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Enhanced Adsorption of Rhodamine B on Biomass of Cypress/False Cypress (*Chamaecyparis lawsoniana*) Fruit: Optimization and Kinetic Study

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Abstract: Many industries use various dyes to beautify their products and discharge the waste into the water without proper treatment. Such wastewater is not only dangerous for aquatic life but it is also toxic to human life and can cause numerous problems, such as skin diseases, and some dyes are carcinogenic or even mutagenic as well. Rhodamine-B (RhB) is one of those synthetic organic dyes which is widely used in textile, paper making, leather manufacturing, stained glass work, cosmetics, and many other industries owing to its high tinting strength, high stability, and bright colour. Therefore, it is essential to either remove or reduce its concentration before releasing it into aquatic streams, as well as to minimize or control the cause of several diseases. Several physical and chemical methods have been used for the removal of different dyes from wastewater; nevertheless, adsorption is one of the best techniques used for the removal of dyes due to its high efficiency and low cost. In this regard, we used *Chamaecyparis lawsoniana* (*C. lawsoniana*) fruit as a bio-adsorbent for the removal of RhB from an aqueous solution. An 85.42% dye adsorption was achieved at optimized conditions (pH 2, 40 ppm initial dye concentration, 105 min, and 50 mg adsorbent). Adsorption occurs by pseudo-second-order kinetics, according to kinetic studies. Several samples from various sources, including tap water, distilled water, river water, and filtered river water, were tested for RhB removal, and the study revealed good results even in river water. Thus, *C. lawsoniana* fruit can be used for its real-world application.

Keywords: rhodamine-B dye; adsorption; *C. lawsoniana* plant fruit; bio-adsorbent; wastewater

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1. Introduction

Water is essential for life. Around 71% of the earth is covered by water. It is used for drinking, washing, bathing, and agricultural purposes, and it has myriad purposes in industries such as processing, washing, diluting, cooling, fabricating, and transporting products [1]. It has been contaminated owing to different human activities and industrialization which is a serious threat to aquatic life and many water-borne diseases. The use of dyes in manufacturing products is one of the factors that contributes to water pollution. When these factories discharge their effluent into water resources, it pollutes the water.

Dyes can be classified into two main categories, i.e., natural and synthetic dyes. Other forms of natural dyes include madder (made from madder root), which comes from plants, and Tyrian purple (made from sea snails), which comes from animals. Synthetic dyes include azo and non-azo dyes. There are several different varieties of azo dyes, including basic, acidic, reactive, dispersion, mordant, and sulfur dyes [2]. Dyes are mostly synthetic and have complex aromatic structures; therefore, they are very stable and non-biodegradable [3]. There are more than 10,000 commercially available dyes nowadays [4].

Many industries, such as textiles, rubber, plastics, printing, leather, cosmetics, pharmaceutical, etc., use different dyes to colour their products. Consequently, they are producing a considerable amount of coloured wastewater. The textile industry, among other industries, makes extensive use of dyes to colour materials. Out of the large amount 7×10^7 t that are produced annually, the textile sector uses more than 10,000 t of synthetic dyes annually [2,5]. If not adequately managed, these dyes are released into aquatic ecosystems such rivers, lakes, ponds, and streams along with wastewater, posing substantial ecotoxicological risks and having negative impacts on living things. This is because they do not bind strongly to fabric [6].

