Green synthesis of *Quercus coccifera* hydrochar in subcritical water medium and evaluation of its adsorption performance in BR18 dye

Mohammed Saleh, Zeynep Bilici, Yasin Ozay, Erdal Yabalak, Mutlu Yalvac and Nadir Dizge

**ABSTRACT**

In this study, we investigated the production conditions of hydrochar produced from *Quercus coccifera*, which is an inexpensive and easy available adsorbent, for the adsorption of Basic Red 18 (BR18) azo dye. Hydrochar was produced in the eco-friendly subcritical water medium (SWM). The effects of the pH (2–10), adsorbent size (45–106 μm), adsorbent dose (0.5–1.5 g/L), dyes concentrations (40–455 mg/L), and contact time (5–120 min) were studied through the optimization experiments. The optimum condition was obtained at pH 10, particle size of 45 μm, particle amount of 1.5 g/L, dyes concentration of 455 mg/L, and 60 minutes. The removal efficiency increased sharply for the first 5 min after that the removal efficiency reached a steady state at the 60 min with maximum removal of 88.7%. The kinetic studies for the adsorption of BR18 dye in aqueous solution using hydrochar showed the second-order kinetics. Langmuir and Freundlich isotherm models were used to explain the relationship between adsorbent and adsorbate and Freundlich isotherm was the most suitable model because of its high regression coefficient ($R^2$) value. The intraparticle diffusion model was used to determine the adsorption mechanism of the BR18 onto *Q. coccifera* fruit. Desorption studies were also carried out using different type acids and different molarity.

**Key words** | azo dye adsorption, hydrochar, *Quercus coccifera*, subcritical water

**HIGHLIGHTS**

- Hydrochar from *Quercus coccifera* was produced by subcritical water to obtain solid products.
- The biochar was used as adsorbents to remove BR18 dye from aqueous solution.
- Hydrochar showed the highest dye removal efficiency as 88.7% with 194.6 mg/g adsorption capacity.
- The equilibrium adsorption was best described by the Freundlich isotherm model.
INTRODUCTION

Water pollution is one of the important issues in the world (Saleh et al. 2019). The sources of pollution are different since water enters all the life activities. The treatment of polluted water had the attention of researchers over the world. The textile industry is a major pollutant by generating hazardous and colored wastewater that had bad effects on human life and the environment (Patel & Vashi 2015). Textile industries release concentrated colored wastewater as a result of the dyeing process. For instants, the discharged textile wastewater reached 3 billion tons over the world (Antczak et al. 2013; Li & Wang 2013). Cationic dyes like Basic red 18 BR18 dissolve simply in the water, causing reducing in the transparency of the water and obstacle the sunlight from water crossing. The sunlight blocking affects the present flora and fauna negatively (Nagpal & Kakkar 2020). Chong et al. (2014) stated that cationic dyes are carcinoogenic and do not degrade naturally. So far, many researchers have tried to treat dyed wastewater using different methods. For the biological treatment systems, bacteria (Pearce et al. 2006; Lavanya et al. 2014), algae (Elumalai & Saravanan 2016), fungi (Krastanov et al. 2013), enzyme (Darwesh et al. 2019), and yeast (Martorell et al. 2018) were used in the biodegradation of dyes. Chemical treatment methods were also used in dye degradations. Advanced oxidation processes (AOPs) (Al-Kdasi et al. 2004; Miklos et al. 2018), coagulation-floculation (Verma et al. 2012; Dotto et al. 2019), electrocoagulation (EC) (Naje et al. 2016), electro-Fenton (EF) (Rosales et al. 2009), and anodic oxidation (AO) (dos Santos et al. 2019) were utilized in treating of textile wastewater. Except for the electrochemical methods, the chemical treatment can be considered more expensive than the biological methods (Crini & Lichtfouse 2019). The mass transfer concept has also been utilized in dye removal from wastewater through what called the physical process. It includes the adsorption process (Rafatullah et al. 2010), membrane filtration (Jegatheesan et al. 2016), and ion-exchange methods (Bayramoglu et al. 2020). The low-cost issues, simplicity in design, high efficiency, and the easy in operation make the adsorption process more favorable than others (Asfaram et al. 2017).

