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 (k_2) 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

<div align="center">**Table 1.** Selected properties of RhB dye</div>

Common name	Rhodamine B
Chemical name	[9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride.
Chemical formula	$C_{28}H_{31}ClN_2O_3$
Maximum wavelength	553 nm
Appearance	Red to violet powder
Molecular weight	479.02 g/mol
Structure	
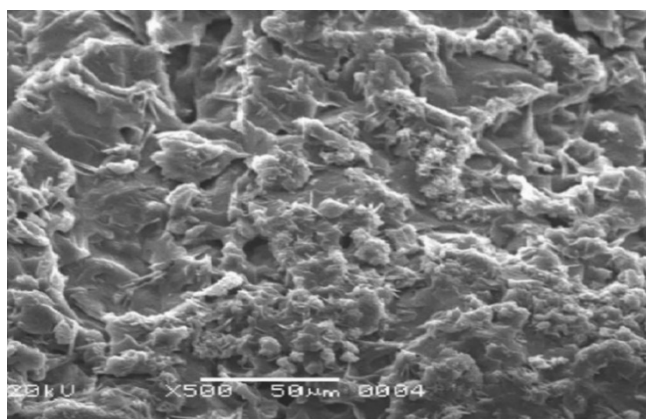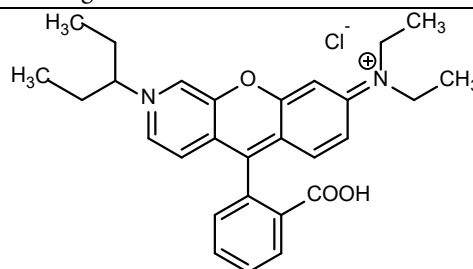
Fig 1. SEM image of waste PPs

from simulated produced water [25-26]. They have shown great efficiency in remediating polluted water sources by the adsorption of chloride ions [27] and malachite green [28]. Moreover, the raw pomegranate peel bio-sorbent was used for the copper removal [29]. Also, the simulated wastewater was treated by the adsorption of ciprofloxacin using the pomegranate peels and then characterized by different techniques such as Zeta sizer and scanning electron microscopy [30]. SEM image plays a significant role in understanding the key changes in the surface of biomass [31]. To understand the surface morphology via SEM, the morphological features of waste PPs are shown in Fig. 1 [31].

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 λ_{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]:

$$\%E = \frac{A_b - A_a}{A_{fa}} \times 100 \tag{1}$$

$$q_e = (A_b - A_a) \times \frac{V_{(L)}}{m_{(g)}} \tag{2}$$

Fig 2. Dried PPs (a) and PPs powder (53 μm) (b)

$$D = (\frac{\%E}{100} - \%E) \times \frac{V_{(mL)}}{m_{(g)}} \qquad (3)$$

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, 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 as before.

To investigate the effect of temperature on the RhB uptake onto PPs, 50 mL of RhB at 5 mg L^{-1} were shaken with PPs (0.1 ± 0.001 g) for 10 min at different temperatures (15–65 °C) in a mechanical shaker. Then adsorbents were filtrated, and the percent extraction of RhB that retained onto PPs solution was measured at 553 nm 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, 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.
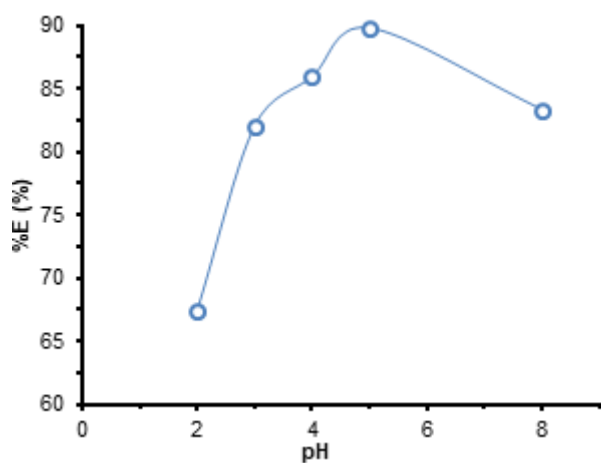
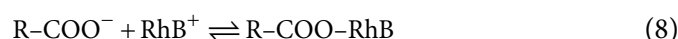**Fig 3.** pH effect on the extraction percentage of RhB dye from aqueous solution using PPs after 60 min shaking at 25 °C