One of these dyes, rhodamine-B (RhB), is a carcinogenic xanthine dye that is synthesized and is widely utilized in industries. It is used in paper industry, fireworks, pot-metal glass, crackers, paint, and leather industry. RhB is a poisonous dye that, when discharged into water supplies, has the potential to seriously harm the ecosystem. When humans and other living things use contaminated water, it may irritate their eyes, skin, and respiratory tracts, in addition to having other negative effects because of its carcinogenicity, neurotoxicity, toxicity, and chronic toxicity. Therefore, before being released into the environment, wastewater should be treated to remove RhB. Through the use of various adsorbents, primarily biomasses, numerous studies have revealed various strategies for removing RhB from wastewater. Modified *Volvariella volvacea*, baker's yeast, *Turbinaria conoides*, biosorbent made from inactivated Aspergillus oryzae cells, banana peel powder, green microalgae *Chlorella pyrenoidosa*, furfural industrial processing waste, and jute stick powder have all been introduced for this purpose in order to remove RhB from aqueous solutions, and the treatment methods have been discussed. Such research exposes the thermodynamic and kinetic parameters [7–15]. Additionally revealed are azo dyes' toxicity assessment and microbial degradation [16]. RhB dye is removed from wastewater using a variety of chemical, biological, and physiochemical separation processes, including chemical precipitation, coagulation–flocculation, oxidation, ion exchange, membrane filtration, and adsorption [17]. Adsorption is a form of physiochemical procedure that is thought to be superior to all others because it is highly effective, affordable, straightforward to build, simple to operate, and insensitive to a harmful substance [18,19]. The adsorption process' effectiveness is determined by the physical and chemical properties of the adsorbent and adsorbate. The adsorption capacity, surface area, accessibility, and overall cost of an adsorbent all affect its selectivity. There are many adsorbents that have been used to remove dyes from wastewater, including agricultural solid waste based activated carbon [20–22], mineral [23], clay [24], water lettuce and agro-wastes [25], *Nepenthes rafflesiana* pitcher and leaves [26], and commercial activated carbon [5]. However, these adsorbents need to be modified before being used. In this experiment, we investigated the possibility of removing the dye RhB from an aqueous solution using an adsorbent prepared from the sun-dried, powdered fruit of the *Chamaecyparis lawsoniana* (*C. lawsoniana*) plant, which was applied directly without any surface modification by chemicals. Native to southwestern Oregon and northwestern California [27], *C. lawsoniana* is also found in Taiwan, China, and Japan [28], and it is regularly seen in various parts of Pakistan. This plant's fruit was chosen as an adsorbent due to its useful qualities, including high efficacy, ease of availability, and low cost. Additionally, it can effectively remove RhB dye from wastewater as well as from tap water and river water. Therefore, we sought a straightforward, low-cost, and environmentally friendly hazardous dye removal technique. The next step was to demonstrate a practical use for wastewater treatment. This paper reveals the kinetics of RhB adsorption on the fruit powder of false cypress. In order to determine how the selected adsorbent might be employed in the real world to shield live species from the negative impacts of water pollution, real water samples were also tested.

2. Materials and Methods

2.1. Preparation of Adsorbent

The adsorbent used in this experiment was the fruit of *Chamaecyparis lawsoniana* (*C. lawsoniana*), a tree that grows in Pakistan's Khyber Pakhtunkhwa province. *C. lawsoniana* is an ornamental, evergreen plant maintained primarily for aesthetic appeal, making its fruit readily available (Figure 1a). To remove any dirt and impurities, the fruit was repeatedly washed with tap water and then with distilled water. It was left to dry in the sun before being pounded into powder. Then, this powder was used right away for adsorption without sieving (Figure 1b).

Figure 1. (**a**) *C. lawsoniana* plant. (**b**) Sun-dried and powdered fruit of *C. lawsoniana*.

2.2. Preparation of Adsorbate Aqueous Solution

Rhodamine B dye ($C_{28}H_{31}ClN_2O_3$) analytical grade, 99% was acquired from Sigma-Aldrich (Unit 6A, Arrow Trading Estate, Audenshaw, Manchester, UK). Next, 0.5 g of RhB dye was dissolved in a small amount of distilled water in a 1000 mL of volumetric flask to prepare the adsorbate solution. After adding distilled water to the required level and vigorously stirring for five minutes to achieve homogeneity, a 500 ppm stock solution was produced. This stock solution was used to prepare dilutions of required concentration.

2.3. Experimental Method and Measurements

Adsorption tests were conducted using a 10 mL dye solution in a 100 mL beaker and a digital orbital shaker set to 200 rpm. A similar procedure was used to analyse the impact of various parameters on the adsorption of the RhB dye, including adsorbate and adsorbent concentration, pH, and ionic strength. The dye solutions were removed from the flasks and filtered to remove the adsorbent after shaking at predefined intervals. The dye concentration was estimated by measuring the filtrate's absorbance at 554 nm with a UV-vis spectrophotometer. The wavelength at which RhB dye (20 ppm) absorbs maximum was determined by plotting the absorbance as a function of wavelength, as demonstrated in Figure S1. In every experiment, the dye concentration was determined at the wavelength of maximum absorption, i.e., 554 nm, both before and after adsorption. The adsorption capacity of the adsorbent at equilibrium (Qe (mg/g)) was calculated by using Equation (1).

$$Qe = \frac{Ci - Ce}{m} V \quad (1)$$

where Ci = the initial concentration (ppm) of dye solution, Ce = the equilibrium concentration of dye solution in ppm, V = the volume of solution in L, and m represents the mass of adsorbent in g. Similarly, % removal was calculated using Equation (2).

$$\%\ Removal = \frac{Ci - Ce}{Ci} \times 100 \tag{2}$$

A variety of reaction parameters, including pH, dye/adsorbate concentration, contact time, adsorbent dose, and ionic strength, were optimized for the best RhB removal performance of the selected adsorbent.

2.4. Instrumentation

A digital orbital shaker (a product of PCSIR Pakistan) was used at room temperature to properly mix the biosorbent and dye, and a UV-visible spectrophotometer (Model UV 3000 Hamburg, Germany) was used to measure the absorbance.

