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Original Article

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Reactive Blue 203 dye Removal Using Biosorbent: A Study of Isotherms, Kinetics, and Thermodynamics

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Abstract

Nowadays, due to increasing usage of dye in various industries and its destructive effects on health and environment, it is necessary to remove dyes from industrial wastes. Although few studies can be found on using pine cone for removal of different dyes, it has not been used yet to remove Reactive Blue 203 (RB203) dye. The purpose of this study is to investigate RB203 dye adsorption using activated carbon produced from pine cone. Optimal values of influencing factors for RB203 dye removal were obtained. The results showed that the maximum removal was occurred at a pH of 2, temperature of 30˚C, dye concentration of 30 mg/L, adsorbent dosage of 100 mg/L, and contact time of 15 min. The maximum removal percentage was 98.48%. In order to study the synthesized activated carbon, some characterization methods including scanning electron microscopy (SEM), Fourier-transform infrared (FT-IR) spectroscopy and Brunauer-Emmett-Teller (BET) have been used. Investigation of adsorption isotherm models revealed that adsorption of RB203dye can be described through D-R and Temkin isotherm models. Additionally, RB203 dye removal follows the pseudo-first-order kinetic equation.

Keywords: Pine cone, Adsorption, Activated carbon, Thermodynamics, Coloring agents, Kinetics

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1. Introduction

Currently, thousands of dyes are consumed in paper, food, textile, rubber, plastic, carpet, and cosmetic industries around the world; therefore, parts of this material from these industries enter the environment through the wastewater (1). The entrance of dyes may disrupt the photosynthesis in aquatic plants by reducing the penetration of light. Even at very low concentrations, the dyes reduce the clarity of the water. Since some dyes and combinations resulting from their decomposition are toxic, mutagenic, and carcinogenic, dye removal from the wastewater is very necessary. The most important dyes that enter the environment through dyeing industries are reactive dyes (2,3). Reactive dyes are vital for dyeing cellulose fibers due to the speed and intensity of dyeing.

Due to the solubility of reactive dyes in water, it is very difficult to remove them by coagulation and biological decomposition (4). Different methods including advanced oxidation (5), reverse osmosis (6), electrochemical method (7), ozonation (8), and biological methods such as the use of fungi and bacteria (9) have been used for dye removal. Each of these methods has some advantages and disadvantages. For example, in reverse osmosis, energy consumption is high because it requires high pressure. In the clotting method and coagulation with collagens, a lot of sludge is produced. The photochemical oxidation method is not economical and produces secondary products (10).

Among the physical methods, adsorption is the most important and practical methods (11). Adsorption is an inexpensive method, with a simple design, easy application and high efficiency (12,13). There are different useful adsorbents such as activated carbon, silica gel, activated alumina, and zeolites. Recently, many studies have been conducted by researchers about the use of natural adsorbents. Agricultural wastes can be used as a cost-effective, accessible and environmentally friendly adsorbent for dye removal from industrial wastewater (14). In previous studies, dye adsorption has been investigated by activated carbon from agricultural wastes such as hazelnut, coffee bean, corn, bamboo, sesame cotton, apricot stone, cherry stone, coconut skin, palm tree, rice husk, and grape tree branch (15-18). Although several investigations have been carried out on using pine cone to remove various dyes, it has not yet been employed to remove Reactive Blue 203 (RB203) dye. RB203 is an important anionic dye which is highly toxic. This dye is frequently used in textile industries; therefore, it is important to investigate RB203 dye removal. Pine cone powder is an abundant and inexpensive adsorbent which can be efficiently used to remove dye from wastewater. Since a large amount of pine cone is grown worldwide, it is accessible for wide usage. In this study, equilibrium studies were carried out using 6 different models of isotherm equations to describe dye adsorption mathematically. The aim of this study was to investigate the removal of RB203 dye using activated carbon produced from pine cone. Moreover, different isotherms, kinetics, and thermodynamic studies were done which are essential to design a wastewater treatment plant on a large scale.

