How to Cite:

Adsorption of Remazol Brilliant Blue R from Aquatic Solution Using Natural Adsorbent (Pistachio Hull)

ABSTRACT
This study examines that adsorption of Remazol Brillant Blue R (RBBR) from aquatic solution was studied using pistachio hull (PH) as an adsorbent. The removal efficiency of pistachio hull was studied as a function of, pH, initial dye concentration, adsorbent dose and time via batch method at room temperature. Langmuir and Freundlich Isotherms applied to obtained data from experiments. The correlation coefficient values shown that the data fit the Langmuir Isotherm ($R^2=0.9989$) compare to Freundlich Isotherm ($R^2=0.7825$). Maximum adsorption capacity was observed as 16.739 mg/g. Thermodynamic parameters also studied. The value of Gibbs Free Energy, ($ΔG=2.696$ kJ/mol) is positive. This value is indicated that the adsorption was not a spontaneous one. According to the experimental data, pistachio hull can be used as an appropriate, no cost and easy obtainable adsorbent for the removal of Remazol Brilliant Blue R dye.

Keywords: Remazol Brillant Blue R, Langmuir, SEM, Pistachio Hull, pH

1. INTRODUCTION
Textile, plastic, paper industries used dyes as colorants. These industries discharged wastewater with color to the aqueous environment. Color in the water is the very important problem in the world. It is unhealthy for ecosystem. It is necessary to color removal from wastewater. There are many methods for treatment of wastewater such as adsorption [1], ion exchange [2], chemical oxidation [3], photodegradation [4]. Some of them are very expensive and have same difficulties to operation. Adsorption is the best way to removal of dye from wastewater. There are many adsorbent in the world. Activated carbon has a high adsorption capacity is the most popular adsorbent. However, in recent years, low cost adsorbents have received growing attention in literatures. PH is waste of pistachio peeling factories at no cost. In this present study, we reported that adsorption of Remazol Brilliant Blue R from aquatic solution using natural adsorbent (Pistachio Hull). Isotherm models (Langmuir and Freundlich) applied to obtained data from experiments. Langmuir isotherm is the best fit for this study. Thermodynamic parameters also studied. PH can be used no cost and easy obtainable wastes for the removal of Remazol Brilliant Blue R dye.
2. RESEARCH SIGNIFICANCE

Recently, water pollution has gained attention in the world. In some areas, they have reached or even exceeded the unacceptable level. Many researches have shown that water pollution was widely cause damage to aquatic environment. The aim of this study was to assess the investigation of adsorption of Remazol Brilliant Blue R from aqueous solution using natural adsorbent (pistachio hull).

3. EXPERIMENTAL METHOD-PROCESS

The following rules should be followed for page layout. It is recommended that you use a template ready to fulfill the terms of spelling rules.

3.1. Material

The PH used as an adsorbent in the study was obtained at a factory in Nizip on August 2016 and stored at +4°C. Raw pistachio and waste PH are shown in Figure 1.

Figure 1. Raw pistachio and waste PH

Remazol Brilliant Blue R was used as textile dye in the study. Remazol Brilliant Blue R is a dye that is toxic and irreversible class of organic contaminants [5]. The properties of Remazol Brilliant Blue R are given in Table 1.

Table 1. Properties of Remazol Brilliant Blue R

<table>
<thead>
<tr>
<th>Remazol Brilliant Blue R</th>
<th>Molecular Weight (g/mol)</th>
<th>626.54</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Color</td>
<td>Blue</td>
</tr>
<tr>
<td></td>
<td>λ_{max} (nm)</td>
<td>582</td>
</tr>
<tr>
<td></td>
<td>Dyepurity</td>
<td>&lt;90%</td>
</tr>
<tr>
<td></td>
<td>Chemical Formula</td>
<td>C_{22}H_{16}N_{2}Na_{2}O_{11}S_{3}</td>
</tr>
<tr>
<td></td>
<td>Structure</td>
<td>![Structure Image]</td>
</tr>
</tbody>
</table>
3.2. Preparation of Adsorbent

The pistachio hulls were obtained from a factory in Gaziantep-Turkey. In order to prepare the adsorbent, pistachio hulls were separated from pistachio shell and then washed many times. After, pistachio hulls were dried at 60°C for 24 h, they allowed to cool in desiccators. It was ground into fine powder to use as an adsorbent in the following experiments.