3. Results and Discussion

3.1. Comparison of the Adsorption Efficiency of Different Parts of *C. lawsoniana* Plant

Comparative research on the adsorption efficiency of *C. lawsoniana*'s fruit, leaves, and bark was carried outin order to choose the most appropriate section. As a result, all three components were dried and ground in a manner akin to that described for fruit in the experimental section. The powder was then used as an adsorbent. To examine the adsorption efficiency, a 50 ppm solution of RhB was prepared, and 10 mL of it was added to each of three 100 mL beakers. Figure 2 compares the percent RhB removal, the dye concentration at equilibrium after adsorption (Ce), and the adsorbent's adsorption capacity at equilibrium (Qe). Fruit was more effective than leaves and bark at removing RhB dye from an aqueous solution. As a result, the fruit's ability to remove RhB dye from the aqueous solution was further investigated in order to clean wastewater in the real world.

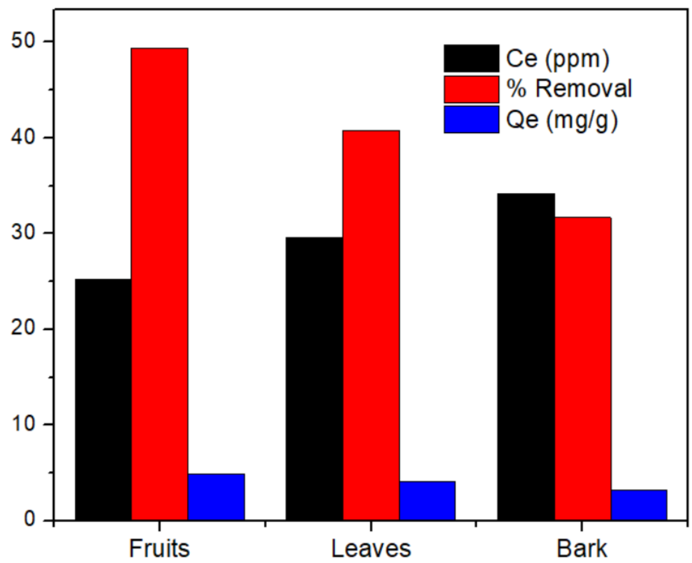

Figure 2. Comparison of different parts of *C. lawsoniana* in terms of Ce, Qe, and % RhB removal at 10 mL of RhB (50 ppm), 50 mg of adsorbent, and a contact time of 70 min.

3.2. Effect of pH on Adsorption of RhB

The pH of a 20 ppm RhB solution was changed using 0.1 M HCl solution and 0.1 M NaOH solution in the range of 1–14 to study the effect of pH on adsorption. After maintaining the desired pH, the absorbance was measured, 40 mg of powdered fruit of *C. lawsoniana* was added to each beaker, and the beakers were shaken vigorously on a digital shaker for 70 min. Following shaking, filter paper was used to remove adsorbent particles from each solution. The solution's absorbance was then measured, and Figure 3 shows the effect of pH on adsorption of RhB dye. The colour of RhB did not change following the addition of HCl and NaOH solutions, preserving the pH of the solutions in the range of 1–14, demonstrating that the pH had a major effect on the adsorption process.

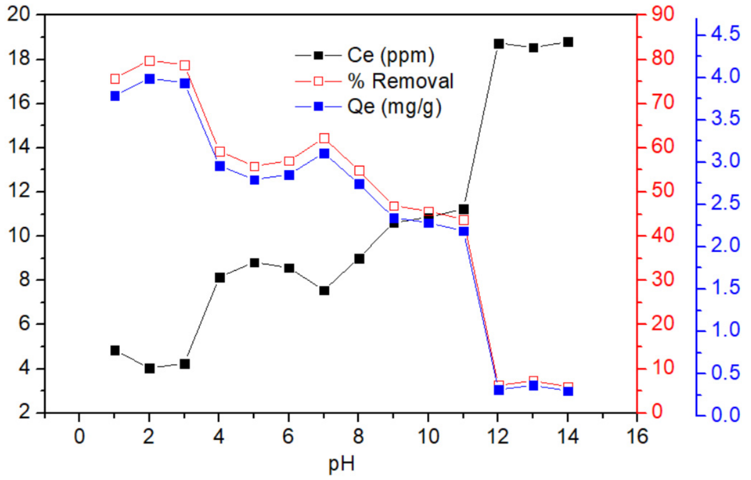

Figure 3. Effect of pH on adsorption of RhB dye under experimental conditions, i.e., 10 mL of aqueous solution of RhB (20 ppm), 40 mg of adsorbent, and a contact time of 70 min.