2. Materials and Methods

2.1. Reagents and Materials

The RB203 dye with the formula of $C_{25}H_{29}N_5O_{21}S_6Na_4$ and a molecular weight of 617.54 g/mol was obtained from Alvan Company, Hamedan, Iran. HNO_3, NaOH, H_3PO_4 were purchased from Sigma-Aldrich Company. Pine cones were obtained from the campus of Jami Institute of Technology of Isfahan in Iran.

In order to prepare the standard solution, at first, the stock solution (1000 mg/L) was prepared. Then, other solutions were obtained by diluting the stock solution. To adjust pH, HNO_3 and NaOH (0.1 M) were used.

2.2. Apparatus

A single-radiation UV-visible spectrophotometer (UV-2100PC, JENUS, China) was used for absorbance measurements of samples. In this study, the concentration of RB203 dye was spectrophotometrically measured at a wavelength of 625 nm (19). A digital pH meter (Jenway 3020, UK) was used for pH measurements. The adsorbent was separated from the solution by centrifugation (Sigma101, 5000 rpm). In order to mix the solutions, a magnetic stirrer (MR3001, Heidolph, Germany) was used. A furnace with vacuum chamber under helium gas (Heraeus, Germany) was used to produce activated carbon from pine cone. The morphology of activated carbon derived fro m pine cone was evaluated using a scanning electron microscope (SEM) (XLC30, Philips, Netherland). A digital scale (Extended Taiwanese model) with a precision of 0.001 g was used to measure the materials. FT-IR (Tensor model, Germany) was used to study the functional groups of active carbon derived from pine cone. In this study, all the experiments were performed in duplicate to ensure that the results are trustworthy.

2.3. Preparation of Adsorbent

First, pine cones were crushed and washed several times with distilled water to eliminate possible contamination. Then, it was placed at 80˚C temperature for 24 hours until it was completely dried. In the end, it was turned into powder. To produce activated carbon derived from pine cone, 20 mL of 1M H_3PO_4 was added to 10 g of pine cone powder for chemical activation and then it was completely mixed and washed with distilled water to remove excess acid from the adsorbent surface (20). The modified powder with phosphoric acid was then placed in a furnace with vacuum chamber under helium gas at 650˚C for 2 hours (21).

2.4. Evaluation of Effective Parameters

2.4.1. Evaluation of pH

One of the important factors in dye removal experiments is the investigation of the effect of pH. The pH value is a very effective parameter in the adsorption process because hydroxyl and hydrogen ions are adsorbed on the adsorbent, so the adsorption of other ions is affected by the pH of the solution. For investigating the effect of pH, 6 dishes containing 50 mL of dye solution with a concentration of 30 mg/L were prepared. Then, 0.05 g of activated carbon from the pine cone as adsorbent was added to the dishes. The pH values of the solutions (1, 2, 3, 4, 8 and 12) were adjusted by HNO_3 and NaOH (1M). After 15 minutes, the solutions were placed in a centrifuge machine for better separation. Finally, the solutions were filtered using filter paper. The absorption of solutions was then read by the UV-visible spectrophotometer at a wave length of 625 nm and compared with the initial absorbance before adding adsorbents.

2.4.2. Evaluation of Adsorbent Dosage

The adsorbent dosage is another factor affecting dye removal in the adsorption process. The removal percentage of RB203 dye was separately calculated for 50 cc solutions with a concentration of 30 mg/L dye, a pH of 2, and a contact time of 15 minutes for dosages of 0.005, 0.01, 0.05, 0.1, 0.3 and 1 g of activated carbon from pine cones as adsorbent. All experiments were carried out at ambient temperature.

2.4.3. Effect of Dye Concentration on Removal Process

Another effective parameter studied in this work is the effect of the initial concentration of the RB203 dye solution on dye removal by carbon activated from pine cones. For this purpose, 6 containers containing 50 cc of dye were prepared at 5, 10, 20, 30, 40 and 50 mg/L concentrations. Then, 100 mg/L of adsorbent was added to each container and the pH of all containers was adjusted to 2. Then, the dye removal percentage was calculated at the contact time of 15 minutes.