Fig 4. PPs dose effect on the sorption distribution of RhB dye (5 mg L⁻¹) from aqueous solution after 60 min shaking at pH ≈ 5 and 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:

$$ROH_2^+ \rightleftharpoons R–OH + H^+ \tag{4}$$

$$R–OH \rightleftharpoons R–O^- + H^+ \tag{5}$$

$$R–O^- + RhB^+ \rightleftharpoons R–O–RhB \tag{6}$$

$$R–COOH \rightleftharpoons R–COO^- + H^+ \tag{7}$$

$$R–COO^- + RhB^+ \rightleftharpoons R–COO–RhB \tag{8}$$

where R represents the PPs surface; $R–OH_2^+$, 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
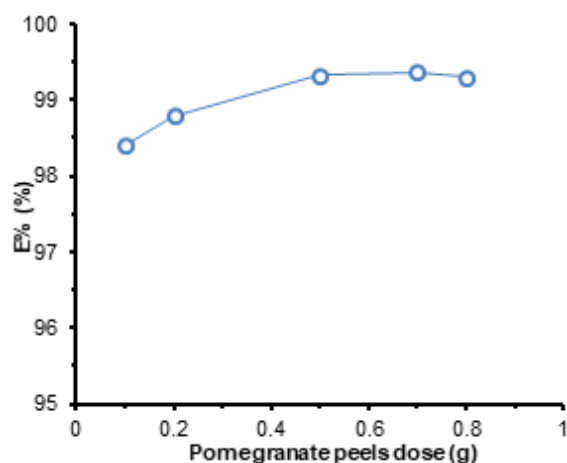
The study of sorbent mass is necessary and very useful to find the optimum amount of sorbent required. The data represented in Fig. 4 indicated the sorption percentage of RhB slightly increased from 98.39 to 99.32% with increasing natural sorbent mass from 0.1 to 0.8 ± 0.001 g with 5 mg L⁻¹ of RhB at 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].
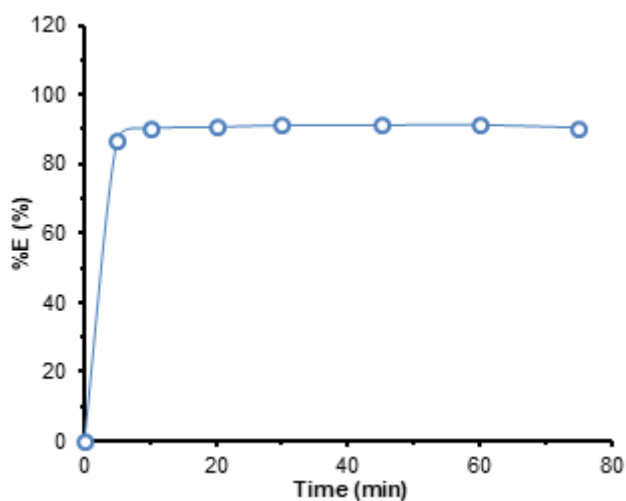
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Fig 5. Time contact effect on the removal of RhB dye (5 mg L⁻¹) by 0.1 g PPs at pH ≈ 5 and 25 °C

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 (q_e) onto PPs *versus* their
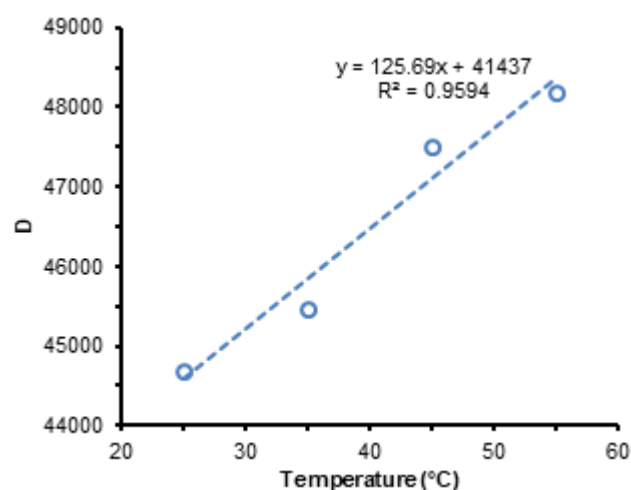