3.3. Adsorption Experiments

All After pistachio hulls were washed in tap water and pure water, the material was dried at 80°C for 2 days and sieved from 20-30-35-50 and 70 mesh screens and used as an adsorbent. Remazol Brilliant Blue R (C_{22}H_{16}N_{2}Na_{2}O_{11}S_{3}) was purchased from (Carlo Erba Reagent). It is a reactive dyestuff. This dye was commercial product. Experiments were performed in 750mL erlenmeyer flasks including 5g of pistachio hulls with 500mL of Remazol Brilliant Blue R solution. All the biosorption experiments were performed at room temperature (25°C) via batch method and four set (25mg/L, 50mg/L, 75mg/L and 100mg/L). The solution was shaken by a mechanical shaker (Edmund Bühler GmbH) at the constant agitation time (100rpm) during 120 min. Then the supernatant was centrifuged at 6000rpm and 5 minutes in a centrifuge (Hettich Zentrifugen) after the batch tests. The absorbance of Remazol Brilliant Blue R was measured at maximum wavelength (λ_{max}:582nm) by UV-VIS Spectrophotometer (T 90). The incubation time was tested in a time from 5 to 120 min. All experiments were repeated three times. The dye removal percentage was calculated by:

\[
\text{Removal} \% = \left( \frac{C_0 - C_e}{C_0} \right) \times 100
\]  

\(C_0\): The liquid-phase concentrations of the adsorbate at initial
\(C_e\): The liquid-phase concentrations of the adsorbate at equilibrium concentrations

The adsorption amount of Remazol Brilliant Blue R was calculated as follows, Equation 2:

\[
\text{Amount of adsorption} (Q) = \frac{(C_0 - C_f)V}{m}
\]

\(C_0\): The initial dye concentration (mg/L)
\(C_f\): The dye concentration after adsorption,
\(V\): Dye volume (mL)
\(m\): Adsorbent mass (g) [10].

4. RESULTS AND DISCUSSION

4.1. SEM Images of Pistachio Hull

Unloaded and dye loaded adsorbent in SEM images are indicated in Figure 2. According to Figure 3, there are many pours in unloaded PH. After adsorption, the pours filled with dye molecules.
4.2. Effect of Contact Time

The effects of contact time for Remazol Brilliant Blue R dye adsorption on pistachio hull shown in Figure 4. According to Figure 2, the adsorption of Remazol Brilliant Blue R was fast at first, after that it decreased until it reached plateau. Researchers statement that the rate of adsorption was higher at first for adsorbents have large surface area [6].

Figure 2. Unloaded adsorbent in SEM Images

Figure 3. SEM images of dye loaded pistachio hull

Figure 4. Effect of contact time on Remazol Brilliant Blue R dye adsorption on pistachio hull
4.3. Effect of pH

The effect of pH was studied at pH values between 2 and 10. It has been observed that the capacity of adsorption decreases with increasing pH values in the acidic medium. It was observed that capacity of adsorption increased slightly after pH 6 and then remained constant. It was found that optimum pH is 2 in adsorption on pistachio hull of Remazol Brilliant Blue R (Figure 5). Ahmad et al. (2015) studied removal of Remazol Brilliant Blue R onto Durian seed activated carbon. They found the maximum removal was get at pH 2 (95.17%). Sathishkumar et al., (2012), used Jatropha curcas pods (agro-industrial waste) for removal of Remazol Brilliant Blue R. They found that optimum pH is 3 for the system [7]. Also, similar result was obtained by researchers [8 and 9].

![Figure 5. Effect of pH on pistachio hull](image)

4.4. Effect of Concentration

Figure 6 shown effect of concentration on Remazol Brilliant Blue R dye adsorption on pistachio hull. As shown in Figure 6, initially increased dye concentrations showed an increase adsorption capacity \( q_t \) (mg g\(^{-1}\)) and then it was found to be in equilibrium.

![Figure 6. Effect of concentration on Remazol Brilliant Blue R dye adsorption on pistachio hull](image)

4.5. Effect of Adsorbent Dose

The variation of adsorption capacity with adsorbent dose is shown in Figure 7. As shown in Figure 7 the adsorption capacity
increased with decrease in adsorbent dosage. Similar results found that [11 and 12].