The principal in the adsorption process is the attaching of adsorbate on the surface of the solid adsorbent. Based on the attachment manner, the adsorption process can be categorized into physisorption or chemisorption (Gupta & Suhas 2009). Different materials were used as adsorbents for dye removal. Activated carbon (Tan et al. 2008), alumina (Banerjee et al. 2019), zeolite (Brião et al. 2018), bio-adsorbents (Gupta et al. 2017), biochar (Biswas et al. 2020), and subcritical water hydrolysis (Abaide et al. 2019) were utilized in the adsorption process.

Hydrochar is a stable carbon-rich solid product obtained by different methods from different types of biomasses. Additionally, subcritical water medium (SWM) has been used as an effective medium in synthesis, extraction, oxidation, solubility processes, and many other fields as well as provides a unique medium for converting carbonaceous materials into hydrochar (Nural et al. 2018; Yabalak 2018a; Lee et al. 2019). Subcritical water is defined as water heated in the range of 373–647 K and pressurized enough to keep the water liquid at this temperature (Yabalak 2018b). Conversion of biomass to hydrochar in the SWM is an advantageous alternative to classical torrefaction, pyrolysis, or gasification processes due to providing high conversion yield of biomass to hydrochar and water-soluble components of the biomass that cannot be obtained in other methods (Chuntanapum & Matsumura 2009; Kumar &
Gupta 2009). Besides, subcritical water provides a reactive medium based on its molecular properties and SWM is a more economical one since it does not require a pre-drying step, thus high costs (Chuntanapum & Matsumura 2009). Recently, the production of biochar, more particularly hydrochar, and their usage in various processes in environmental and agricultural applications have received great attention. Furthermore, it has been reported that biochar has high effectiveness in removing many organic pollutants from water and soil (Fang et al. 2014). To the best of our knowledge, it is the first attempt to investigate the production of hydrochar from Quercus coccifera L. (Q. coccifera) in unique eco-friendly SWM as well as evaluate its effects as an adsorbent in the removal of dye contaminant in the aqueous solution.

MATERIALS AND METHODS

Collection and preparing of Quercus Coccifera L.

The specimens of Q. coccifera fruit were collected from Mersin, Yenişehir, Akkent, open-field, 20–40 m in 21.10.2018. Q. coccifera fruits with their outer thick shell (hereinafter called hat) were washed with distilled water to remove the resin and other impurities on them and they were kept in room temperature in a dark until completely dry for 20 days.

Hydrochar production in the subcritical water medium

Home-made stainless-steel reactor, which was demonstrated in detail in previous work, was used in the production of hydrochar in the subcritical water medium (Yabalak 2018b). The production process was schematized in Figure 1. Briefly, 30 g of dried Q. coccifera fruit and their hats were put into the reactor and 150 mL of pure water was added on. After closing and screwing the reactor, the inner pressure was fixed at 100 bar. The temperature of the reactor was increased to 513 K and kept constant for 3 h. At the end of the treatment time, the reactor was depressurized and unscrewed. The obtained hydrochar was filtered through ordinary filter paper and dried in an oven at 373 K. 21.8 g of obtained dry hydrochar indicated 72.8% of hydrochar yield from the conversion of Q. coccifera. This value is quite high compared to pyrolysis, dry torrefaction, gasification, and even hydrothermal carbonization methods reported in literature (Lee et al. 2019).

Adsorbate preparation

In this study, a cationic dye (Basic red 18 - BR18) was examined. The properties of BR18 dye are shown in Table 1. A stock solution (1,000 ppm) was prepared and kept until the end of the experiments. The proposed concentrations were diluted from the stock solution. Sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄) with different molarities (1–5) M were utilized in pH’s arrangements.

Adsorbent characterization

Brunauer Emmett-Teller (BET) analysis was employed to determine the surface area, total pore volume, microporous volume, and pore diameter using adsorption and desorption isotherms of N₂ gas (MicroActive for TriStar II Plus 2.00). The adsorbent surface area was determined by plotting the linear form of the Brunauer Emmett-Teller equation. The total volume was calculated at the relative pressure (p/p₀) 0.99 (Schneider 1993). The microporous volume and the pore diameter were determined by the method of Boer and by the ratio of 4 V_total/BET surface, respectively (Barrett et al. 1951).