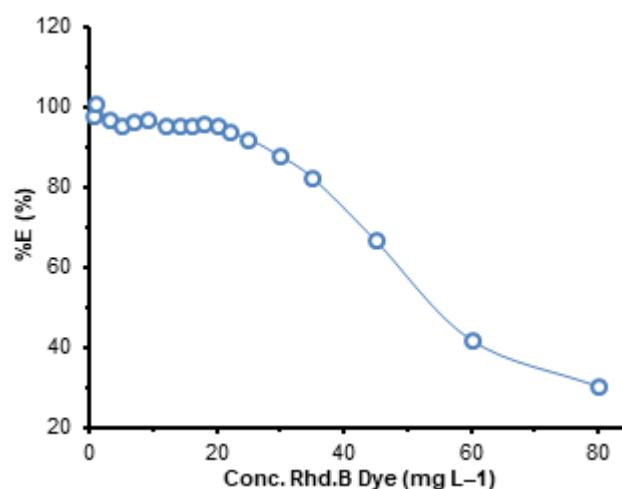**Fig 6.** Various temperatures effect on the sorption of RhB dye (5 mg L⁻¹) at pH ≈ 5 using 0.1 g of PPs after 10 min shaking

Fig 7. Initial concentration effect on the uptake of RhB dye at pH ≈ 5 using 0.1g of PPs after 10 min shaking

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]:

$$C_e/q_e = C_e/q_e + 1/K_L q_m \tag{9}$$

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].

$$R_L = 1/1 + K_L C_0 \tag{10}$$

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
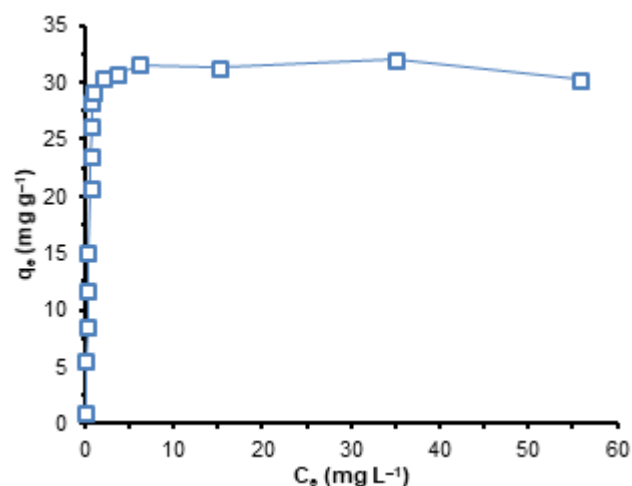
Fig 8. Sorption isotherm of RhB dye amount onto 0.1 g PPs at pH ≈ 5 after 10 min shaking

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

Isotherm model	Parameter	Value
Langmuir	q_m (mg g^{-1})	7.37
	k_L (L g^{-1})	1.369
	R^2	0.994
Freundlich	k_f (L g^{-1})	25.22
	1/n	0.6766
	R^2	0.9127
D-R	E (kJ mol^{-1})	15.80
	R^2	0.9998

