at room temperature.

After shaking, the PPs were filtrated by Whatman No. 5 qualitative filter paper. The filtrates were analyzed using a UV-Vis spectrophotometer at \(\lambda_{\text{max}}\) of 553 nm. The extraction percentage (% E), the uptake of RhB at equilibrium (\(q_e\)) per unit mass of solid sorbent (mg/g), and the distribution ratio (D) of RhB onto the PPs were evaluated using the following equations [32]:

\[
\%E = \frac{A_b - A_a}{A_{fa}} \times 100
\]

\[
q_e = (A_b - A_a) \times \frac{V(L)}{m(g)}
\]

![Fig 2. Dried PPs (a) and PPs powder (53 µm) (b)](image-url)
\[
D = \left( \frac{\%E - \%E}{100} \right) \times \frac{V_{(mL)}}{m_{(g)}}
\]

where; \( V \) represents the volume of the solution (mL), \( A_b \) and \( A_a \) are the absorbance before and after the extraction, respectively. The parameter (m) represents the mass of the sorbent (g). The extraction percentage (%E) and the distribution ratio (D) are the mean of three independent measurements. In addition, the precision in most cases was ± 0.2%.

To study the effect of pH, a series of solutions (50 mL) of 5 mg L⁻¹ of RhB with an accurate weight (0.1 ± 0.001 g) of the PPs were adjusted to different pH values (1–10) in the presence of 0.1 M HCl and 0.1 M NaOH. The standard solutions of RhB were individually mechanically shaken for 60 min using a mechanical shaker at room temperature. The amount of RhB dye adsorbed per gram of the adsorbent at equilibrium (\( q_e, \text{mg g}^{-1} \)) and at pH values can be calculated, as previous from Eq. (2).

To examine the influence of PPs dose on sorption of RhB, series of aqueous solutions (50 mL) containing RhB at 5 mg L⁻¹ level at optimum pH were also shaken for 60 min at room temperature with different weights (0.1 – 0.8 ± 0.001 g) of PPs. After shaking, the percent extraction of RhB that retained onto PPs was then determined from the absorbance at 553 nm before and after extraction using Eq. (1).

To study the effect of contact time on uptake of RhB from aqueous solution using the PPs, an accurate weight of the PPs (0.1 ± 0.001 g) was shaken with 5 mg L⁻¹ of RhB concentration (50 mL) at the optimized pH for various time intervals up to 60 min at room temperature. After shaking, the amount of RhB retained onto PPs was then determined from the absorbance at 553 nm before and after extraction using Eq. (1).

To study the effect of contact time on uptake of RhB from aqueous solution using the PPs, an accurate weight of the PPs (0.1 ± 0.001 g) was shaken with 5 mg L⁻¹ of RhB concentration (50 mL) at the optimized pH for various time intervals up to 60 min at room temperature. After shaking, the amount of RhB retained onto PPs was then determined from the absorbance at 553 nm before and after extraction using Eq. (1).

To study the adsorption capacity of prepared adsorbent PPs under batch conditions, various concentrations (0.5–80 mg L⁻¹) of RhB in 50 mL aqueous solution at optimum parameters were individually mixed with the PPs (0.1 ± 0.001 g) and shaken for 10 min at room temperature. After shaking, the adsorption capacity (\( q_e, \text{mg g}^{-1} \)) was calculated from Eq. (2). The experimental adsorption isotherms data were calculated by classical adsorption isotherms.

**Analytical applications**

The environmental samples of water collected from Jeddah City, KSA, including tap water, drink water, seawater, and well water. The samples of tap water were acquired from the chemistry laboratory at King Fahd Medical Research Center, and the drink water samples were purchased from a local store, seawater sample collected from North beach in Jeddah.

The application was performed by filtrating the given 50 mL of each type of water through 0.45 µm cellulose membrane filter prior to analysis. A concentration of 5 mg L⁻¹ RhB was then introduced to each type of water. The pH was adjusted again to 5 in the presence of an appropriate amount of natural sorbent and then was shaken separately for 10 min. All samples were analyzed using the standard addition method under the same batch conditions as described before, and the RhB dye amount retained was measured as described before.