![Figure 1](http://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2020.607/820525/wst2020607.pdf)  
**Figure 1** | The hydrochar production process in the SWM.
The adsorbent surface morphology was observed by scanning electron microscope (SEM- Zeiss, Supra 55). Fourier transform infrared spectroscopy (FT/IR-6700, Jasco) was utilized to investigate the function group presents on the surface of the adsorbent. The function groups were scanned for the bands between 450 and 4,000 cm\(^{-1}\).

The surface charge changes of the prepared hydrochar during the pH optimization were measured using zeta potential (Malvern Zeta Sizer Nano ZS).

Batch studies

The adsorption of the cationic dye (BR18) onto the prepared hydrochar was assessed by the batch method. All the experiments were carried on 50 mL solutions using 250 mL Erlenmeyer flasks (Isolab). They were agitated at a speed of 155 rpm using an orbital shaker (Biosan PSU-20i) at room temperature (25 ± 2°C). The changes in dyes concentrations were measured using a spectrophotometer (Hack DR-3900) at the aforementioned wavelengths. The removal efficiencies and adsorption capacities were calculated using Equations (1) and (2), respectively;

Removal efficiency (%) = \( \frac{(C_i - C_e)}{C_i} \times 100 \)  \hspace{1cm} (1)

\( q_e = \frac{(C_i - C_e) \times V}{m} \)  \hspace{1cm} (2)

where \( C_i \) and \( C_e \) are the concentration of the dye before and after the adsorption process (mg/L), \( q_e \) is the adsorption capacity (mg/g), \( V \) is the volume of the aqueous solution (L), and \( m \) is the mass of the prepared hydrochar (g).

The effects of the pH (2–10), adsorbent size (45–150 \( \mu \)m), adsorbent dose (0.5–1.5 g/L), dyes concentrations (50–455 mg/L), and contact time (5–120 min) were studied through the optimization experiments. The optimum conditions were obtained by studying the factors one by one.

Adsorption kinetic

In this study, Lagergren’s pseudo-first-order model (Equation (3)) and pseudo-second-order model (Equation (4)) were used to describe the adsorption of BR18 onto the prepared adsorbent. The samples were collected over time until the final concentrations became very close to each other. The obtained data were linearized, and the correlation coefficients were calculated.

\[
\log \left( \frac{q_e - q_t}{q_e} \right) = \log q_e - \frac{K_1}{2.303} t
\]  \hspace{1cm} (3)

\[
\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{1}{q_e} t
\]  \hspace{1cm} (4)

where \( q_e \) and \( q_t \) are the capacities of the adsorption at the equilibrium and at time \( t \) (mg/g), \( K_1 \) is Lagergren’s constant (1/min), \( K_2 \) is the second-order constant (mg/g·min).

Weber–Morris equation or intraparticle diffusion assumes that the intraparticle diffusion is the rate-limiting step in the overall biosorption process, as shown in Equation (5);

\[
q_t = k_i t^{0.5} + C
\]  \hspace{1cm} (5)

where \( K_i \) is intraparticle diffusion rate constant (mg·g·min\(^{-1/2}\)), \( C \) is a boundary layer thickness constant.

Adsorption isotherm

The adsorption isotherm is an important issue to elucidate the interaction between the adsorbent and the adsorbate. The isotherms experiments were executed by changing the dose of the adsorbent while the other factors were still constant. The initial concentration, final concentration, and the adsorption capacities were plotted using the linear form of the Langmuir (Langmuir 1918), Freundlich (Freundlich 1906), Temkin (Temkin & Pyzhov 1940), Dubinin-Radushkevich (D-R) (Dąbrowski 2001), Redlich – Peterson (Redlich & Peterson 1959), and Sips (Blanchard et al. 1984) equations which are shown in Table 2.