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:

$$\log q_e = \log K_F + 1/n \log C_e \qquad (11)$$

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.
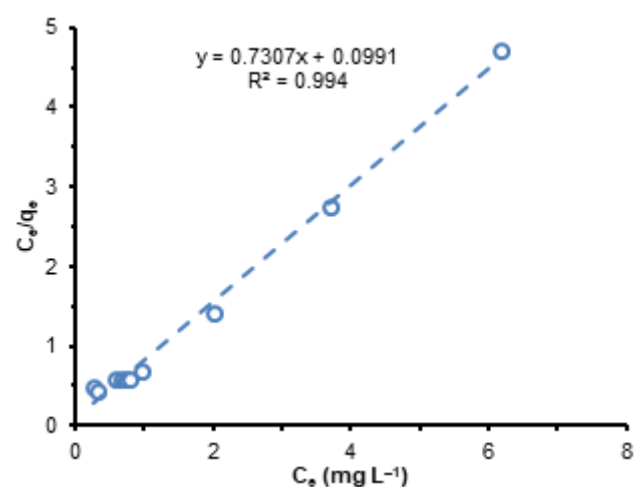

Fig 9. Langmuir sorption isotherm of RhB dye uptake onto 0.1 g PPs at pH ≈ 5 after 10 min shaking

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

Adsorbent	Conc. RhB, mg/L	q_m, mg/g (Langmuir)	Reference
Acid treated banana peel	20	9.52	[37]
Banana peel powder	25	3.8	[41]
Chestnut peel	20	2.97	[42]
Orange peel	10	3.23	[21]
Pomegranate peel	15	7.37	Present work

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]:

$$\ln(q_e - q_t) = \log q_e - k_1 t \tag{12}$$

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]:

$$t/q_t = 1/k_2 q^2_e + t/q_e \tag{13}$$

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
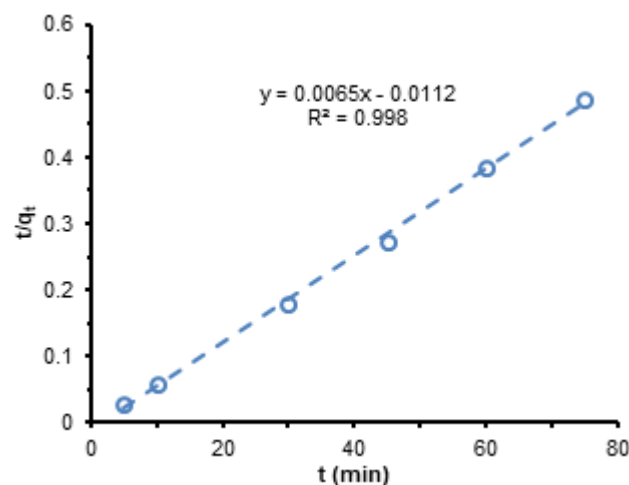
Fig 10. Pseudo-second-order plot of RhB dye uptake by 0.1 g PPs at pH ≈ 5 after 10 min shaking

optimum conditions [44]. The thermodynamic activation parameters of the process, such as activation enthalpy (ΔH), Gibbs free energy (ΔG), which is the fundamental criterion to determine if a process occurs spontaneously, and the entropy (ΔS) where calculated from the equations below [26,45-46]:

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{14}$$

$$\Delta G = \Delta H - T\Delta S \tag{15}$$

$$\Delta G = -RT \ln K_c \tag{16}$$

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:

$$K_c = \frac{F_e}{1 - F_e} \tag{17}$$

ΔH and ΔS 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]:

$$\log D = \frac{-\Delta H}{2.303 RT} + C \tag{18}$$

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 ΔH 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 ($\Delta S = 42.17$ 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.
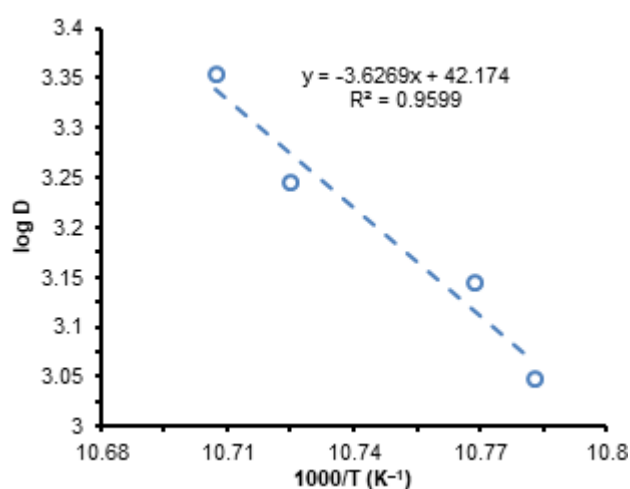