**RESULTS AND DISCUSSION**

**Retention Profile of RhB Dye onto PPs**

**Effect of different pH of the adsorption of RhB onto PPs**

The most critical parameter that affects the RhB adsorption onto PPs (53 µm) surface is the pH of the solution where it controls the PPs surface charge. To investigate the pH effect on the PPs (53 µm) affinity toward RhB, different pH of samples solutions was studied through ranging from 2.00 to 9.00 (Fig. 3). Fig. 3 showed that the percentage of extraction depends on the pH of the solution. The value of pH from 2.00 to 5.00 increased the removal percentage of RhB dye from 67.4 to 89.8%, which indicates that PPs was most selective toward RhB at pH = 5. The extraction percentage of RhB onto PPs was calculated by Eq. 1.
Fig 3. pH effect on the extraction percentage of RhB dye from aqueous solution using PPs after 60 min shaking at 25 °C.

The low adsorption capacity at low pH values is the result of a competition between the cationic dye and hydrogen ions for the same active adsorption sites [33]. pH effect on the RhB interaction with the surface functional groups onto PPs has been clarified as follows:

\[
\begin{align*}
  &\text{ROH}_2 \rightleftharpoons \text{R–OH} + \text{H}^+ \\
  &\text{R–OH} \rightleftharpoons \text{R–O}^- + \text{H}^+ \\
  &\text{R–O}^- + \text{RhB}^+ \rightleftharpoons \text{R–O–RhB} \\
  &\text{R–COOH} \rightleftharpoons \text{R–COO}^- + \text{H}^+ \\
  &\text{R–COO}^- + \text{RhB}^+ \rightleftharpoons \text{R–COO–RhB}
\end{align*}
\]

where R represents the PPs surface; R–OH₂⁺, R–OH and R–O⁻ represent protonated, neutral, and ionized surface hydroxyl functional groups; R–O–RhB and R–COO–RhB are the formation of the bonding complexes. At pH < 5, the adsorption is unfavorable because of repulsive electrostatic interactions between cationic dye and positively charged functional groups [33]. At pH = 5, ion association has taken place between the negative charged surface of PPs and positive charge RhB molecules [34]. This shows that RhB molecules bind to hydroxyl and carboxyl groups that are found on the surface of PPs (Eq. (6), (8)). This proves that the principal adsorption mechanism for the removal of RhB dye could be the chemical ion exchange process [34-35].

**Effect of different sorbent masses**

The study of sorbent mass is necessary and very useful to find the optimum amount of sorbent required. The data represented in Fig. 4 indicated the sorption percentage of RhB slightly increased from 98.39 to 99.32% with increasing natural sorbent mass from 0.1 to 0.8 ± 0.001 g with 5 mg L⁻¹ of RhB at pH = 5. This behavior belongs to the increasing of adsorption with increasing the mass of adsorbent can be attributed to higher adsorbent surface area and the obtainability of more adsorption sites [32]. In fact, Fig. 4 showed there is no significant difference. Therefore, 0.1 g was chosen for later removal studies. The extraction percentage of RhB was calculated by Eq. (1).

**Effect of contact time**

The influence of shaking time (0.0–75 min) on the retention of RhB (5 mg L⁻¹) from the aqueous media at pH = 5 by PPs was carried out at room temperature. The results are demonstrated in Fig. 5 in which the sorption of tested RhB onto PPs sorbent was fast and reached its maximum adsorption after 10 min of shaking time. Consequently, a 10 min shaking period was adopted in the subsequent experiments. In the primary stages, the separation of the RhB by PPs increased rapidly due to the presence of a large number of available surface sites for adsorption. By increasing time in the post-stage (plateau portion), the residual available surface sites are hard to be taken as a result of the repulsive forces between the RhB molecules on the sorbent and bulk phases [33].
Effect of different temperatures on the sorption of RhB dye onto PPs

The enthalpy and the entropy changes during adsorption were informatively studied as temperature dependence reactions [1,36]. The effect of solution temperature on the distribution ratio of RhB from aqueous solution using PPs observed in Fig. 6, which shows an increase of removal efficiency of RhB from 25 to 55 °C due to the high mobility of RhB toward available binding sites onto PPs but the percentage extraction of RhB (5 mg L⁻¹) increased from 94.5 to 98.18% at pH ≈ 5 that mean the adsorption process is an endothermic process in nature.

