Ecological Life Sciences
ISSN: 1308 7258 (NWSAELS)
ID: 2018.13.2.5A0099

Status : Original Study
Received: October 2017
Accepted: April 2018

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DOI	http://dx.doi.org/10.12739/NWSA.2018.13.2.5A0099		
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ADSORPTION OF REMAZOL BRILLANT 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 16.739mg/g. Thermodynamic parameters also studied. The value of Gibbs Free Energy, (ΔG=2.696kJ/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 Brillant 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 Brillant 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 Brillant Blue R dye.

How to Cite:
Savcı, S., Yalvaç, M., and Karaman, Z., (2018). Adsorption of Remazol Brillant Blue R from Aquatic Solution Using Natural Adsorbent (Pistachio Hull), **Ecological Life Sciences (NWSAELS)**, 13(2): 103-113. DOI: 10.12739/NWSA.2018.13.2.5A0099.

2. RESEARCH SIGNIFICANCE

Recently, water pollution has gained attantion 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 thye investigation of adsorption of Remazol Brillant 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.

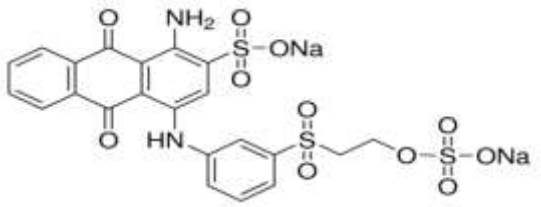
3.1. Material

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

Table 1. Properties of Remazol Brillant Blue R

Remazol Brillant Blue R	
Molecular Weight (g/mol)	626.54
Color	Blue
λ_{max} (nm)	582
Dyepurity	<90%
Chemical Formula	$C_{22}H_{16}N_2Na_2O_{11}S_3$
Structure	

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^{0}C for 2 days and sieved from 20-30-35-50 and 70 mesh screens and used as an adsorbent. Remazol Brillant Blue R ($C_{22}H_{16}N_2Na_2O_{11}S_3$) 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 Brillant 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 Brillant 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:

$$\text{Removal } (\%) = \frac{(C_o - Ce)}{C_o} * 100 \quad (1)$$

C_o(mg/L): The liquid-phase concentrations of the adsorbate at initial

Ce(mg/L): The liquid-phase concentrations of the adsorbate at equilibrium concentrations
The adsorption amount of Remazol Brillant Blue R was calculated as follows, Equation 2:

$$\text{Amount of adsorption } (Q) = \frac{(C_o - C_t)V}{m} \quad (2)$$

C_o: The initial dye concentration (mg/L)
C_t: 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.

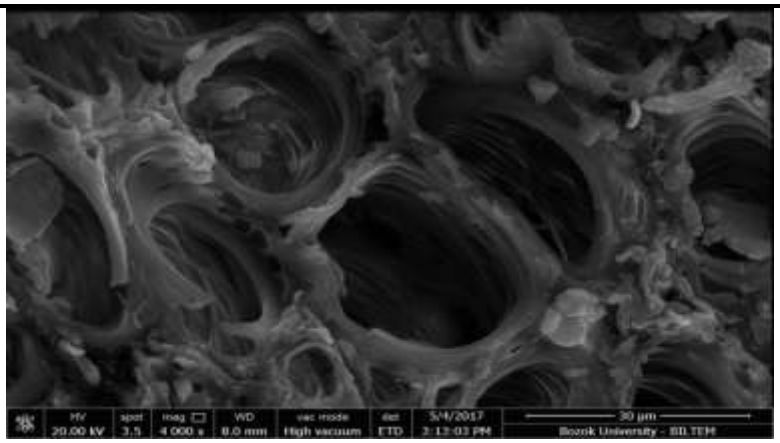


Figure 2. Unloaded adsorbent in SEM Images

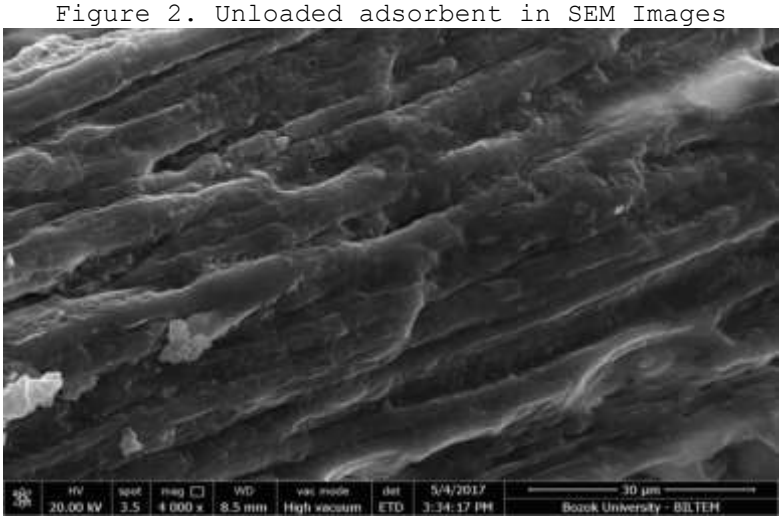


Figure 3. SEM images of dye loaded pistachio hull

4.2. Effect of Contact Time

The effects of contact time for Remazol Brillant Blue R dye adsorption on pistachio hull shown in Figure 4. According to Figure 2, the adsorption of Remazol Brillant 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].