2.4.4. Evaluation of the Contact Time

The contact time in the dye removal process through adsorption is also one of the most important factors. To investigate the effect of contact time on the removal of RB203 dye, 6 containers containing 50 cc of dye at a concentration of 30 mg/L and a pH of 3 and 100 mg/L of adsorbent were prepared. Then, the percentage of dye removal at contact times 5, 10, 15, 30, 45, and 60 minutes were calculated. All experiments were carried out at ambient temperature.

2.4.5. Evaluation of the Temperature

Temperature is another important parameter in the study of the chemical-physical process since the absorption capacity will change with increasing or decreasing temperature. To investigate the effect of temperature on the RB203 dye removal, 6 containers containing 50 cc of dye at a concentration of 30 mg/L and a pH of 3 and 100 mg/L of adsorbent were prepared. Then, the percentages of dye removal at the contact time of 15 minutes and temperatures of 25, 30, 35, 40, 45 and 50°C were calculated.

2.5. Equilibrium Isotherm Modeling

Adsorption isotherms indicate the relationship between the amount adsorbed on the adsorbent and the adsorbed concentration in solution in equilibrium. There are many models to express the relationship between the adsorption and the residual dye concentration in solution. In this study, Langmuir, Freundlich, Temkin, Generalized, Dubinin-Radushkevich (D-R), and Jovanovic isotherms were investigated (22,23).

Langmuir isotherm: At first Langmuir isotherm was developed to describe gas-solid phase adsorption. Langmuir isotherm calculates the surface coverage by balancing the relative rates of adsorption and desorption. Adsorption depends on the fraction of the adsorbent surface that is free, while desorption depends on the fraction of the adsorbent that is covered. Langmuir isotherm model is used to investigate the sorption of aqueous compounds in the solid phase.

Langmuir isotherm is shown in equation (1).

$$\frac{C_e}{(x/m)} = \frac{1}{ab} + \frac{1}{a}C_e \quad (1)$$

Where C_e is the equilibrium concentration of the adsorbed dye in the solution after adsorption, *x/m* is the amount of adsorbed dye per weight of the adsorbent, and the parameters *a* and *b* are Langmuir constants.

Freundlich isotherm: The Freundlich equation expresses the adsorption for a heterogeneous surface. Freundlich isotherm expresses the energy of active sites and their exponential distribution on heterogeneous surfaces. The linear form of the Freundlich isotherm is defined as equation (2).

$$\log(\frac{x}{m}) = \log K_f + \frac{1}{n}\log(C_e) \quad (2)$$

Where *n* and K_f are the constant coefficients of the Freundlich isotherm.

Temkin isotherm: The effects of indirect adsorbate/adsorbate interactions on the adsorption process can be estimated through the Temkin isotherm model. However, it should be noted that Temkin isotherm model is valid only for an intermediate range of ion concentrations (24).

The linear form of Temkin isotherm is shown in equation (3).

$$q_e = \frac{RT}{b_T}\ln K_T + \frac{RT}{b_T}\ln C_e \quad \mathbf{(3)}$$

Where q_e is the equilibrium adsorption capacity, R is common gas constant, *R* is universal gas constant (8.314 J/mol.K), *T* is absolute temperature, and $\frac{1}{b_T}$ is the Temkin constant (24).

Generalized isotherm: The Generalized isotherm is shown in equation (4).

$$\ln\left[\left(\frac{q_{max}}{q_e}\right) - 1\right] = \ln(K_G) - N\ln(C_e) \quad (4)$$

Where K_G is the saturation constant, *N* is the cooperative binding constant, and q_{max} is the maximum adsorption capacity of the adsorbent.

D-R isotherm: The D-R model explains the adsorption mechanism using Gaussian energy distribution on heterogeneous surfaces (25). The D-R model, like the Tamkin model, is valid only for an intermediate range of ion concentrations. The D-R isotherm is shown in equation (5).

$$\ln q_e = \ln q_m - B[RT\ln\left(1 + \frac{1}{C_e}\right)]^2 \quad (5)$$

Where *B* is the Dubinin-Radushkevich constant, which is related to energy.