Effect of different concentrations of RhB dye

The effect of initial concentration on the extraction percentage of RhB by studied adsorbents was showed in Fig. 7. The experimental results showed that increasing the dye ion concentration from 0.5 mg to 80 mg L⁻¹ causes decreasing in the removal percentage of RhB from 97.62 to 30.17%. The decrease of adsorption capacity with raising the initial RhB dye concentration is due to the competing of dye ions for available binding sites of adsorption and because of the possible aggregation of RhB molecules onto the solid phase extractor. At lower RhB dye concentration, the active sites more ability to saturate, and adsorption capacity approaches higher value [33]. Therefore, 5 mg L⁻¹ of RhB was chosen for all later other experiments.

Sorption Isotherms of RhB Dye onto PPs

The mechanism of the interaction of RhB dye on the PPs surface was described by the sorption isotherms. The equilibrium studies contingent upon the nature of the sorption system is beneficial for calculating the maximum sorption capacity of the PPs toward RhB dye. They are also beneficial for determining some significant surface properties of the selected biomass [37-38]. At a wide range of concentrations RhB dye (0.5–80 mg/L), the sorption behavior of RhB dye at pH = 5 onto PPs were investigated. At the perfect parameters, the plot of the amount of RhB retained (qₑ) onto PPs versus their

![Fig 6. Various temperatures effect on the sorption of RhB dye (5 mg L⁻¹) at pH = 5 using 0.1 g of PPs after 10 min shaking](image_url)

![Fig 7. Initial concentration effect on the uptake of RhB dye at pH = 5 using 0.1g of PPs after 10 min shaking](image_url)
equilibrium concentrations in the bulk aqueous solution is shown in Fig. 8. The isotherm showed a strong RhB–PPs interaction. At low concentrations (0.1–6 mg L\(^{-1}\)) of RhB, a sharp rise in the RhB retained, followed by a slight increase at a concentration higher than 15 mg L\(^{-1}\). This is due to the surface coverage of the PPs could be low, and the vacant vigorous sites of PPs are not completely occupied by RhB. On increasing analyte concentration, the linearity of the plot decreases because the surface coverage increases, and the available active sites of the PPs for RhB are limited. The sorption isotherm was found 31.95 ± 0.02 mg g\(^{-1}\) for the sorption capacity of RhB onto PPs.

The equilibrium data were subjected to the adsorption isotherm models, e.g., Langmuir, Freundlich, and Dubinin–Radushkevich (D-R) over a wide range of equilibrium concentration through linear regression at optimum conditions\([37-38]\). Adsorption equilibrium is found when RhB contacted with the PPs for adequate time. The perfect close-fitting model is subjected to its agreeability to the experimental data with the correlation coefficient that is close to unity. The parameters data of the three isotherms studied models are represented in Table 2.

The uptake behavior of RhB dye from the aqueous solution onto PPs was subjected to the Langmuir model, which shows that a single layer of molecules on the PPs surface is absorbed, so adsorption is restricted to a monolayer only. Since PPs surface is homogeneous, the adsorption energy is uniform for all sites. As a result, RhB doesn’t transmigrate in the plane of the PPs surface. As an RhB dye occupies a site, no more adsorption can take place in that site, the intermolecular attractive forces a rapid decrease as distance increases. There is no interaction between RhB molecules adsorbed on adjacent sites, in which the adsorption is localized on the surface. Langmuir model is expressed by the following equation\([39]\):

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}
\]  

(9)

where \(C_e\) is the concentration of adsorbate at equilibrium (mg L\(^{-1}\)), \(q_e\) is the equilibrium quantity of adsorbate per unit mass of the sorbent (mg g\(^{-1}\)), \(q_m\) is the monolayer maximum adsorption capacity of RhB per unit mass of sorbent (mg g\(^{-1}\)), and \(K_L\) is Langmuir constant related to the binding energy of RhB sorption (L mg\(^{-1}\)), which determined from the slope and intercept of linear plot respectively, \(K_L\) can be correlated with the variation of the suitable area and porosity of the sorbent which indicates that large surface area and high pore volume will give a higher adsorption capacity.