Figure 3 demonstrates that the adsorbent exhibited the highest adsorption capacity between pH 1–3 with an 80% removal of RhB. The efficiency of the adsorbent steadily declined when the acidity was reduced, and up to pH 11, RhB was removed by 45%. The adsorption capacity was shown to rapidly decline in alkaline solution before maintaining constant at pH 12–14 with just 5% RhB removal. At these lower pH levels, i.e., pH < 4, the RhB dye molecules exist in monomeric and cationic forms, which makes adsorbent more effective at removing the dye. The dye molecule does produce dimer since it is in the zwitterionic state at higher pH values, i.e., pH > 4.0. Kooh et al. [29] hypothesized that the electrostatic forces might not be the only cause driving dye adsorption at the adsorbent surface despite the positive charge of the RhB molecule. RhB monomers are smaller than RhB dimers, which makes them easier to diffuse into the micropores of the adsorbent surface. As a result, the capacity for dye adsorption removal was better at lower pH levels.

3.3. Effect of Ionic Strength on Adsorption of RhB

The effect of ionic strength was studied on the adsorption efficiency of the powdered fruit of *C. lawsoniana* to remove RhB. The ionic strength of the solution was varied by the addition of the neutral salt i.e., NaCl. The adsorption was studied at pH 2, 40 ppm RhB, 50 mg of adsorbent, and a contact time of 105 min (i.e., optimized conditions) in 0.1 to 0.5 M NaCl. The experiment was repeated three times for accuracy. The results showed that the adsorption process is unaffected by the ionic strength (Figure 4). Therefore, confirming that the diffusion of RhB on the adsorbent's surface plays a major role in the adsorption of dye rather than electrostatic interactions between RhB and adsorbent. According to the kinetic studies, the rate constant, and therefore the rate of reaction, increases with ionic strength when an interaction occurs between similar charges and decreases when the interaction occurs between dissimilar charges. However, no effect is shown when an ionic species interacts with a neutral species, therefore helping to conclude that the adsorption may entirely occur by diffusion of monomeric RhB into the micropores of the adsorbent surface in strong acidic environments. Thus, the *C. lawsoniana* fruit can be effectively used in saline water to remove various pollutants.

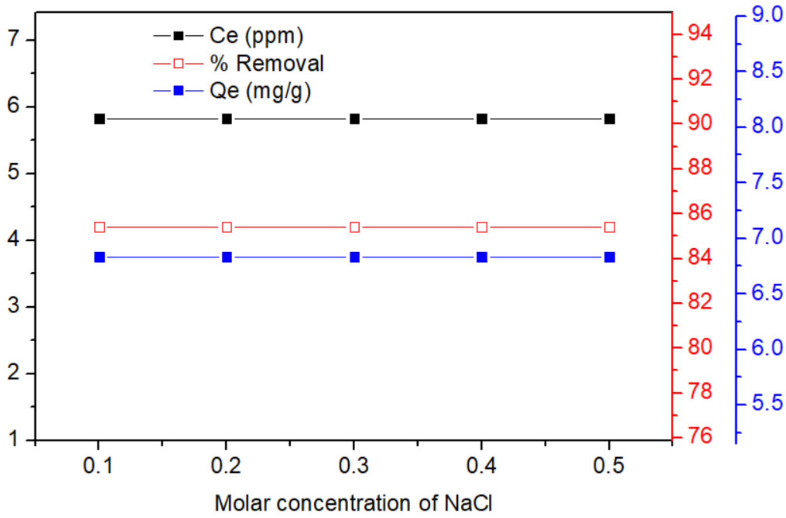

Figure 4. Effect of ionic strength on the adsorption of RhB by *C. lawsoniana* at pH 2, 40 ppm RhB, 50 mg of adsorbent, and acontact time of 105 min.

3.4. Effect of Initial Concentration of Dye on Adsorption of RhB

The effect of increasing dye concentration, from 10 to 70 ppm, on adsorption parameters, including the percent removal of RhB, adsorbent's adsorption capacity, and equilibrium dye concentration at pH 2, was examined. The highest percent removal (80.87%) of RhB at a concentration of 40 ppm dye is shown in Figure 5. Further raising the dye's concentration lowers the percentage of elimination. Due to the increasing percentage removal of RhB, the equilibrium dye concentration was initially low at a low initial dye concentration and high at a high initial dye concentration because of less precent removal. As the dye concentration rises, the equilibrium shifts slightly in favour of adsorption, increasing the amount of dye loaded per unit mass of the adsorbent, while the adsorption capacity (Qe) of the adsorbent grows gradually and nearly remains constant (~7 mg/g) between 40 and 60 ppm RhB with a slight increase (Qe = 7.5 mg/g) up to 70 ppm. This might be because the active sites of the adsorbent that are available for adsorption were occupied by the adsorbent. Thus, 50 mg of adsorbent can effectively remove dye up to the concentration of 40 ppm in a 70 min time period.