Jovanovic isotherm: This model is used to describe adsorption equilibria on heterogeneous surfaces. The linear form of the Jovanovic model is shown in equation (6).

$$\ln q_e = \ln q_{max} - K_J C_e \quad (6)$$

Where K_J is a constant coefficient of Jovanovic and q_{max} is maximum uptake of adsorbate obtained from the plot of $\ln q_e$ versus C_e (26).

2.6. Analytical Methods

To calculate the maximum wavelength of the RB203 dye, the absorbance of a 100 mg/L solution in the range of 200 to 700 nm was read by UV-visual spectrophotometer. The maximum absorption of RB203 was achieved at 625 wavelengths. In all subsequent experiments, the wavelength was adjusted to 625 nm. Equation (7) was used to determine the percentage of removal of dye:

$$\text{Decolourization}(\%) = \frac{A_0 - A}{A_0} \times 100 \quad (7)$$

In this equation, A_0 is the initial absorption rate of dye solution without the presence of absorbent and A is the final absorbance value of the dye solution after adding the adsorbent (19). To prepare the calibration curve, solutions with different concentrations (in mg/L range) were prepared and subsequently, the absorbance of each solution was read by UV-visual spectrophotometer. Using the calibration curve, the value of $R^2=0.9922$ was achieved.

3. Results and Discussion

3.1. Characterizations of Adsorbent

The SEM was used to determine the size of activated carbon particles obtained from the pine cones (Figure 1). BET test was used to determine the surface area of dry powders (Figure 2A). The results of BET test are summarized in Table 1. In addition, FTIR spectra were selected to study the functional groups of activated carbon derived from the pine cones (Figure 2B).

In addition, FTIR spectra were selected to study the functional groups of activated carbon derived from the pine cones. The peak area of 1500 and 3350 cm^{-1} is related to tensile and bending vibrations of the NH_2 group from the absorbing structural unit. The peak appearing in the 1230 cm^{-1} region of the N-C gradient vibrations and the absorbing bar in the 2900 cm^{-1} region shows the tensile vibrations of the H-C aliphatic (CH_3) sp^3 (Figure 2B).

According to the NH_2 functional group, which is found in the active carbon structure of the pine cone, one can justify RB203, which is an anionic dye. The adsorption mechanism of RB203 dye is shown below (equation 8- 10) (27).

$$-NH_2\ (\text{pinecone}) \overset{H^+}{\leftrightarrow} -NH_3^+ \qquad (8)$$

$$\text{dye} - SO_3Na \xleftrightarrow{\text{dissociation}} \text{dye} - SO_3^- + Na^+ \qquad (9)$$

$$-NH_3^+ + \text{dye} - SO_3^- \longleftrightarrow NH_3^+\ {}^-O_3S - \text{Dye} \qquad (10)$$

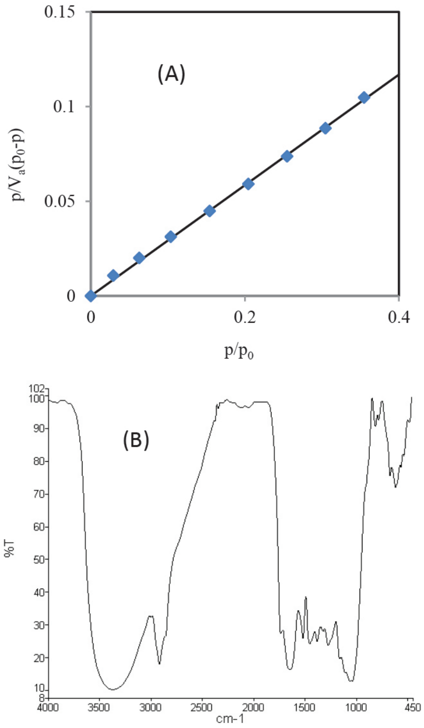

Figure 2. BET Plot of N2 Adsorption–desorption Isotherms of Pure Activated Carbon (A) and FT-IR Spectra Related to Activated Carbon from Pine Cones (B).