**Table 1** Properties of cationic BR18 dye (Fathy et al. 2017)

| Properties of cationic BR18 dye (Fathy et al. 2017) |  
|-----------------|---|
| Chemical formula | \( \text{C}_{19}\text{H}_{25}\text{ClN}_{5}\text{O}_{2} \) |
| Chemical structure (2D) | ![Chemical structure (2D)](image1) |
| Chemical structure (3D) | ![Chemical structure (3D)](image2) |
| Molecular weight (g/mol) | 390.89 |
| Wavelength (nm) | 486 |
Desorption studies were done as described in the previous works (Saleh et al. 2019). Briefly, at the end of the adsorption process, the adsorbent was separated from the aqueous solution. First, the effect of acid type was investigated and HCl, H₂SO₄, HNO₃, and H₃PO₄ were tested. Second, different molarity of the acid (0.5, 1, 2.5, and 5 M) was tested. The desorption conditions were selected to be the same as the adsorption conditions (agitation speed: 150 rpm, solution volume: 50 mL, temperature: 25 ± 2 °C). The desorption efficiency was calculated using Equation (15):

\[
\text{Desorption Efficiency} \% = \frac{\text{Desorbed Dye Concentration}}{\text{Adsorbed Dye Concentration}} \times 100
\]  

**RESULTS AND DISCUSSION**

**Hydrochar characterization**

The prepared hydrochar was sieved <45 μm, 45–106 μm, and >106 μm and analysed by the BET analysis using the adsorption and desorption of N₂ gas. Three different particle sizes were analysed to determine the physical properties of the adsorbent. BET surfaces areas, the total volumes of the pores, microporous volumes, and the diameters of the pores were determined and shown in Table 3.

As shown in Table 3, the adsorbent with the particle size of less than 45 μm has the maximum surface area with a value of 25.2718 m²/g. Also, the total pore volume is inversely related to particle size. The maximum pore diameter is 17.88 nm, which is larger than the BR18 size. This reflects that the dye can be adsorbed toward the pores of the adsorbent.
The hydrochar surface morphology was also identified by SEM analysis. SEM analyses occurred before and after the adsorption process to note the changes. The changes in surface morphology are shown in Figure 2. As shown in Figures 2(a) and 2(b), the adsorbent has a heterogeneous, rough, and porous surface. SEM results also support the adsorption of BR18 onto the surface of the prepared hydrochar since the pores were filled and no pores were noticed after the absorption process (Figures 2(c) and 2(d)).

The Energy Dispersive X-Ray Analysis (EDX) was carried out to determine the elements in the adsorbents. A comparison between the raw adsorbent and the adsorbent at the end of the adsorption process is shown in Table 4. It can be stated that carbon, nitrogen, and oxygen are the dominant elements in the adsorbent. The concentrations of the nitrogen and chlorine increased at the end of the adsorption process. This is another proof that the adsorption of the BR18 onto the Q. coccifera fruit has successfully occurred as the BR18 has nitrogen and chlorine elements in its structure.

The FTIR analysis for the raw adsorbent and the dyed adsorbent were performed and shown in Figure 3. The results show that there are some changes between the FTIR for the adsorbent before and after the adsorption process. The alkene compound class (functional group C= C bending) observed at peak 790 cm\(^{-1}\) before the adsorption process disappeared after the adsorption process. Also, the peak at the band 1,428 cm\(^{-1}\) with functional group O-H bending was not noticed at the end of the adsorption process. In contrast, three peaks were recorded for the band from 1,141 to 1,336 cm\(^{-1}\). The peak at the band 1,141.65 cm\(^{-1}\) can be related to an amine compound with a functional group of C-N stretching. The functional group C-O stretching was also noticed at the band of 1,213.01 cm\(^{-1}\). The peak at the band 1,336 cm\(^{-1}\) was referred to O-H bending functional group. In addition to these changes, peaks shifting were noticed at many bands.