The dimensionless constant separation factor \(R_L\) is expressing the essential characteristics of the Langmuir isotherm\([40]\).

\[
R_L = \frac{1}{1 + K_L C_0}
\]  

(10)

where \(K_L\) is Langmuir constant (mg g\(^{-1}\)), and \(C_0\) is the initial concentration of adsorbate (mg g\(^{-1}\)). \(R_L\) values show the adsorption to be disapproving at \(R_L > 1\), linear when \(R_L = 1\), favorable when \(0 < R_L < 1\), and irreversible when \(R_L = 0\).

The plot of \(C_e/q_e\) versus \(C_e\) over the entire RhB concentration range, as seen in Fig. 9. The plot was linear with a good correlation factor (\(R^2 = 0.994\)), which indicates favorable adsorption. Moreover, the previous

![Fig 8. Sorption isotherm of RhB dye amount onto 0.1 g PPs at pH = 5 after 10 min shaking](image)

Table 2. Isotherm models and their parameters for RhB dye sorption from model solution onto natural sorbent

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>(q_m) (mg g(^{-1}))</td>
<td>7.37</td>
</tr>
<tr>
<td></td>
<td>(k_L) (L g(^{-1}))</td>
<td>1.369</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.994</td>
</tr>
<tr>
<td></td>
<td>(K_L) (L g(^{-1}))</td>
<td>25.22</td>
</tr>
<tr>
<td>Freundlich</td>
<td>(1/n)</td>
<td>0.6766</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9127</td>
</tr>
<tr>
<td>D-R</td>
<td>(E) (kJ mol(^{-1}))</td>
<td>15.80</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.9998</td>
</tr>
</tbody>
</table>
relation confirms that the characteristics of analyte adsorption onto the sorbent followed the Langmuir adsorption model. The Langmuir parameters $q_m$ and $K_L$ were calculated from the slope and intercept were found equal 7.37 ± 1.0 mg g$^{-1}$ and 1.369 L mg$^{-1}$, respectively, the low value of $K_L$ obtained indicated that PPs has a high affinity for RhB. Thus, PPs are most likely to contain fixed individual sites, each of which equally adsorbs only one RhB molecule forming a monolayer [29]. These data confirm that an added component for "surface adsorption" participated in RhB dye uptake. The dimensionless constant equilibrium parameter $R_L$ of Langmuir isotherm is given by the Eq. (10), the adsorption of RhB on PPs is favorable adsorption as the $R_L$ values obtained (0.09) at all initial concentrations lie between 0 and 1. This proposes the applicability of this PPs for RhB removal.

The Freundlich isotherm model is an empirical equation and another form of Langmuir that can be useful to multilayer adsorption. This model indicates that the surface of the adsorbent is heterogeneous in which the active sites and their energies distribute exponentially. Firstly, the stronger binding sites are occupied continuously up to the adsorption energy is exponentially decreased upon the completion of the adsorption process [35]. The linear form of the Freundlich model is expressed by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  \hspace{1cm} (11)

where $K_F$ is adsorption capacity (L mg$^{-1}$) and $1/n$ is adsorption intensity; it also shows the relative distribution of the energy and the heterogeneity of the adsorbate sites.

The value of slope $(1/n)$ ranges between 0 and 1. If the value of $(1/n)$ gets close to zero, the surface of the adsorbent becomes more heterogeneous, while a value of $(1/n)$ that is above unity indicates unfavorable adsorption isotherms. Since the value of $(1/n)$ is found to be 0.6766, which is more than 0.1, so the adsorption isotherm approaches irreversible isotherm. This isotherm did not much fit the experimental data ($R^2 = 0.9127$). The constants $1/n$ and $K_F$ were attained from the slope and intercept of the linear plot were found equal 0.6766 and 25.22 mg g$^{-1}$ (L mg$^{-1}$)$^{1/n}$, respectively (Table 2). Moreover, the value of $1/n < 1$ indicates favorable adsorption isotherm for the sorption of RhB onto PPs sorbent. The value of $n$ obtained (1.5) lies within this range, which implies that PPs have a high affinity for RhB in solution.