3.1. The effect of pH on the Dye Removal Process

According to Figure 3, the best pH value is 2. It was found that by decreasing the pH, the efficiency of the adsorption increases sharply and the efficiency decreases with increasing pH. In other words, at acidic pH, NH_2 groups of activated carbon from pine cone are protonated and converted to NH_3^+. The NH_3^+ groups are indispensable for the interaction between the sulfonic group in the RB203 dye and activated carbon. As a result, it increased the electrostatic interaction between functional groups in dye and adsorbent. At a pH higher than 7, the concentration of hydroxyl ions in the solution increases. The hydroxyl ions compete with dye ions for adsorbing on active sites of adsorbent and cause a reduction in efficiency (17).

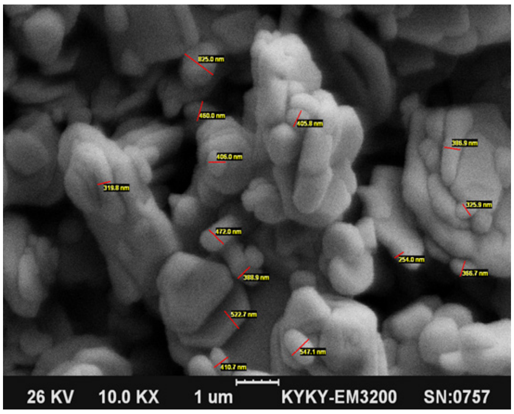

Figure 1. SEM Image of Activated Carbon from Pine Cone.

3.2. Effect of Adsorbent Dosage on Dye Removal Process

The results (Figure 4A) showed that the highest amount of dye removal (98.48%) was obtained using 0.05 g of the desired adsorbent. As the adsorbent dosage is increased, the amount of adsorption of reactive blue dye 203 is expected to increase. Because the number of active adsorption sites increases on the adsorbent, which can be placed in the dye. However, after a while, with the increase of adsorbent amount due to the limited dye concentration, a large number of adsorption sites will remain free (28).

Table 1. Pore Characterization of Pure Activated Carbon From Pine Cone

Adsorbent	Total pore volume (cm^3/g)	Mean pore diameter (nm)	Special surface area (m^2/g)
Activated carbon derived from pine cone	0.00811	2.17	14.8

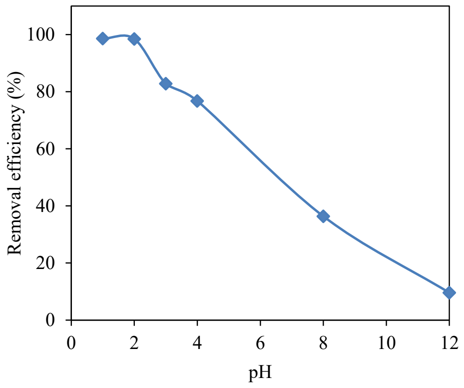

Figure 3. The Effect of pH on the Removal of RB203 by Activated Carbon.

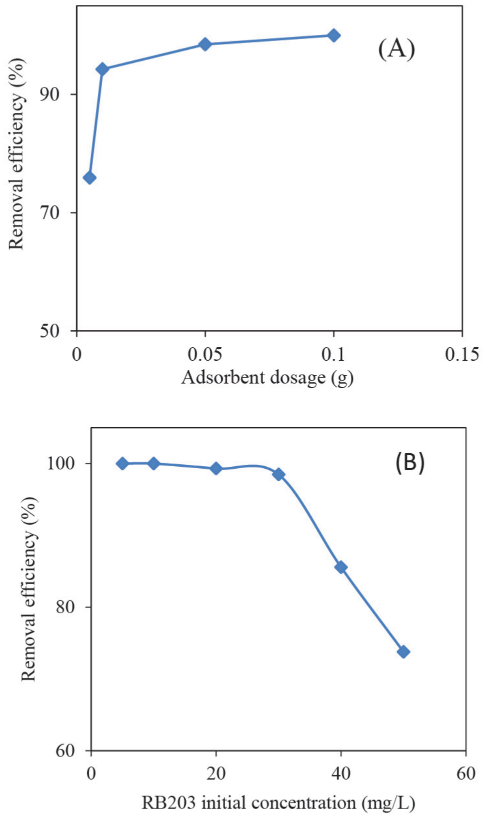

Figure 4. The Effect of Adsorbent Dosage (A) and RB203 Concentration on the Dye Removal (B)