| Parameter          | Unit | < 45 \(\mu\)m | 45–106 \(\mu\)m | > 106 \(\mu\)m |
|--------------------|------|----------------|----------------|--------------|
| BET surface area   | (m\(^2\)/g) | 25.27180         | 11.03790        | 5.22000      |
| Total pore volume  | (cm\(^3\)/g) | 0.11298           | 0.04515         | 0.01018      |
| Micro pore volume  | (cm\(^3\)/g) | 0.06897           | 0.00635         | 0.02487      |
| Mesoporous volume  | (cm\(^3\)/g) | 0.00109           | 0.00022         | 0.00059      |
| Pore diameter      | nm   | 17.88191         | 16.36362        | 7.79847      |

| Element | Before adsorption | After adsorption |
|---------|-------------------|------------------|
|         | Weight (%) | Atomic (%) | Weight (%) | Atomic (%) |
| C       | 62.58    | 68.31      | 60.88    | 66.91      |
| N       | 9.55     | 8.91       | 11.06    | 10.42      |
| O       | 27.64    | 22.65      | 26.91    | 22.20      |
| Na      | 0.07     | 0.04       | 0.30     | 0.17       |
| Cl      | 0.05     | 0.02       | 0.42     | 0.16       |
| Ca      | 0.11     | 0.04       | 0.43     | 0.14       |

Figure 2 | SEM for the prepared adsorbent before the adsorption process for (a) 5 \(\mu\)m, (b) 1 \(\mu\)m and after the adsorption process for (c) 5 \(\mu\)m, (d) 1 \(\mu\)m.
The FTIR results support the realization of the adsorption process.

The effect of pH

The concentration of hydrogen ion (pH) is the most important parameter in the adsorption process. It controls the protonation and deprotonation process on the adsorbent surface. To explore the effect of pH on the removal efficiency of the BR18 by adsorption process, 1 g/L of the adsorbent added to 100 mg/L of the dye concentration at constant temperature (25 ± 2 °C) and agitation speed (150 rpm). The effects of pH on the adsorption capacity and the removal efficiency are shown in Figure 4(a). The dye uptake and the adsorption capacity increased with the pH increases. The removal efficiency increased from 2% at pH 2 to reach 72% at pH 10. The capacity also increased from 2 mg/g to reach 80 mg/g.

The zeta potential analysis for the adsorbent and the adsorbate under different pHs was studied. The adsorbent and the adsorbate were dissolved in 25 mL of distilled water and measured by a zeta-meter (Malvern Zeta Sizer Nano ZS). The zeta potentials for the adsorbent at all pH values were negative (Figure 4(b)), while the adsorbate was positive at all the measured pH. Because the adsorbent and the adsorbate have different charges, they will have an attractive force. The values of the zeta potential for the adsorbent sharply decreased from 5.87 mV at pH 2 to reach −43.93 mV at pH 10. As the zeta potential for the adsorbent decreased with the increases in the pH, the attractive force between the hydrochar and BR18 increased. Which results in the increasing of the removal efficiency.

The effect of particle size

The effect of the adsorbent particle size on the adsorption efficiency was investigated. Three different particle sizes were used in the experiments while the other parameters were kept constant (dye concentration: 110 mg/L, contact time: 60 min, adsorbent dosage: 1 g/L, and volume: 50 mL). The results showed that the maximum removal efficiency was obtained when the particle size was smaller than 45 μm with an efficiency of 89.1% (Table 5). These results can be explained by the surface area of the adsorbent. As shown in BET results, the particle sizes have an inverse relationship with the surface area.

The effect of adsorbent amount

The effect of the adsorbent amount on the removal efficiency was investigated. hydrochar was added in different
quantities (0.5, 1.0, 1.5 g/L) into solutions with a concentration of 125 mg/L. The results show that the maximum removal efficiency occurred at 1.5 g/L (Table 6).

The effect of contact time and initial concentration

The effects of contact time (0–120 min) on the uptake of BR18 by Q. coccifera fruit at an initial concentration of 280 mg/L was studied and shown in Figure 5(a). The removal efficiency increased sharply for the first 5 min after that the removal efficiency reached a steady state at the 60 min with maximum removal of 87.9%. After that, the removal efficiency did not change and hence 60 min was chosen as the optimum contact time. The removal of the BR18 from the aqueous solution had done in two steps; the rapid-step (first five minutes) where the active sites on the adsorbent surface were empty, as the number of the active sites decreased (attached with the dye), the removal speed decreased where the second step realized.