Fig 11. Vant- Hoff plot of RhB dye retention onto 0.1 g PPs at pH ≈ 5 after 10 min shaking

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

Samples	Concentration (mg L^{-1})	% Extraction*
	5	89.8 ± 9.85
Well water	10	87.75 ± 10.0
	15	87.63 ± 9.45
	5	92.23 ± 7.65
Tap water	10	86.23 ± 9.88
	15	89.84 ± 9.43
	5	93.45 ± 5.85
Bottle water	10	93.78 ± 6.05
	15	92.92 ± 6.85
	5	97.86 ± 1.88
Sea water	10	89.37 ± 9.85
	15	94.97 ± 4.45

*Average (n = 3)

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.

■ 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

[1] Tahir, M.A., Bhatti, H.N., Hussain, I., Bhatti, I.A., and Asghar, M., 2020, Sol–gel synthesis of

mesoporous silica–iron composite: Kinetics, equilibrium and thermodynamics studies for the adsorption of Turquoise-Blue X-GB dye, *Z. Phys. Chem.*, 234 (2), 233–253.

[2] Shannon, M.A., Bohn, P.W., Elimelech, M., Georgiadis, J.G., Mariñas, B.J., and Mayes, A.M., 2008, Science and technology for water purification in the coming decades, *Nature*, 452 (7185), 301–310.

[3] Kurniawan, T.A., Sillanpää, M.E.T., and Sillanpää, M., 2012, Nanoadsorbents for remediation of aquatic environment: Local and practical solutions for global water pollution problems, *Crit. Rev. Env. Sci. Technol.*, 42 (12), 1233–1295.

[4] Alcamo, J., Henrichs, T., and Rösch, T., 2017, *World Water in 2025: Global Modeling and Scenario Analysis for the World Commission on Water for the 21ˢᵗ Century*, Center for Environmental Systems Research, University of Kassel, Germany.

[5] Cosgrove, W.J., and Rijsberman, F.R., 2014, *World Water Vision: Making Water Everybody's Business*, Routledge, United Kingdom.

[6] Maneerung, T., Liew, J., Dai, Y., Kawi, S., Chong, C., and Wang, C.H., 2016, Activated carbon derived from carbon residue from biomass gasification and its application for dye adsorption: Kinetics, isotherms and thermodynamic studies, *Bioresour. Technol.*, 200, 350–359.

[7] Namasivayam, C., Radhika, R., and Suba, S., 2001, Uptake of dyes by a promising locally available agricultural solid waste: Coir pith, *Waste Manage.*, 21 (4), 381–387.

[8] Kulyukhin, S.A., Krasavina, E.P., Rumer, I.A., and Gordeev, A.V., 2019, Use of layered double oxides and hydroxides of Mg and Al for removing dyes from aqueous solutions containing 137Cs, 90Sr, 90Y, and U(VI), *Radiochemistry*, 61 (5), 585–591.

[9] Eslami, A., Yazdanbakhsh, A.R., and Momayyezi, M.H., 2015, Removal of reactive dyes from textile wastewater using sonochemical process: effective parameters study, *JRH*, 5 (2), 184–192.

[10] Mahmoudabadi, T.Z., Talebi, P., and Jalili, M., 2019, Removing disperse red 60 and reactive blue 19 dyes

removal by using *Alcea rosea* root mucilage as a natural coagulant, *AMB Express*, 9 (1), 113.

[11] Zhou, Y., Lu, J., Zhou, Y., and Liu, Y., 2019, Recent advances for dyes removal using novel adsorbents: A review, *Environ. Pollut.*, 252, 352–365.

[12] Bhatti, H.N., Safa, Y., Yakout, S.M., Shair, O.H., Iqbal, M., and Nazir, A., 2020, Efficient removal of dyes using carboxymethyl cellulose/alginate/polyvinyl alcohol/rice husk composite: Adsorption/desorption, kinetics and recycling studies, *Int. J. Biol. Macromol.*, 150, 861–870.