3.3. Effect of Dye Concentration on Removal Process

According to the results of Figure 4B, the dye concentration of 30 mg/L was chosen as the optimum concentration for the mentioned conditions. The results showed that the dye removal efficiency decreases with increasing dye concentration because adsorbents have a limited number of active sites that are saturated at high dye concentrations. In this situation, the adsorbent surface is no longer able to adsorb more dye. Consequently, the percentage of dye removal is reduced. On the other hand, with increasing initial dye concentration, the adsorbent capacity increases, which may be due to the high proton motive force for the mass transfer in the initial dye concentration (29).

3.4. The Effect of Contact Time on the Dye Removal Process

As shown in Figure 5A, with increasing contact time from 5 to 15 minutes, the adsorption efficiency was increased. Because adsorbents have a number of active sites, with increasing contact time, dye adsorption increases on the adsorbent surface. After the optimal time (15 minutes), adsorption sites were saturated, so after this time, there was no significant change in the dye removal percentage (30).

3.5. The effect of temperature on the dye removal process

According to the results of Figure 5B, it could be concluded that, with increasing temperature, the dye removal efficiency decreases. If the amount of adsorption increases with increasing temperature, this might be due to an increase in the number of active sites and an increase in the mobility of dye molecules. If the amount of adsorption decreases while temperature increases,

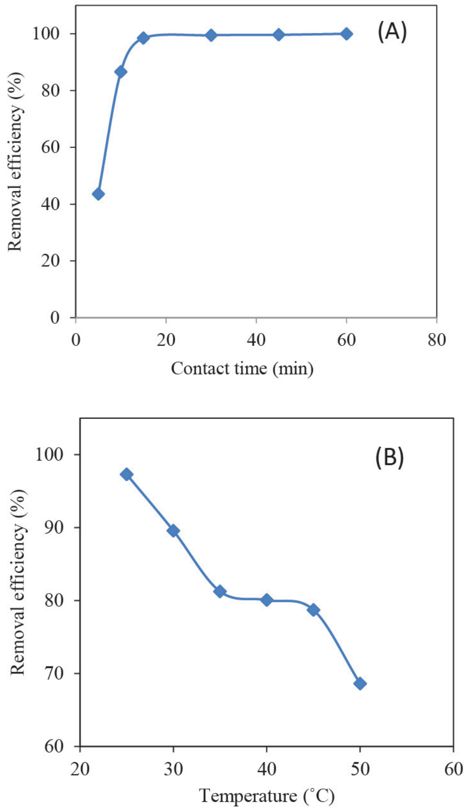

Figure 5. The Effect of Contact Time (A) and Temperature on the Removal of Dye (B)

it indicates that the adsorption process is exothermic. This suggests that with increasing the temperature, the adsorption forces between the active sites and the dye species are reduced at the adsorbent level, which results in the reduction in the amount of adsorption (31).

3.6. The Isotherms

In this work, the equilibrium data for the adsorption of RB203 dye onto activated carbon derived pine cone were analyzed using 6 isotherm models including Langmuir, Freundlich, Generalized, D-R, and Jovanovic isotherms (Figure 6). The best fit isotherm was introduced based on the values of the R^2 of the linear regression plot. As shown in Figure 6, the R^2 values of the D-R and Temkin the isotherm were estimated to be 0.997 and 0.992, respectively. Therefore, D-R and Temkin models are the best models to describe the adsorption data for the RB203 dye removal. Therefore, according to D-R's model, a heterogeneous surface or constant sorption potential was assumed. Moreover, the Temkin isotherm model, like the Freundlich isotherm model, assumes that the fall in the heat of sorption is linear rather than logarithmic (25).