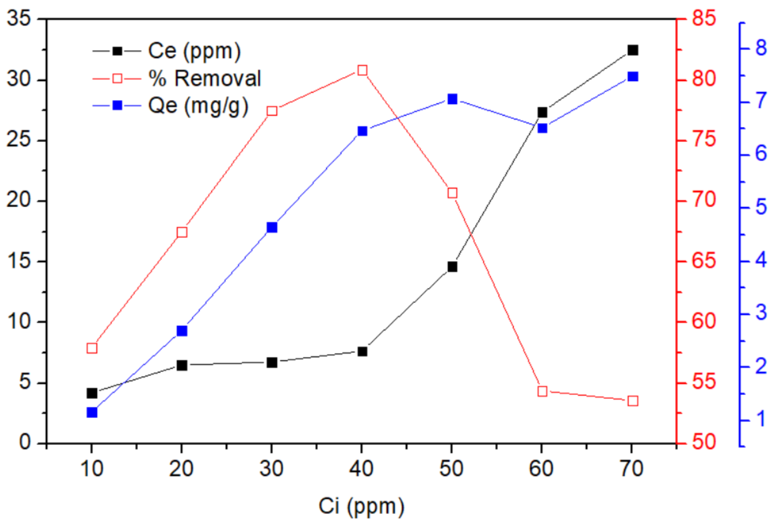

Figure 5. Effect of initial concentration of dye on the adsorption parameters at 10 mL solution of RhB (10–70 ppm), 50 mg of adsorbent, a contact time of 70 min, and a pH of 2.

3.5. Effect of Contact Time on the Adsorption of RhB

The amount of time that the adsorbent spends in contact with the adsorbate has a major effect on the rate of adsorption. As a result, contact time has a significant role in the adsorption process. Greater adsorption will be encouraged by a longer contact time. After the pH and initial dye concentration were optimized, the optimal time to achieve maximum adsorption was identified. The adsorption parameters in Figure 6 show that the maximum adsorption occurs at 105 min. At 105 min, both the maximum percent removal and the adsorbent's adsorption capacity are reached, and since it is conceivable that all the adsorbent's active sites are occupied at that time, no more adsorption may take place. The 105 min contact duration between the adsorbent and the adsorbate was therefore the subject of additional investigations.

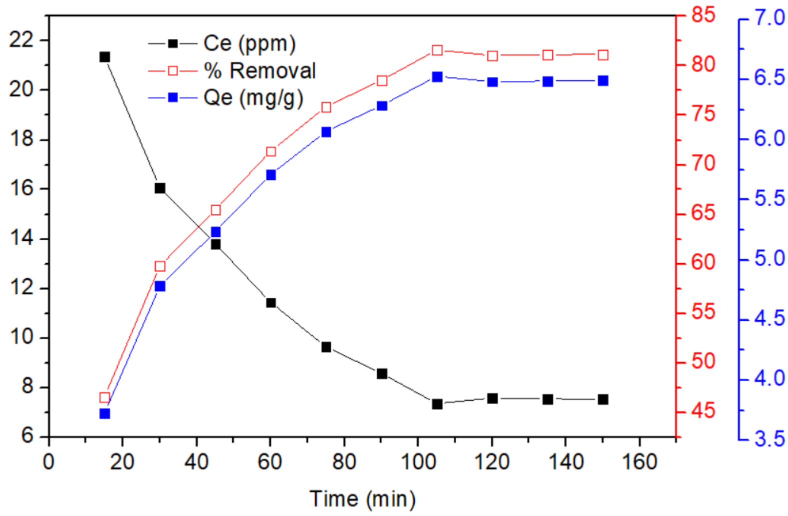

Figure 6. Effect of contact time between adsorbent and adsorbate on the adsorption of RhB at experimental conditions such as 10 mL of 40 ppm solution of RhB and 50 mg of adsorbent at pH 2.