[13] Noreen, S., Bhatti, H.N., Iqbal, M., Hussain, F., and Sarim, F.M., 2020, Chitosan, starch, polyaniline and polypyrrole biocomposite with sugarcane bagasse for the efficient removal of Acid Black dye, *Int. J. Biol. Macromol.*, 147, 439–452.

[14] Gupta, V.K., and Suhas, 2009, Application of low-cost adsorbents for dye removal – A review, *J. Environ. Manage.*, 90 (8), 2313–2342.

[15] Forgacs, E., Cserháti, T., and Oros, G., 2004, Removal of synthetic dyes from wastewaters: A review, *Environ. Int.*, 30 (7), 953–971.

[16] Aguiar, J.E., Cecilia, J.A., Tavares, P.A.S., Azevedo, D.C.S., Castellón, E.R., Lucena, S.M.P., and Silva Junior, I.J., 2017, Adsorption study of reactive dyes onto porous clay heterostructures, *Appl. Clay Sci.*, 135, 35–44.

[17] Senthilkumar, T., Chattopadhyay, S.K., and Miranda, L.R., 2017, Optimization of activated carbon preparation from pomegranate peel (P*unica granatum* peel) using RSM, *Chem. Eng. Commun.*, 204 (2), 238–248.

[18] Yu, S., Wang, X., Ai, Y., Tan, X., Hayat, T., Hu, W., and Wang, X., 2016, Experimental and theoretical studies on competitive adsorption of aromatic compounds on reduced graphene oxides, *J. Mater. Chem. A*, 4 (15), 5654–5662.

[19] Maurya, I.C., Singh, S., Srivastava, P., Maiti, B., and Bahadur, L., 2019, Natural dye extract from *Cassia fistula* and its application in dye-sensitized solar cell: Experimental and density functional theory studies, *Opt. Mater.*, 90, 273–280.

[20] Mozafarjalali, M., Hajiani, M., and Haji, A., 2020, Efficiency of *Aptenia cordifolia* mucilage in removal of anion dyes from aqueous solution, *IJNC*, 7 (2), 111–124.

[21] Namasivayam, C., Muniasamy, N., Gayatri, K., Rani, M., and Ranganathan, K., 1996, Removal of dyes from aqueous solutions by cellulosic waste orange peel, *Bioresour. Technol.*, 57 (1), 37–43.

[22] Hage, R., and Lienke, A., 2006, Applications of transition-metal catalysts to textile and wood-pulp bleaching, *Angew. Chem. Int. Ed.*, 45 (2), 206–222.

[23] Afsharnia, M., Saeidi, M., Zarei, A., Narooie, M.R., and Biglari, H., 2016, Phenol removal from aqueous environment by adsorption onto pomegranate peel carbon, *Electron. Physician*, 8 (11), 3248–3256.

[24] Ververi, M., and Goula, A.M., 2019, Pomegranate peel and orange juice by-product as new biosorbents of phenolic compounds from olive mill wastewaters, *Chem. Eng. Process. Process Intensif.*, 138, 86–96.

[25] Saadi, R., Saadi, Z., Fazaeli, R., and Fard, N.E., 2015, Monolayer and multilayer adsorption isotherm models for sorption from aqueous media, *Korean J. Chem. Eng.*, 32 (5), 787–799.

[26] Liu, Y., and Liu, Y.J., 2008, Biosorption isotherms, kinetics and thermodynamics, *Sep. Purif. Technol.*, 61 (3), 229–242.

[27] Al Jaaf, H.J.M., 2020, Adsorption of chloride ion from polluted water using pomegranate peels powder and tea leaves, *J. Eng. Sustainable Dev.*, 24 (1), 70–78.

[28] Gündüz, F., and Bayrak, B., 2017, Biosorption of malachite green from an aqueous solution using pomegranate peel: Equilibrium modelling, kinetic and thermodynamic studies, *J. Mol. Liq.*, 243, 790–798.

[29] Ben-Ali, S., Souissi-Najar, S., and Ouederni, A., 2017, Comments on "Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal", *J. Cleaner Prod.*, 154, 269–275.