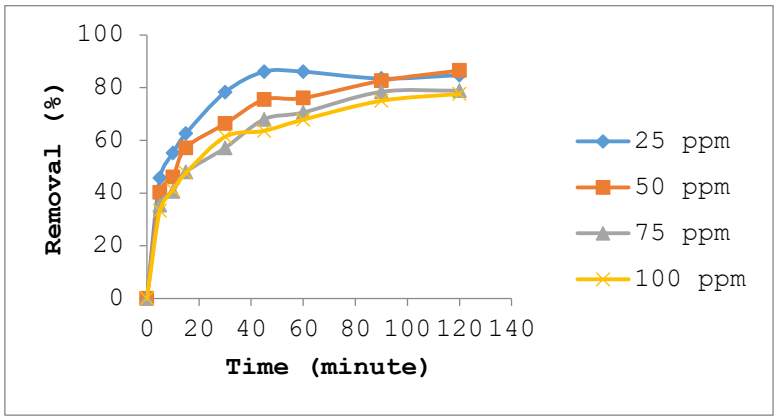


Figure 4. Effect of contact time on Remazol Brillant Blue R dye adsorption on pistachio hull

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 Brillant Blue R (Figure 5). Ahmad et al (2015) studied removal of Remazol Brillant 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 Brillant Blue R. They found that optimum pH is 3 for the system [7]. Also, similar result was obtained by researchers [8 and 9].

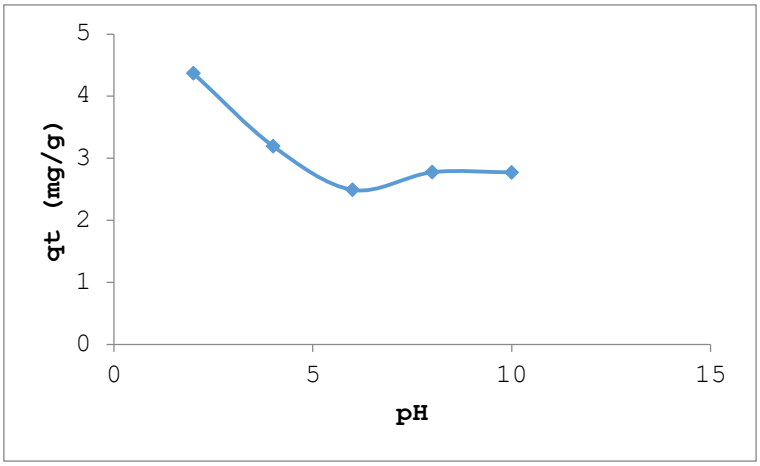


Figure 5. Effect of pH on pistachio hull

4.4. Effect of Concentration

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

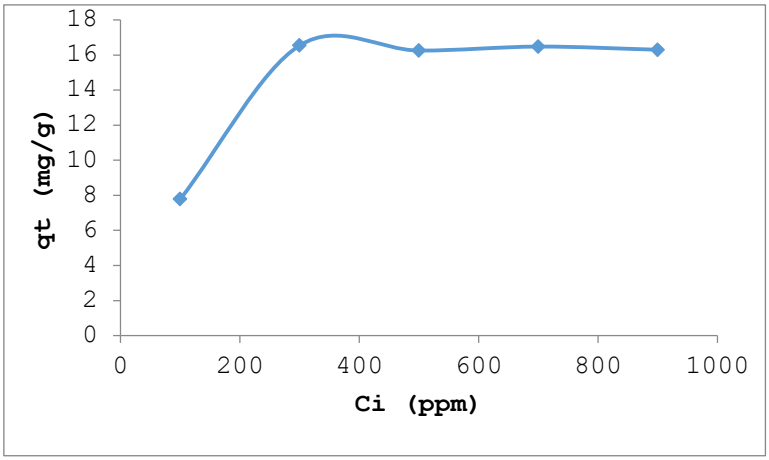


Figure 6. Effect of concentration on Remazol Brillant Blue R dye adsorption on pistachio hull

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].