3.6. Effect of Adsorbent Dose on the Adsorption of RhB

The mass of the adsorbent is crucial to the adsorption process. Therefore, it is essential to optimize the mass of adsorbent at which maximum adsorption takes place. Each adsorbent has a unique adsorption capacity, which has quantifiable identification such as the amount of adsorbate that is loaded onto or taken up by each unit mass of the adsorbent in mg/g. A stock solution containing 40 ppm of adsorbate (RhB dye) was prepared, and the pH was maintained at 2. The solution was divided into eight equal-sized beakers, each holding 10 mL of the solution. Then, different adsorbent dosages (from the powdered fruit of the *C. lawsoniana* plant), ranging from 10 to 80 mg, were added to RhB dye solutions, which were then shaken for 105 min on a digital orbital shaker. Following that, filtration was performed, and the filtrate's final absorbance was recorded. As indicated in Figure 7, the adsorption parameters were determined and displayed against the dose of the adsorbate. It is important to note that the elimination of RhB dye rose steadily as the adsorbent dose increased. Qe was 6.833 mg/g for 50 mg of adsorbent, and the removal rate was 85.42%. This is due to the fact that more adsorbent increases the surface area and number of pores, which leads to greater removal efficiency given the availability of the higher number of active sites [30]. After 50 mg of adsorbent, there is no discernible difference in the percent removal because the adsorbent aggregates, making it impossible for the adsorbate to effectively access the active sites. As a result, as the amount of adsorbent is increased, the adsorption capacity (Qe) and equilibrium dye concentration decrease.

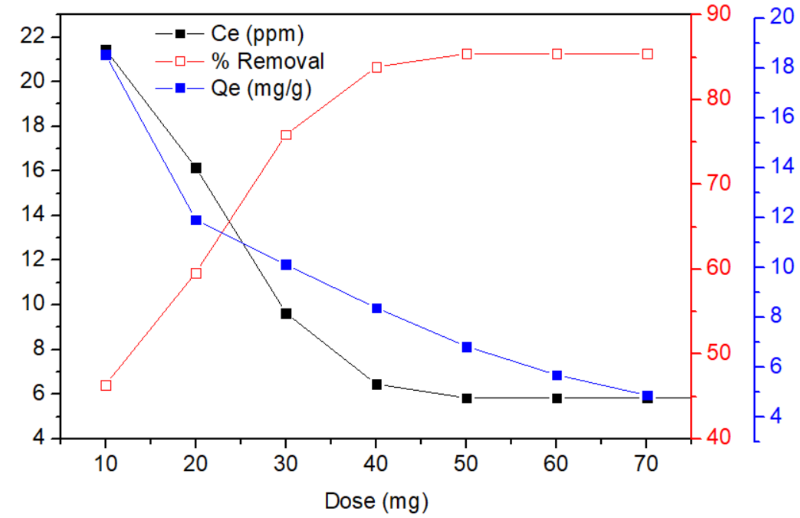

Figure 7. Effect of adsorbent dose on the adsorption of RhB.

3.7. Comparative Analysis of the Adsorption of RhB in Real Water Samples

Different aqueous media, including tap water, distilled water, river water, and filtered river water, were used to prepare the solutions in order to test the effectiveness of the adsorbent for removing the RhB dye at the commercial level. Adsorption was carried out under optimal conditions, including pH 2, a contact time of 105 min, 50 mg of adsorbent, and a dye solution with a concentration of 40 ppm. The comparison of Ce, Qe, and the percentage of RhB removed in various water samples is shown in Figure 8. It is clear that the adsorbent performs well not just with distilled water but also with tap water, river water, and filtered river water. The statistics show that RhB was eliminated from tap water, river water, filtered river water, and distilled water with the following mathematical percentages: 85.42, 76.00, 74.18, and 65.17, respectively. In order to conserve water resources, this adsorbent made from *C. lawsoniana* fruit can be used commercially to treat wastewater including dye pollutants such as RhB and other contaminants.

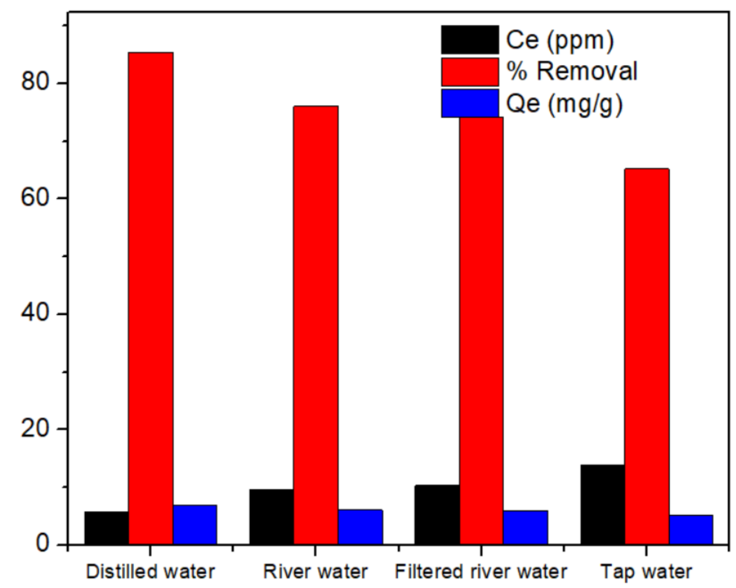

Figure 8. Comparative analysis of the adsorbent's efficiency in real water samples at 10 mL of 40 ppm dye solution, pH 2, a contact time of 105 min, and an adsorbent dose of 50 mg.