Moreover, the adsorption capacity of PPs for removal RhB dye was compared with many adsorbents peels that are summarized in Table 3. These data revealed that the natural PPs is an excellent extractor for selective separation of RhB at trace concentration levels from aqueous solutions.

![Fig 9. Langmuir sorption isotherm of RhB dye uptake onto 0.1 g PPs at pH = 5 after 10 min shaking](image)

**Table 3.** Adsorption Capacity of natural adsorbents peels for removal RhB dye

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Conc. RhB, mg/L</th>
<th>$q_m$, mg/g (Langmuir)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid treated banana peel</td>
<td>20</td>
<td>9.52</td>
<td>[37]</td>
</tr>
<tr>
<td>Banana peel powder</td>
<td>25</td>
<td>3.8</td>
<td>[41]</td>
</tr>
<tr>
<td>Chestnut peel powder</td>
<td>20</td>
<td>2.97</td>
<td>[42]</td>
</tr>
<tr>
<td>Orange peel</td>
<td>10</td>
<td>3.23</td>
<td>[21]</td>
</tr>
<tr>
<td>Pomegranate peel</td>
<td>15</td>
<td>7.37</td>
<td>Present work</td>
</tr>
</tbody>
</table>
Kinetic Behavior of RhB Dye Adsorption onto PPs

Predicting the rate at which the sorption of pollutants occurs in a given system is one of the essential factors in the sorption system. Thus, determining the most probable kinetic mode for describing the analyte retention is subjected to pseudo-first-order and pseudo-second-order, which are the most common models to assign the retention step [37-38]. The data were subjected to the Lagergren model (pseudo-first-order) expressed by the following Lagergren model [43]:

\[
\ln(q_e - q_t) = \ln(q_e) - k_1t
\]

where \( q_e \) and \( q_t \) (mg g\(^{-1}\)) are the sorption capacities at equilibrium and at time \( t \), respectively, and \( k_1 \) (min\(^{-1}\)) is the pseudo-first-order adsorption rate constant for RhB uptake per min by the PPs extractor. The values of \( k_1 \) and \( q_e \) are determined from the slope. The parameters \( K_L \) and \( q_e \) can be determined from the linear plot of \( \ln(q_e - q_t) \) versus \( t \). A nonlinear plot of \( \ln(q_e - q_t) \) versus \( t \) was obtained low correlation value \((R^2 = 0.9422)\). As a result, RhB uptake by PPs does not fit well with the pseudo-first-order rate equation.

Hence, the data were further subjected to pseudo-second-order that expressed by the equation [37-38]:

\[
t/q_t = 1/k_2q_e^2 + t/q_e
\]

where \( k_2 \) (g mg\(^{-1}\) min\(^{-1}\)) is the pseudo-second-order rate constant.

The plot of \( t/q_t \) versus \( t \) was found linear with an excellent correlation value \((R^2 = 0.998)\) (Fig. 10). The calculated value of \( k_2 \) was found equal to 0.04 g mg\(^{-1}\) min\(^{-1}\). Thus, it can be concluded that RhB retention by the used PPs fitted well with the second-order model. Good agreement between the experimental value of \( q_e \) (175.86 mg g\(^{-1}\)) and the calculated value of \( q_e \) (152.73 mg g\(^{-1}\)) for the pseudo-second-order kinetic model. These findings confirm the suitability of the pseudo-second-order rate equation for the RhB adsorption using PPs from aqueous solutions.

Thermodynamic Behavior of RhB Dye Retention onto PPs

The sorption behavior of RhB by PPs was investigated at different temperatures (298–328 K) to determine the nature of RhB dye uptake onto PPs at optimum conditions [44]. The thermodynamic activation parameters of the process, such as activation enthalpy (\( \Delta H \)), Gibbs free energy (\( \Delta G \)), which is the fundamental criterion to determine if a process occurs spontaneously, and the entropy (\( \Delta S \)) where calculated from the equations below [26,45-46]:

\[
\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}
\]

\[
\Delta G = \Delta H - T \Delta S
\]

\[
\Delta G = -RT \ln K_c
\]

The \( K_c \) values of RhB sorption by the PPs are dependent on the fractional attainment \((F_e)\) of the sorption process, and the values of \( K_c \) can be calculated using the following equation:

\[
K_c = \frac{F_e}{1 - F_e}
\]

\( \Delta H \) and \( \Delta S \) determined from the slope and intercept (Eq. (14)), respectively, of plotting \( \ln K_c \) against \( 1/T \).