Also Table 2 illustrates the results of using different isotherm models for dye removal by various adsorbents.

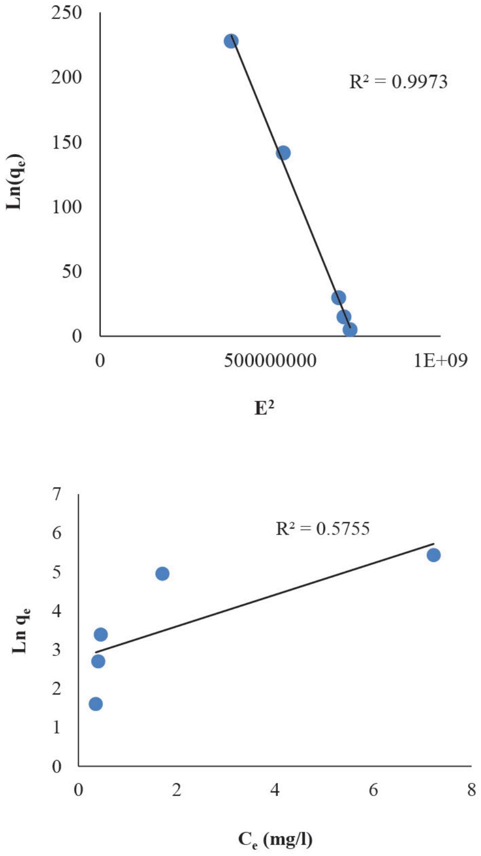

Figure 6. The Results of Fitting for Langmuir, Freundlich, Temkin, Generalized, D-R and Jovanovic Isotherms

3.7. Adsorption Kinetics

Speed is one of the important parameters in every process. By analyzing the speed of the process and adapting it to the most popular kinetic models, a mechanism of reaction can be obtained. In this study, two models were used to evaluate the kinetics of the reaction.

3.7.1. Pseudo-first-order Equation

The linear form of the pseudo-first-order kinetics is equation (11).

$$\ln\left(q_{eq} - q_t\right) = \ln q_{eq} - K_1 t \quad (11)$$

Where q_e and q_t are the amount of RB203 dye adsorbed (mg/g) at equilibrium and at time t (min) and K_1 is the rate constant of adsorption (min^{-1}). Assuming that the variation is linear, K_1 was determined from the slope of the ln ($q_e - q_t$) graph versus t (39).

3.7.2. Pseudo-second-order Equation

In a pseudo-second-order kinetic model, it is assumed that the adsorption process can be controlled by chemical absorption. The pseudo-second-order kinetic form is equation (12).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (12)$$

If the pseudo-second-order equation is applicable, then the t/q_t graph versus t must show a linear relationship. K_2 is the pseudo-second-order kinetic constant calculated from the t/q_t graph versus t (40). Considering the value of R^2 obtained from the graphs of the first and second pseudo-order equations, it can be concluded that the RB203 dye removal follows the pseudo-first-order equation (Figure 7). The R^2 value of the pseudo-first-order was 0.9427. Additionally, it indicates that the reaction is more inclined towards physisorption.

3.8. Standard Free Energy Change

By studying thermodynamics, endothermic and exothermic properties of processes can be investigated. The most important properties of an adsorption process

Table 2. The Results of Different Isotherm Studies on Dye Removal Using Various Adsorbents

Adsorbent	Dye	Isotherm model	Ref
Garlic peel	Direct Red 12B	Langmuir	32
Tamarind hull	Cationic dyes	Freundlich	33
Soy meal hull	Direct red 80 and 81)	Langmuir	34
Pine cone	Basic Red 46	Langmuir	35
Princess tree leaf	Basic Red 46	Langmuir	36
Chitosan	Methylene blue	Freundlich	37
Tea waste	Basic dyes	Freundlich and Langmuir	38
Mango seed	Methylene blue	Freundlich	18
This work	Reactive blue203	D-R and Temkin	-