The initial concentration is one of the most affecting factors in the adsorption process. The adsorption capacity for the prepared hydrochar at different initial concentrations is shown in Figure 5(b). The capacity increased sharply with the increase in the initial concentration of BR18 until 280.8 mg/L. Then the graph became flatter. This can be related to the availability of active sites. The capacity increased from 20.9 mg/g at a concentration of 40 mg/L to 194.6 mg/g at a concentration of 454 mg/L.

Kinetic studies

The obtained data were fitted to the Lagergren’s pseudo-first-order and pseudo-second-order models to determine the adsorption kinetic. The linear form of the Lagergren’s pseudo-first-order and pseudo-second-order expressed in Equations (3) and (4) were fitted at different concentrations to obtain the maximum correlation coefficients. The chi-square errors (X²) were tested using the SciDavis program to study the linearization errors. Table 7 shows the kinetics models parameters and also shows the X² results. Because of the high values of correlation coefficients, the X² errors are very small, and the calculated capacities are very close to the experimental capacities, the adsorption of BR18 onto Q. coccifera fruit is fitted to the pseudo-second-order model (Figure 6). According to the Pseudo-second-order model, the rate of the adsorbate adsorption is related proportionally to the available sites on the surface of the adsorbent.

According to Gau & Wang (2019), the pseudo-second-order model can occur in three ways; at low concentrations, at the final stage of the adsorption, and when the adsorbent

Table 5 | Effect of particle size on the removal efficiency of BR18 by Q. coccifera fruit

| Particle size | Initial concentration (mg/L) | Final concentration (mg/L) | Removal efficiency (%) |
|---------------|-----------------------------|---------------------------|------------------------|
| <45 μm        | 110                         | 12                        | 89.1                   |
| 45–106 μm     | 110                         | 18                        | 83.6                   |
| <106 μm       | 110                         | 30                        | 72.7                   |

Table 6 | Effect of hydrochar amount on the removal efficiency of BR18

| Hydrochar amount (g/L) | Removal efficiency (%) |
|------------------------|------------------------|
| 0.5                    | 66%                    |
| 1.0                    | 76%                    |
| 1.5                    | 91%                    |

Figure 5 | (a) The changes in the removal efficiency and the concentration over time and (b) The changes in the adsorption capacities related to the initial concentration.
is abundant with active sites (Qiu & Zheng 2009). The fitting of the current study to the pseudo-second-order model can be referred to the BR18 attaching to the active sites presents on the surface of the prepared adsorbent. Unfortunately, neither Lagergren’s pseudo-first-order nor pseudo-second-order models predict the solute diffusion into the adsorbent.

The intraparticle diffusion model was used to determine the adsorption mechanism of the BR18 onto Q. coccifera fruit. The square root of time was plotted versus the adsorption capacity, as shown in Figure 7. The IDM plot shows multiple linear sections with no passing through the origin point. The multilinearity reflects the effects of different mechanisms. The first mechanism indicates film diffusion, which involves the BR18 movements slowly from the boundary layer to the surface of the Q. coccifera fruit. The moving from the surface to the adsorbent pores and the attaching to the active pores reflected the second and the third mechanisms. As a result of the IDM graph, the main mechanism in the adsorption of BR18 onto Q. coccifera fruit is film diffusion (graph has not passed through the origin point), and the Intraparticule resistance has a role in the adsorption (because of multi linearity).