[30] Mekhamer, W., and Al-Tamimi, S., 2019, Removal of ciprofloxacin from simulated wastewater by pomegranate peels, *Environ. Sci. Pollut. Res.*, 26 (3), 2297–2304.

[31] Siddiqui, M., Nizamuddin, S., Mubarak, N.M., Shirin, K., Aijaz, M., Hussain, M., and Baloch, H.A., 2019, Characterization and process optimization of biochar produced using novel biomass, waste pomegranate peel: a response surface methodology approach, *Waste Biomass Valorization*, 10 (3), 521–532.

[32] Ghaneian, M.T., Jamshidi, B., Dehvari, M., and Amrollahi, M., 2015, Pomegranate seed powder as a new biosorbent of reactive red 198 dye from aqueous solutions: Adsorption equilibrium and kinetic studies, *Res. Chem. Intermed.*, 41 (5), 3223–3234.

[33] Ben-Ali, S., Jaouali, I., Souissi-Najar, S., and Ouederni, A., 2017, Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal, *J. Clean. Prod.*, 142, 3809–3821.

[34] Shen, K., and Gondal, M.A., 2017, Removal of hazardous Rhodamine dye from water by adsorption onto exhausted coffee ground, *J. Saudi Chem. Soc.*, 21 (Suppl. 1), S120–S127.

[35] Boparai, H.K., Joseph, M., and O'Carroll, D.M., 2011, Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles, *J. Hazard. Mater.*, 186 (1), 458–465.

[36] Saha, P., and Chowdhury, S., 2011, "Insight into adsorption thermodynamics" in *Thermodynamics*, Eds. Tadashi, M., IntechOpen, Rijeka, 349–364.

[37] Oyekanmi, A.A., Ahmad, A., Hossain, K., and Rafatullah, M., 2019, Adsorption of Rhodamine B dye from aqueous solution onto acid treated banana peel: Response surface methodology, kinetics and isotherm studies, *PloS One*, 14 (5), e0216878.

[38] Chin, M., Cisneros, C., Araiza, S.M., Vargas, K.M., Ishihara, K.M., and Tian, F., 2018, Rhodamine B degradation by nanosized zeolitic imidazolate framework-8 (ZIF-8), *RSC Adv.*, 8 (47), 26987–26997.

[39] Dąbrowski, A., 2001, Adsorption – From theory to practice, *Adv. Colloid Interface Sci.*, 93 (1-3), 135–224.

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

the degradation of Congo Red in aqueous solution, *Open J. Phys. Chem.*, 5 (3), 56–70.

[41] Singh, S., Parveen, N., and Gupta, H., 2018, Adsorptive decontamination of rhodamine-B from water using banana peel powder: A biosorbent, *Environ. Technol. Innovation*, 12, 189–195.

[42] Khan, T.A., Nazir, M., and Khan, E.A., 2013, Adsorptive removal of rhodamine B from textile wastewater using water chestnut (*Trapa natans* L.) peel: Adsorption dynamics and kinetic studies, *Toxicol. Environ. Chem.*, 95 (6), 919–931.

[43] Lagergren, S.K., 1898, About the theory of so-called adsorption of soluble substances, *Kungl. Svenska Vetenskapsakad. Handl.*, 24 (4), 1–39.

[44] Bello, O.S., Alabi, E.O., Adegoke, K.A., Adegboyega, S.A., Inyinbor, A.A., and Dada, A.O., 2020, Rhodamine B dye sequestration using *Gmelina aborea* leaf powder, *Heliyon*, 6 (1), e02872.

[45] Chakraborty, S., Chowdhury, S., and Saha, P.D., 2011, Adsorption of crystal violet from aqueous solution onto NaOH-modified rice husk, *Carbohydr. Polym.*, 86 (4), 1533–1541.

[46] El-Shahawi, M., Othman, M.A., and Abdel-Fadeel, M.A., 2005, Kinetics, thermodynamic and chromatographic behaviour of the uranyl ions sorption from aqueous thiocyanate media onto polyurethane foams, *Anal. Chim. Acta*, 546 (2), 221–228.