Figure 7. Effect of Adsorbent Dose of Remazol Brilliant Blue R dye adsorption on pistachio hull

4.6. Adsorption Isotherms

The isotherm constants are summarized Table 2. The $R^2$ values (Table 2) show that the Langmuir model has more precise coefficients than the Freundlich model. The Langmuir isotherm provided a homogeneous adsorption mechanism. Langmuir model is given by Equation 3 [13].

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L}C_e$$  \hspace{1cm} (3)

$C_e$: The equilibrium concentration of adsorbate in solution after adsorption (mg/L),
$q_e$: The equilibrium solid phase concentration (mg/g),
$K_L$ (L/g), $a_L$ (L/mg): The Langmuir constants.

However, the Freundlich isotherm can be expressed by Equation 4:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (4)

$K_f$ (L/g): The adsorption capacity
$1/n$: Intensity of adsorption

Table 2. Parameters for isotherms obtained from equilibrium models

<table>
<thead>
<tr>
<th>Parameter (unit)</th>
<th>Methylene Blue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td></td>
</tr>
<tr>
<td>$K_L$ (L/g)</td>
<td>1.299</td>
</tr>
<tr>
<td>$a_L$ (L/mg)</td>
<td>0.0776</td>
</tr>
<tr>
<td>Qmax(mg/g)</td>
<td>16.739</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.9989</td>
</tr>
<tr>
<td>Freundlich Isotherm</td>
<td></td>
</tr>
<tr>
<td>$n$</td>
<td>4.775</td>
</tr>
<tr>
<td>$K_f$</td>
<td>4.615</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.7825</td>
</tr>
</tbody>
</table>

Table 3 described that adsorption capacity of Remazol Brilliant Blue R on pistachio hull in literature. Many researchers used different adsorbents and calculated different adsorption capacities.
Table 3. Adsorption capacity of Remazol Brilliant Blue R on pistachio hull in literature

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>$Q_{max}$ (mg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon from industrial laundry sewage sludge</td>
<td>Remazol Brilliant Blue R</td>
<td>33.47</td>
<td>[14]</td>
</tr>
<tr>
<td>Prosopis juliflora modified with H$_2$O$_2$</td>
<td>Remazol Brilliant Blue R</td>
<td>83.3</td>
<td>[15]</td>
</tr>
<tr>
<td>Pistachio hull waste</td>
<td>Methylene Blue</td>
<td>389</td>
<td>[16]</td>
</tr>
<tr>
<td>Pistachio nut shells activated with KOH (microwave heating)</td>
<td>Methylene Blue</td>
<td>296.57</td>
<td>[17]</td>
</tr>
<tr>
<td>Peanut hull-based activated carbon by microwave</td>
<td>Remazol Brilliant Blue R</td>
<td>149.25</td>
<td>[18]</td>
</tr>
<tr>
<td>Activated Carbon Prepared from Pinang Frond</td>
<td>Remazol Brilliant Blue R</td>
<td>232.59</td>
<td>[19]</td>
</tr>
<tr>
<td>Scenedesmus quadricauda</td>
<td>Remazol Brilliant Blue R</td>
<td>45.70</td>
<td>[8]</td>
</tr>
<tr>
<td>Graphene oxide</td>
<td>Basic Yellow28</td>
<td>68.5</td>
<td>[25]</td>
</tr>
<tr>
<td>Cucurbit [8] uril</td>
<td>Acid blue25</td>
<td>434.8</td>
<td>[26]</td>
</tr>
<tr>
<td>Sodic bentonite</td>
<td>Bezathren-Blue</td>
<td>5.33</td>
<td>[27]</td>
</tr>
<tr>
<td>Pistachio hull</td>
<td>Remazol Brilliant Blue R</td>
<td>16.739</td>
<td>This Study</td>
</tr>
</tbody>
</table>