### Isotherms

The isotherms studies were fulfilled by exposing different dosages of the adsorbent to an initial BR18 concentration of 123 mg/L. The adsorbent and the adsorbate were agitated at 155 rpm at 25 ± 2 °C. The samples were collected and fitted to the aforementioned isotherms. The isotherms parameters are shown in Table 8. In this study, the experimental data were fitted according to the four-parameter isotherms (Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich (D-R)) and based on the three-parameter isotherms (Redlich – Peterson and Sips). Langmuir isotherm has a correlation coefficient of 0.8988. Langmuir supposes the adsorption process will reach the maximum capacity when a saturated monolayer is formed. Freundlich isotherm has the highest correlation coefficient of 0.9527. This isotherm is an empirical isotherm, which assumes...
heterogeneous multilayer formation at the end of the adsorption process. Tempkin isotherm ($R^2 = 0.9192$) includes the heat of the adsorption process. It assumes a linear inverse relationship between the heat of the molecule in the same layer and the surface coverage. Dubinin-Radushkevich has the lowest coefficient with $R^2 = 0.6980$. Redlich–Peterson (R-P) ($R^2 = 0.9483$) depends on three parameters to describe the adsorption mechanism. Redlich–Peterson isotherm assuming the mechanism will be a mix of Langmuir and Freundlich isotherms. According to R-P, no ideal monolayer will be formed. Sips isotherm also has a relatively high correlation coefficient with a value of 0.8769. Sips isotherm can be defined as a combination of Langmuir and Freundlich isotherms. At high concentrations, Sips isotherm can be abbreviated to be Langmuir isotherm. In contrast, it will be reduced to Freundlich isotherms at the low concentrations.

**Thermodynamic**

The thermodynamic parameters (Gibbs free energy, enthalpy, and entropy) were determined using the Equations (12)–(14). The adsorption experiments were conducted at different temperatures (303, 313, 318, and 323 K). At the end of the adsorption experiments, the relationship shown in Equation (12) was plotted and shown in Figure 8.

![Figure 8](image.png)

The change in enthalpy was founded by multiplying the slope value by the universal gas constant. The multiplication of the universal gas constant with the graph intercept led to entropy. The Gibbs free energy for each temperature was determined by Equation (14). Table 9 shows the thermodynamic parameters. Based on the negative sign of the Gibbs free energy, the adsorption process of BR18 onto the Q. coccifera fruit can be considered to be feasible and spontaneous in nature. The adsorption process can be considered as physisorption since the Gibbs free energy is lower than 20 kJ/mol (Singh & Kaur 2016). The Gibbs free energy at 30°C equals −6.011 (kJ/mol) which is higher than the Gibbs free energy for the removal of Methylene Blue (MB) onto bagasse hydrochar −1.24 (kJ/mol) (Biswas et al. 2020). The change in enthalpy was found to be positive. Since that, the adsorption process of BR18 onto Q. coccifera fruit can be imagined as endothermic. The positive sign of the entropy reflects the solid phase randomness and the change in the surface of the adsorbent at the end of the adsorption process. Similar results were obtained by previous works (Afroze et al. 2019; Dawood et al. 2017; Biswas et al. 2020).

**Table 8** | Isotherms parameters for the adsorption of BR18 onto Q. coccifera fruit

| Isotherm            | Parameter | Unit     | Value            |
|---------------------|-----------|----------|------------------|
| Langmuir            | $R^2$     |          | 0.8988           |
|                     | $q_m$     | mg/g     | 263.1579         |
|                     | $b_{BR}$  | L/mg     | 0.0368           |
| Freundlich          | $R^2$     |          | 0.9527           |
|                     | $K_{BR}$  | (mg/g).(L/mg) | 23.2113  |
|                     | $n$       |          | 1.9550           |
| Tempkin             | $R^2$     |          | 0.9192           |
|                     | $b_T$     |          | 42.7415          |
|                     | $A_T$     | L/g      | 0.0110           |
| Dubinin-Radushkevich (D-R) | $R^2$     |          | 0.6980           |
|                     | $K_{sd}$  | mol²/kJ² | 1e − 5           |
|                     | $q_s$     | mg/g     | 141.1750         |
| Redlich – Peterson (R-P) | $R^2$     |          | 0.9483           |
|                     | $\beta$   |          | 0.4885           |
|                     | $a_r$     | L/g      | 0.0431           |
| Sips                | $R^2$     |          | 0.8769           |
|                     | $r$       |          | 0.9500           |
|                     | $q_{inh}$ | mg/g     | 188.6793         |
|                     | $K_s$     | 1/mg     | 0.0618           |