3.8. Comapartive Analysis of the Efficiency of the Sun-Dried Powdered Fruit of C. lawsoniana Plant with Conventional Adsorbents

The effectiveness of the adsorbent was evaluated and compared to other common adsorbents, including silica gel and animal charcoal. According to Figure 9, silica gel removed 87.90% of the RhB dye, animal charcoal removed 88.76%, and *C. lawsoniana* plant's dried powdered fruit removed 85.42%. The amount of RhB dye removed from aqueous solution using this bio-sorbent is therefore very close to that of conventional adsorbents, which are processed to modify their surface before being used to remove dyes. As a result, this bio-sorbent is relatively inexpensive, easily accessible, and can be used without modification. Table 1 compares our investigation with the published literature, and it is evident that the *C. lawsoniana* plant's fruit exhibits higher or comparable adsorption efficiency to other adsorbents reported in the literature.

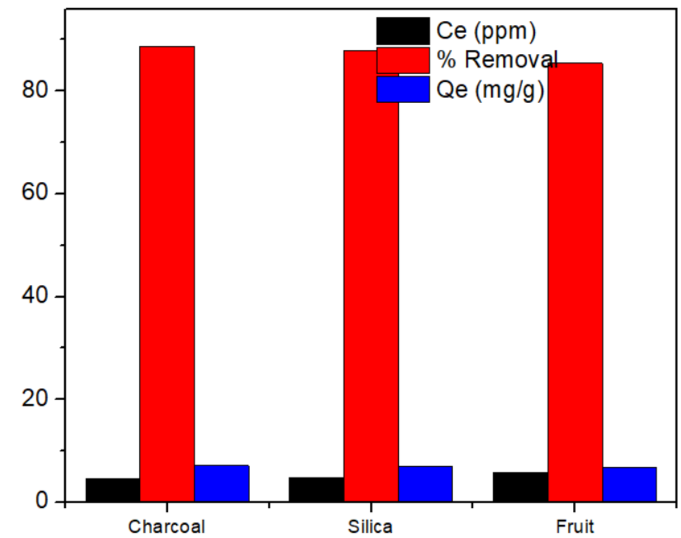

Figure 9. Comparative analysis of the adsorption efficiency of dried powdered fruit of *C. lawsoniana*, animal charcoal, and silica gel at 10 mL of 40 ppm dye solution, pH 2, a contact time of 105 min, and an adsorbent dose of 50 mg.

Table 1. Comparisonof the adsorption capacity of dried powdered fruit of *C. lawsoniana* with other bio-adsorbents.

S.No.	Adsorbent	pH	Conc. (ppm)	Time (min)	Dose (g)	% Removal	References
1	*Artocarpus odoratissimus* leaves	3	100	30	0.5	81	[31]
2	Spent tea leaves	3	20	120	0.25	14	[32]
3	Pinecone charcoal	2.4	75	60	2.0	80	[33]
4	*Causuarina equisetifolia* needles	4.4	20	20	0.04	85	[29]
5	Activated banana peel carbon	2	120	60	12	85	[34]
6	*C. lawsoniana* sundried powdered fruit	2	40 ppm	105	0.5	85.42	This study

3.9. Kinetic Study

The kinetics of RhB dye adsorption by the sun-dried powdered *C. lawsoniana* fruit was studied. The conventional pseudo-first-order (PFO) [35] and pseudo-second-order (PSO) Equations (3) and (4) [36] were applied to determine the order of the adsorption process. Kinetic studies reveal important information about the reaction pathway, the mass transfer mechanism of dye adsorption, and the diffusion rate [37].

$$\log [Qe - Qt] = \log Qe - [k_1/2.303]t \quad (3)$$

$$t/Qt = 1/[k_2Qe^2] + t/Qe \quad (4)$$

where Qt (mg/g) is the adsorption capacity at time t (min), Qe (mg/g) is the adsorption capacity at equilibrium, k_1 (min^{-1}) is the pseudo-first-order rate constant, and k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order rate constant. Figure 10 displays the results of the linear fitting of kinetic models to experimental data points. The PSO model, which has a higher R^2 value when compared to the PFO model given in Table 2, helps to determine the adsorption kinetics. This is shown in Figure 10. Additionally, the pseudo-second-order model's experimental Qe value is quite close to the predicted Qe, indicating that this model is the one that best fits our adsorption experimental data [38].