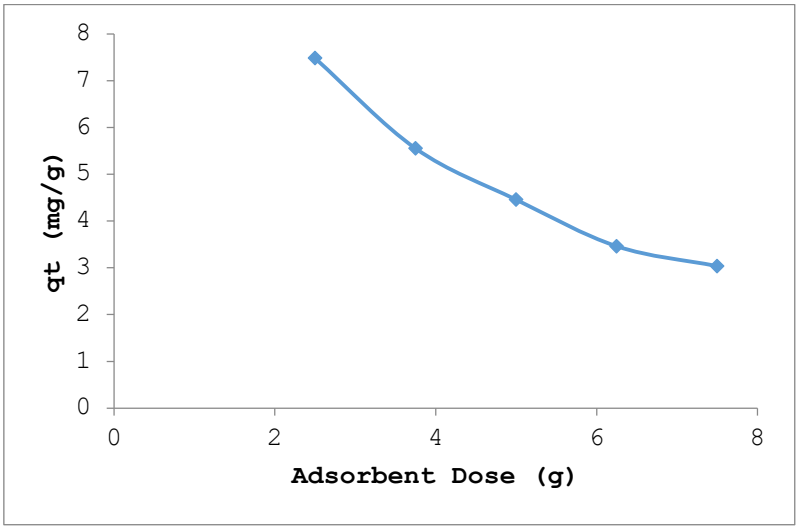


Figure 7. Effect of Adsorbent Dose of Remazol Brillant Blue R dye adsorption on pistachio hull

4.6. Adsorption Isotherms

The isotherm constants are summarized Table 2. The R^2 values (Table 2) show that he 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].

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right)C_e \quad (3)$$

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:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (4)$$

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

Table 2. Parameters for isotherms obtained from equilibrium models

	Parameter (unit)	Methylene Blue
Langmuir	K_L (L/g)	1.299
	a_L (L/mg)	0.0776
	Qmax(mg/g)	16.739
	R^2	0.9989
Freundlich Isotherm	n	4.775
	K_F	4.615
	R^2	0.7825

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

Table 3. Adsorption capacity of Remazol Brillant Blue R on pistachio hull in literature

Adsorbent	Dye	Q_{max} (mg/g)	References
Activated carbon from industrial laundry sewage sludge	Remazol Brillant Blue R	33.47	[14]
Prosopis juliflora modified with H_2O_2	Remazol Brillant Blue R	83.3	[15]
Pistachio hull waste	Methylene Blue	389	[16]
Pistachio nut shells activated with KOH (microwave heating)	Methylene Blue	296.57	[17]
Peanut hull-based activated carbon by microwave	Remazol Brillant Blue R	149.25	[18]
Activated Carbon Prepared from Pinang Frond	Remazol Brillant Blue R	232.59	[19]
Scenedesmus quadricauda	Remazol Brillant Blue R	45.70	[8]
Graphene oxide	Basic Yellow28	68.5	[25]
Cucurbit [8] uril	Acid blue25	434.8	[26]
Sodic bentonite	Bezathren-Blue	5.33	[27]
Pistachio hull	Remazol Brillant Blue R	16.739	This Study

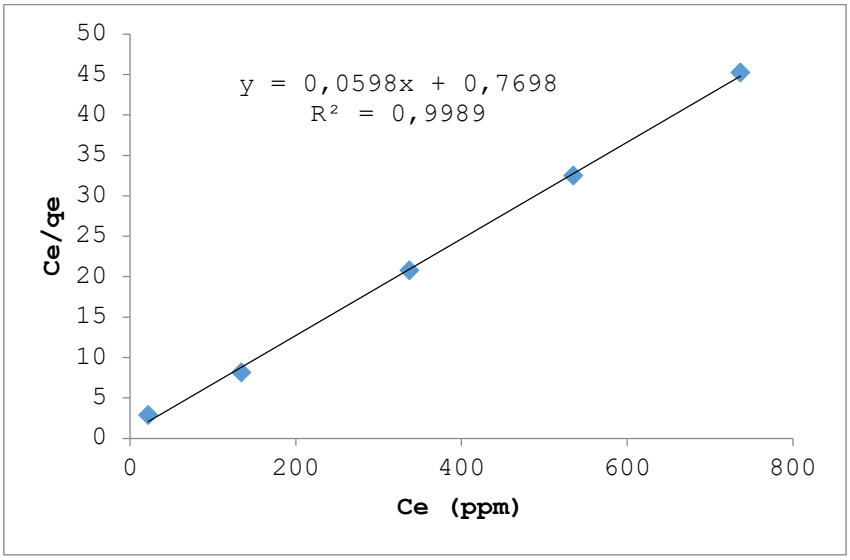


Figure 7. Langmuir Isotherm of Remazol Brillant Blue R on pistachio hull

K_F and n were found to be 4.615 and 4.775 for Remazol Brillant Blue R dye on pistachio hull, respectively (Table 2). Similar results found to be [8] for adsorption of Remazol Brillant Blue R onto immobilized Scenedesmus quadricauda. They explained that values of n>1 for Remazol Brillant Blue R demonstrate a heterogeneous nature of adsorption and positive binding. Langmuir and Freundlich Isotherm models graphics described that Figure 7-8.