The distribution ratio \( (D) \) of PPs according to Van’t Hoff equation, using the following expression [45]:

\[
\log D = -\frac{\Delta H}{2.303RT} + C
\]

where, \( C \) is a constant. RhB uptake from aqueous media of \( pH = 5 \) onto PPs shows decreased D values on increasing temperature. The plot of \( \log D \) against \( 1000/T \) (K\(^{-1}\)) was linear (Fig. 11). The evaluated \( \Delta H \) data for RhB
sorption onto PPs is equal to 30.15 ± 1.01 kJ mol⁻¹.

The positive value of ΔH confirms the endothermic behavior of the adsorption of RhB by PPs from aqueous solution [44]. The adsorption capacity of adsorbent increased with an increase in temperature from 298 to 328 K. The positive value of entropy (ΔS = 42.17 J mol⁻¹ K⁻¹) of the sorption of RhB onto the sorbent surface may be attributed to the increase in the degree of freedom of the RhB molecules is more restricted in the PPs structure than in solution [44]. The negative value of ΔG at all studied temperatures indicated the feasibility and spontaneous nature of RhB sorption onto PPs.

The increase in the ΔG values -1024.19 kJ mol⁻¹ at 298 K, -1445.93 kJ mol⁻¹ at 308 K, and -1356.94 kJ mol⁻¹ at 318 K with increasing temperature because of the spontaneous nature of sorption [44]. It implies that is more favorable at higher temperatures confirming the endothermic sorption process.

Environmental Application

To examine the applicability of the suggested method for RhB detection, it was implemented to extract RhB dye from real water samples. Therefore, different environmental samples of well water, tap water, bottled water, and seawater were collected from Jeddah, Saudi Arabia. Then, the suggested procedure was applied to analyze the samples by above-proposed batch conditions (Table 4). The percentage of RhB dye extraction, using PPs from the real environmental samples, was ranging from 92.82–98.15%. Thus, the proposed method is accurate and applicable to RhB removal from real water samples.

Table 4. Extraction percentage of RhB dye at different concentrations in real water samples using 0.1 g of PPs at pH ≈ 5

<table>
<thead>
<tr>
<th>Samples</th>
<th>Concentration (mg L⁻¹)</th>
<th>% Extraction*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well water</td>
<td>5</td>
<td>89.8 ± 9.85</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>87.75 ± 10.0</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>87.63 ± 9.45</td>
</tr>
<tr>
<td>Tap water</td>
<td>5</td>
<td>92.23 ± 7.65</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>86.23 ± 9.88</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>89.84 ± 9.43</td>
</tr>
<tr>
<td>Bottle water</td>
<td>5</td>
<td>93.45 ± 5.85</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>93.78 ± 6.05</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>92.92 ± 6.85</td>
</tr>
<tr>
<td>Sea water</td>
<td>5</td>
<td>97.86 ± 1.88</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>89.37 ± 9.85</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>94.97 ± 4.45</td>
</tr>
</tbody>
</table>

*Average (n = 3)

CONCLUSION

The current approach demonstrates the efficacy of the natural PPs as a solid phase extractor for selective separation of RhB at trace concentration levels from aqueous solutions. PPs adsorbent also provided high adsorption capacity for RhB dye at pH ≈ 5 at 10 min. Isotherm models such as Langmuir adsorption fitted with the experimental data of RhB adsorption onto PPs sorbent, indicating the adsorption process mainly by a monolayer of RhB onto a homogenous surface of PPs.

The results of kinetics of the RhB retention from the aqueous media towards PPs fitting well with pseudo second order rate equation. The thermodynamic study showed that the sorption process was spontaneous and endothermic in nature, associated with positive entropy value. Overall, the results were reliable, feasible and suitable. Therefore, the proposed method can be successfully used for a selective separation of organic dyes from the real water samples.

REFERENCES


[40] Nimibofa, A., Angaye, S.S., Wankasi, D., and Dikio, E.D., 2015, Synthesis, characterization and application of Mg/Al layered double hydroxide for