Figure 7. Langmuir Isotherm of Remazol Brilliant Blue R on pistachio hull

$y = 0.0598x + 0.7698$
$R^2 = 0.9989$

$K_F$ and $n$ were found to be 4.615 and 4.775 for Remazol Brilliant Blue R dye on pistachio hull, respectively (Table 2). Similar results found to be [8] for adsorption of Remazol Brilliant Blue R onto immobilized Scenedesmus quadricauda. They explained that values of $n>1$ for Remazol Brilliant Blue R demonstrate a heterogeneous nature of adsorption and positive binding. Langmuir and Freundlich Isotherm models graphics described that Figure 7-8.
4.7. Thermodynamic Study
The thermodynamic parameters can be determined using the experimental data in the following equations Eq.5-7:

\[ \Delta G = -RT \ln K_c^0, \quad (K_c=C_a/C_e) \]  
\[ \ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]  
\[ \Delta G = \Delta H - T \Delta S \]  
\( \Delta S \): Changes of entropy,  
\( \Delta H \): Changes of enthalpy  
\( \Delta G \): Gibbs free energy  
\( K_c \): The equilibrium constant  
\( T \): Temperature (K)  
\( R \): The ideal gas constant (8.314 J/(mol K)).  

In equilibrium, the solid phase concentration (mg/L).

Thermodynamic equilibrium constant \((K_c^0)\) can be calculated from the equilibrium constant by plotting equilibrium constant against initial dye concentration. Table 4 shows Gibbs free energy values \((\Delta G: 2.696 \text{kJ/mol})\) for systems. Thermodynamic adsorption studies demonstrated that adsorption process was endothermic.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Dye</th>
<th>( \Delta G^0 ) (kJ/mol)</th>
<th>( T ) (K)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pistachio hull</td>
<td>Remazol Brilliant Blue R</td>
<td>2.696</td>
<td>298</td>
<td>This work</td>
</tr>
<tr>
<td>Titania aerogel</td>
<td>Orange II</td>
<td>1.2</td>
<td>303</td>
<td>[20]</td>
</tr>
<tr>
<td>Sepiolite</td>
<td>Reactive blue 221</td>
<td>47.9</td>
<td>293</td>
<td>[21]</td>
</tr>
<tr>
<td>Activated carbon prepared from coir pith</td>
<td>Congo Red</td>
<td>0.487</td>
<td>308</td>
<td>[22]</td>
</tr>
<tr>
<td>Activated Carbon</td>
<td>Remazol Brilliant Blue R</td>
<td>9.72</td>
<td>303</td>
<td>[23]</td>
</tr>
<tr>
<td>RB</td>
<td>Mordant Red 73</td>
<td>0.36</td>
<td>293</td>
<td>[24]</td>
</tr>
</tbody>
</table>

5. CONCLUSION AND RECOMMENDATIONS
This study involved the adsorption of Remazol Brilliant Blue R onto pistachio hull was studied. The removal efficiency of pistachio hull was studied as a function of, pH, initial dye concentration,
adsorbent dose and time via batch method at room temperature. No modifications have been made to the adsorbent. It can be considered that the adsorption process is effected by the surface charges Dye adsorption was affected by pH (pH=2). According to the experimental data, Remazol Brilliant Blue R adsorption on pistachio hull was determined to be Langmuir isotherm (16.739mg/g). The adsorption was endothermic for thermodynamic adsorption study. The data shown that PH is an effective and no-cost adsorbent for the removal of Remazol Brillant Blue R from aqueous solutions.

ACKNOWLEDGMENT
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NOTICE
This study was presented as an oral presentation at the I. International Scientific and Vocational Studies Congress (BILMES 2017) in Nevşehir/Ürgüp between 5-8 October 2017.

SYMBOLS
PH : Pistachio Hull
PBBP: Remazol Brillant Blue R
C₀ : The liquid-phase concentrations of the adsorbate at initial (mg/L)
Cₑ : The liquid-phase concentrations of the adsorbate at equilibrium concentrations (mg/L)
Cₜ : The dye concentration after adsorption
V : Dye volume (mL)
m : Adsorbent mass (g)
qₑ : The equilibrium solid phase concentration (mg/g)
Kₑ : The Langmuir constants (L/g)
aₑ : The Langmuir constants (L/mg)
Kₑ : The adsorption capacity (L/g)
1/n : Intensity of adsorption
ΔS : Changes of entropy
ΔH : Changes of enthalpy
ΔG : Gibbs free energy
Kₑ : The equilibrium constant
T : Temperature (K)
R : The ideal gas constant (8.314 J/(mol K))
Cₑ : In equilibrium, the solid phase concentration (mg/L).

REFERENCES