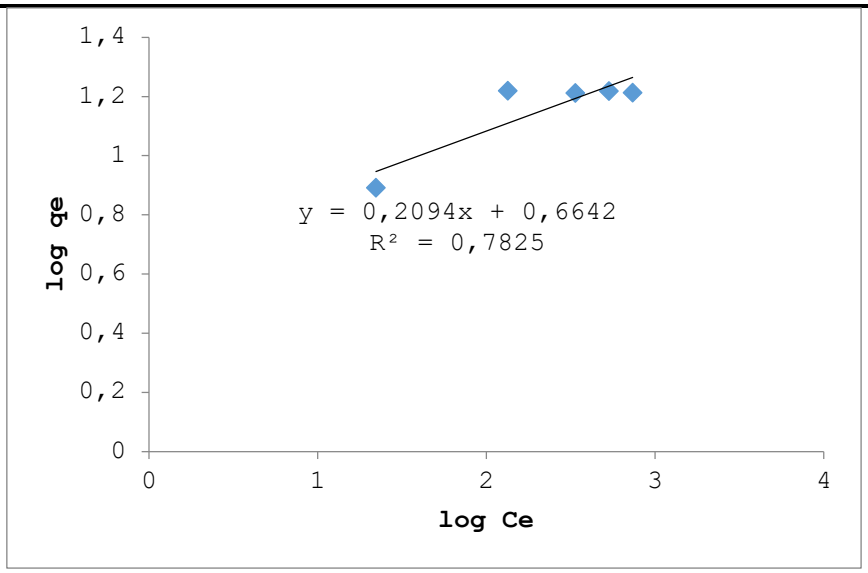


Figure 8. Freundlich Isotherm of Remazol Brillant Blue R on pistachio hull

4.7. Thermodynamic Study

The thermodynamic parameters can be determined using the experimental data in the following equations Eq.5-7 :

$$\Delta G = -RT\ln K_C^0, \quad (K_c=C_a/C_e) \tag{5}$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{6}$$

$$\Delta G = \Delta H - T\Delta S \tag{7}$$

ΔS: Changes of entropy,
ΔH: Changes of enthalpy
ΔG: Gibbs free energy
K_c: The equilibrium constant
T: Temperature (K)
R: The ideal gas constant (8.314J/(mol K)).
Ca: In equilibrium, the solid phase concentration (mg/L).

Thermodynamic equilibrium constant (Kc°) can be calculated from the equilibrium constant by plotting equilibrium constant against initial dye concentration. Table 4 shows Gibbs free energy values (ΔG:2.696kJ/mol) for systems. Thermodynamic adsorption studies demonstrated that adsorption process was endothermic.

Table 4. Gibbs Free Energy Values For Systems

Sorbent	Dye	ΔG° (kJ/mol)	T(K)	References
Pistachio hull	Remazol Brillant Blue R	2.696	298	This work
Titania aerogel	Orange II	1.2	303	[20]
Sepiolite	Reactive blue 221	47.9	293	[21]
Activated carbon prepared from coir pith	Congo Red	0.487	308	[22]
Activated Carbon	Remazol Brillant Blue R	9.72	303	[23]
RB	Mordant Red 73	0.36	293	[24]

5. CONCLUSION AND RECOMMENDATIONS

This study involved the adsorption of Remazol Brillant 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 Brillant 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

Editors thank to Mersin University Project Center Project number: 2017-2-TP2-2526 and Bozok University Scientific Research and Project Department (BAP).

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
C_o : The liquid-phase concentrations of the adsorbate at initial (mg/L)
C_e : The liquid-phase concentrations of the adsorbate at equilibrium concentrations (mg/L)
C_t : The dye concentration after adsorption
V : Dye volume (mL)
m : Adsorbent mass (g)
q_e : The equilibrium solid phase concentration (mg/g)
K_L : The Langmuir constants(L/g)
a_L : The Langmuir constants (L/mg)
K_F : The adsorption capacity(L/g)
1/n : Intensity of adsorption
ΔS : Changes of entropy
ΔH : Changes of enthalpy
ΔG : Gibbs free energy
K_c : The equilibrium constant
T : Temperature (K)
R : The ideal gas constant (8.314 J/(mol K))
C_a : In equilibrium, the solid phase concentration (mg/L).

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