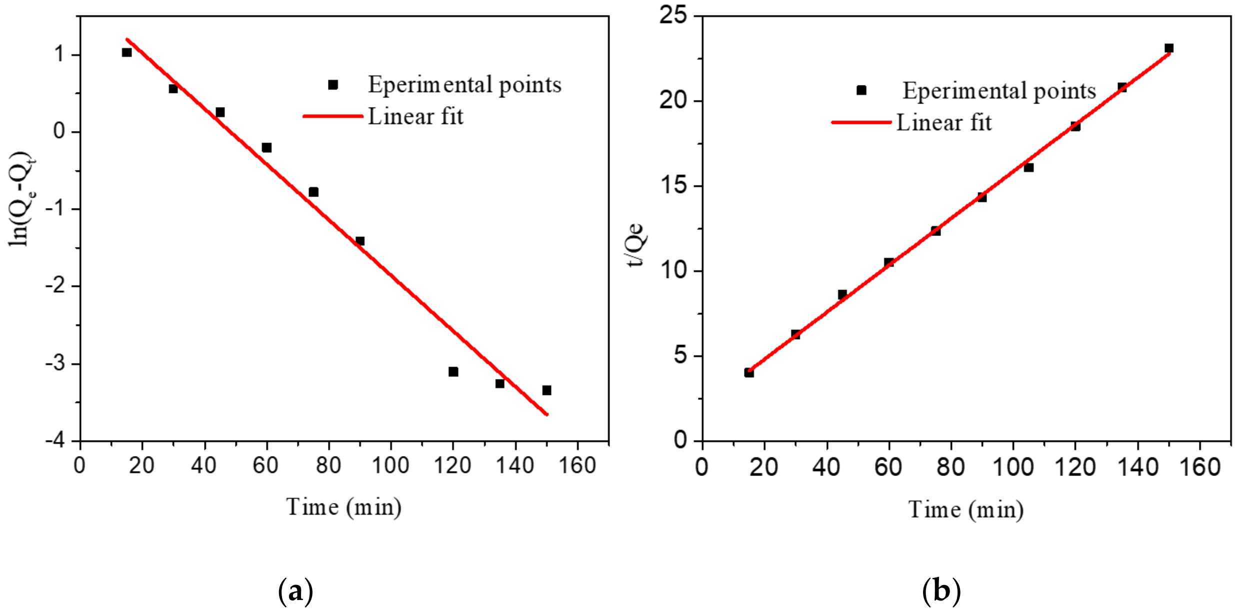

Figure 10. Plots of the (**a**) pseudo-1st-order, and (**b**) pseudo-2nd-order kinetics models for RhB dye adsorption onto *C. lawsoniana* fruit under experimental conditions such as 10 mL of 40 ppm solution of RhB, 50 mg adsorbent at pH 2.

Table 2. Kinetic parameters for RhB dye adsorption onto *C. lawsoniana* fruit.

Experimental	**Pseudo-1st-Order**			**Pseudo-2nd-Order**		
Qe (mg/g)	**Qe (mg/g)**	**k_1 (min^{-1})**	**R^2**	**Qe (mg/g)**	**k_2 (g mg^{-1} min^{-1})**	**R^2**
6.83	5.69	−0.00024	0.97	7.24	0.0092	0.998

4. Conclusions

The bio-adsorbent made from the powdered fruit of the *C. lawsoniana* plant was used in this investigation. In comparison to other conventional and previously reported adsorbents and biosorbents, this study identifies a biosorbent that is affordable, environmentally benign, and accessible. Adsorption is primarily caused by dye diffusion in the adsorbent's (fruit of *C. lawsoniana* plant) surface micropores rather than electrostatic forces between the adsorbent's surface and the adsorbate, according to the effects of various experimental parameters, including the pH, adsorbent and adsorbate concentration, adsorbent and adsorbate contact time, and ionic strength. The study also showed that the adsorption process is the most effective at lower pH levels, which allows our chosen adsorbent to more effectively clean acidic wastewater containing RhB. The adsorbent displayed good performance in all types of water samples, including tap water, distilled water, river water, and filtered river water. As a result, this bio-adsorbent can be used to effectively remove dyes from wastewater on a commercial scale without the need for additional surface treatment by chemicals.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14192987/s1, Figure S1: Absorbance as a function of wavelength for aqueous solution of RhB dye.

Author Contributions: Conceptualization, S.G., M.G. and H.G.; methodology, S.G. and R.K.; software, M.G., H.G., R.K. and G.R.; formal analysis, M.G., H.G., G.R., M.S.K. and H.A.A.; investigation, M.G., H.G., M.S.K. and H.A.A.; resources, S.G. and R.K.; data curation, M.G.; writing—original draft preparation, H.G.; writing—review and editing, R.K.; visualization, H.G. and R.K.; supervision, S.G.; project administration, S.G.; funding acquisition, S.G. and R.K. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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