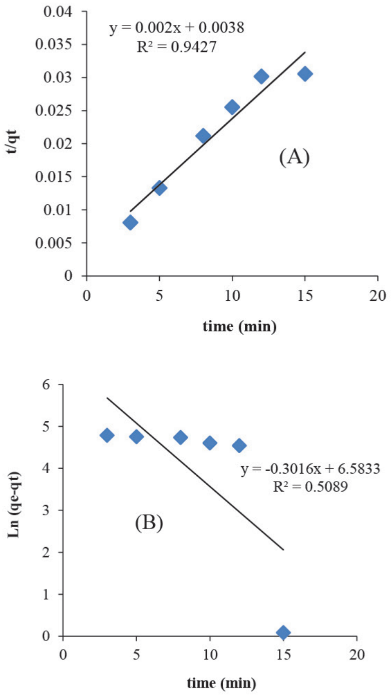

Figure 7. Pseudo-Frist-order Equation (A) and Pseudo-second-Order Equation (B)

include enthalpy changes (ΔH), standard free energy changes (ΔG^0) and entropy changes (ΔS).

Equation (13) is used to determine ΔG^0

$$\Delta G^0 = -RT\ln K_d \quad (13)$$

Where K_d is the equilibrium constant, R is universal gas constant (8.314 J/mol K), and *T* is absolute temperature (41).

K_d was calculated from equation (14).

$$K_d = \frac{q_e}{C_e} \quad (14)$$

Figure 8 shows the plot of lnK_d versus 1/T. Thermodynamic parameters for RB203 dye removal by activated carbon produced by pine cone are summarized in Table 3.

Considering the results of Table 3, the negativity of enthalpy changes is verifying the exothermic nature of RB203 dye adsorption process. The magnitude of enthalpy can give information about the type of adsorption (e.g., physical, chemical or physico-chemical). The negative ΔG° value indicates that the adsorption of RB203 dye is a spontaneous and highly favorable process. The positive ΔS° value reflects the affinity of the pine cone for RB203 dye as well as the increase of randomness at solid-solution interface during dye adsorption (41).

4. Conclusion

In the present work, the process of removing RB203 dye was studied by activated carbon from pine cones as a natural adsorbent. In addition, effective factors in dye removal were considered and optimized. Among the investigated factors, pH was evaluated as the most effective factors on RB203 dye adsorption. As a result, in acidic medium, the maximum removal rate occurred. Among the six isotherm models studied, the equilibrium data fitted well with the D-R and Temkin isotherm models. In addition, the adsorption process follows the pseudo-first-order kinetic equation. When the temperature increases, the dye removal efficiency decreases. Therefore, it could be concluded that the adsorption of RB203 dye was exothermic. Unfortunately, reusability of the biosorbent was not checked in this study; therefore, it is suggested that reusability must be checked for dye removal using pine cones in future studies. The results indicate that the activated carbon produced from pine cone can be used as an excellent adsorbent for removal of RB203 dye from aqueous solution.

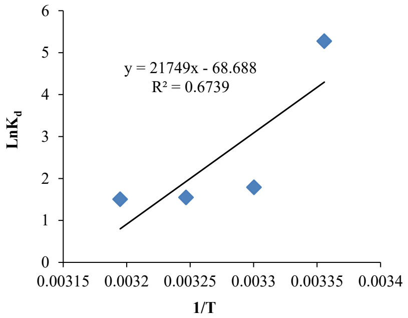

Figure 8. The Plot of the Adsorption of RB203 species onto Activated Carbon.

Table 3. Thermodynamic Parameters for RB203 Dye Removal by Activated Carbon

T (ºK)	ΔH (KJ/mol)	Δs (J/K.mol)	ΔG (KJ/mol)
298	-180.821	571.072	-169998.63

Conflict of Interest Disclosures

The authors declare that there is no conflict of interests that would prejudice the impartiality of this scientific work.

Ethical Issues

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

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