**Table 9** | The thermodynamic parameters for the adsorption of BR18 onto Q. coccifera fruit

| T (°C) | $\Delta H$ (kJ/mol) | $\Delta S$ (J/mol.K) | $\Delta G$ (kJ/mol) |
|--------|----------------------|----------------------|---------------------|
| 30     | 2.670                | 28.648               | −6.011              |
| 40     |                      |                      | −6.297              |
| 45     |                      |                      | −6.440              |
| 50     |                      |                      | −6.584              |
Desorption study

Desorption study was done at the optimum condition of the adsorption process. Different concentrations of HCl were experimented. The desorption percentage increased with the concentration of HCl. The maximum desorption obtained at 5 M HCl with a percentage of 80.4%. The adsorption-desorption process was repeated five times and the removal efficiencies after each cycle are shown in Figure 9. The removal efficiency of the BR18 from the aqueous solution at the prepared hydrochar at the first cycle reached 90.4%. The desorption process was applied several times, for each cycle, the removal efficiency decreased until still constant at the fifth cycle. The removal efficiency at the fifth cycle reached up to 69.2%.

The prepared hydrochar by SWM was used in the adsorption of azo dye. To investigate the feasibility of using this method in producing hydrochar, it was compared with other studies, as shown in Table 10.

CONCLUSION

In this study, the *Q. coccifera* fruit-based hydrochar was prepared successfully in the subcritical water medium. This method is green since no chemicals were used in the production of the hydrochar. Also, it can be considered as an economical method as the preparation temperature did not exceed 240 °C, and the yield reached 72%.

The prepared hydrochar was used as an adsorbent to remove the BR18 dye from the aqueous solution. The adsorption process of the BR18 onto the prepared hydrochar can be considered as a fast process since a drop in concentration was noticed after five minutes. The adsorption process was significantly affected by pH concentration; the maximum removal efficiency was obtained at pH 10. The adsorption process was fitted to the Freundlich isotherm and pseudo-second-order model. The feasibility of the adsorption process was obtained from the thermodynamic experiments. The adsorption process was found to be spontaneous and
endothermic in nature. The adsorbent was used for five cycles. At the end of the fifth cycle, the efficiency reached 70%. According to the aforementioned results, the prepared hydrochar by SWM can be used as an effective adsorbent for BR18 dye from the aqueous solution.

CONFLICT OF INTERESTS

The authors have no conflict of interest in relation to this work.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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Table 10 | Comparison with other studies

| Raw Material          | Biochar/hydrochar Preparation Method | Adsorbate      | Capacity (mg/g) | Isotherm  | Kinetic          | Thermodynamic | References                  |
|-----------------------|------------------------------------|----------------|-----------------|-----------|------------------|---------------|----------------------------|
| Palm Petiole          | Pyrolyzed at 700 °C                | Crystal Violet | 209.0           | Langmuir  | Empiric Avrami   | Endothermic   | Chahinez et al. (2020)      |
| Bovine Bones          | Pyrolyzed at 800 °C                | Basic Red 9    | 49.5            | Langmuir  | Pseudo–First Order | –            | Córtes et al. (2019)       |
| Fish Scales           | Pyrolyzed at 800 °C                | Basic Red 9    | 52.3            | BET       | Pseudo–First Order | –            | Córtes et al. (2019)       |
| Municipal Solid Waste | Pyrolyzed at 400–800 °C            | Methylene Blue | 33.3            | –         | Pseudo–Second Order | Endothermic  | Chen et al. (2015)         |
| Switch grass          | Pyrolyzed at 600 °C                | Orange G       | 8.2             | Langmuir  | Pseudo–Second Order | –            | Park et al. (2019)         |
| Cow Dung              | Pyrolyzed at 500 °C                | Methylene Blue | 19.2            | Langmuir  | Pseudo–Second Order | Endothermic  | Ahmad et al. (2020)        |
| Sewage Sludge         | Pyrolyzed at 550 °C                | Methylene Blue | 29.8            | Langmuir  | Pseudo–Second Order | Endothermic  | De Filippis et al. (2015)  |
| Q. coccifera fruit    | Subcritical water medium           | Basic Red 18   | 194.6           | Freundlich| Pseudo–Second Order | Endothermic  | This study                  |
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