Study the adsorption of remazol brilliant blue dye from aqueous solutions using bioresource activated carbon

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Abstract

Adsorption of Remazol Birilliant blue R dye (RBBR) from aqueous solutions on activated carbon prepared from coconut shell was compared, and where coconut shell was investigated in terms of adsorbent dose, dye concentration, temperature, and pH.

The results were compared for all parameters. The equilibrium adsorption data were interpreted using Langmuir, Freundlich, and Temkin models. The adsorption of of RBBR dye was better represented by the Freundlich equation.

The change in the thermodynamic parameters, like standard free energy ($\Delta G°$), standard enthalpy ($\Delta H°$), and standard entropy ($\Delta S°$) of the adsorption process were calculated, from the results show adsorption process was endothermic.

Key Words: activated carbon, Langmuir model, Freundlich model, Temkin model, Remazol Birllian blue dye, Adsorption.

الخلاصة

تم امتزاز صبغة الريموزال الزرقاء البراقة RBBR من المحاليل المائية باستخدام الكاربون المنشط المحضر من قشور جوز الهند.

تم دراسة قابيلة الامتزاز من خلال دراسة تاثير وزن المادة المازة, تركيز المادة الممتزة, درجة الحرارة, وكذلك الدالة الحامضية.

ان نتائج الامتزاز تم تطبيقها على كل من معادلة لانكماير Langmuir, فرندلج Freundlich, تمكن Tempkin الايسوثرمية, ووجد ان نتائج الامتزاز تطيع بصورة جيدة معادلة فرندلج.

بالاضافة الى ذلك تمت دراسة التغيرات الثرموديناميكية في الطاقة الحرة (ΔG) والانتروبي (ΔS) والانثالبي (ΔH), ومن خلال قيم الانثالبي وجد بان التفاعل هو ماص للحرارة.

الكلمات المفتاحية:الكاربون المنشط, موديل لانكماير Langmuir, موديل فرندلج Freundlich, موديل تمكن Tempkin , صبغة الريموزال الزرقاء البراقة, الامتزاز.

Introduction

Dyes are being widely used in textile, dyeing, paper printing, color photography and other industries[1-3] . In textile dyeing industries the reactive dyes are used due to their superior fastness in the applied fabric, high photolytic stability, high solubility and resistance to microbial attack[4-7]

Synthetic dyes, classified by their chromophores, have different and stable chemical structures to meet various coloring requirements and often are not degraded and/or removed by conventional physical and chemical processes[8]. These dyes contain chromophoric groups such as azo, anthraquinone, triarylmethane etc. and reactive groups e.g. vinyl sulphone, chlorotriazine, trichloropyrimidine etc.

Remazol Brilliant Blue R (RBBR) is a reactive dye, frequently used as a starting material in the production of polymeric dyes[9]. It represents an important class of toxic and recalcitrant organopollutants[10]. They consist of a chromophore and a functional group that binds the dyestuff to the fiber[11]

There are various conventional methods of removing dyes including, ozonation[12], membrane separation[13], coagulation[14] and adsorption method[15-19]

The adsorption method is considered the better one among these methods due to its low cost, simple design and easy operation. One of the best and economical types of adsorbent surface is the activated carbons (ACs). ACs are widely used for the removal of dyes from wastewater.

The aim of this paper was to examine adsorption characteristic for RBBR on activated carbon derived from coconut shell. The effect of different factors such as initial dye concentration, temperature, adsorbent dose and pH were investigated.

Materials and Methods

Materials

Remazol Brilliant Blue R(RBBR) purchased from Sigma–Aldrich Company Ltd., an anthraquinone-based dye, was chosen as the adsorbate in this study. Distilled water was used to prepare all solutions. The chemical formula of RBBR (Fig.1) is $C_{22}H_{16}N_2Na_2O_{11}S_3$, with the molecular weight of 625.56 g/mol. All other chemicals used in this experiment were of analytical grade.

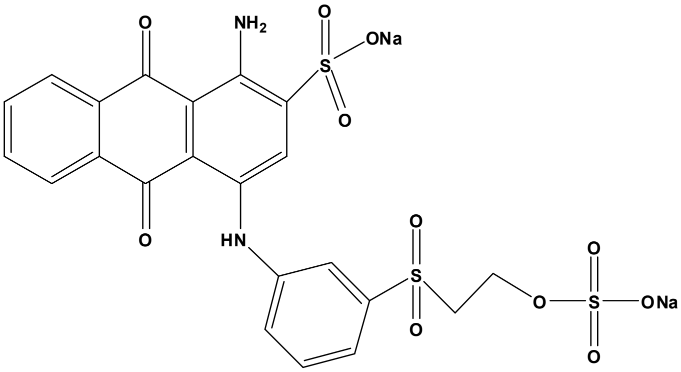

Figure 1:Chemical Structure of Remazol Birlliant blue RBBR

Preparation of Coconut Shell Activated Carbon (AC)

10 g of the dried coconut shell is impregnated with 50 mL of 60 % (wt/wt) H_2SO_4 solution, so it has to have an impregnation ratio of 3:1(wt. H_2SO_4: wt. Coconut shell). The H_2SO_4 soaked sample is left overnight and the excess water is evaporated in an oven at 100°C to ensure complete absorbance of the H_2SO_4 on to the coconut shell powder. The acid soaked samples are semi-carbonized in a hot air oven at a preset furnace temperature of 500°C for 2 h under a self-generated atmosphere. After activation, the samples are washed repetitively with distilled water to remove residual acid. The product is finally air dried at 105°C, before being manually ground to a fine powder and sieved to a size below 75 µm, which are utilized for product characterization.

Equilibrium adsorption isotherms

Equilibrium adsorption isotherms for RBBR was undertaken at 25 ± 1 °C, and pH 6.7. A mass of 0.075 ± 0.001 g of activated carbon (75 µm) was added to 100 cm^3 conical flasks containing 100.0 cm^3 of RBBR of (200 ppm) concentration. The conical flasks were placed in a thermostated shaker for 1 hr until equilibrium was achieved.

The effect of pH solution on adsorption behavior of the RBBR dye on the activated carbon 0.75 $g.L^{-1}$ was studied for (200 ppm) concentration at varying pH of solution (2,3, 4.7, 6.7, 9, 10, and 11), using 0.1 M HCl or 0.1 M NaOH solutions (prior to the addition of the adsorbent). The conical flasks were placed in the shaker at 25 ± 1 °C for 1 hr.

Also the effect of temperature on adsorption behavior of the reactive dye on the activated carbon (0.75 $g.L^{-1}$) was studied for varying concentrations: (10-300 ppm) at three temperatures (283, 298, and 313K), and pH 6.7. The concentration of RBBR was determined using UV–visible spectrophotometer at maximum wavelength of 595 nm. The RBBR uptake at equilibrium, *qe* (mg/g), was calculated by Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad (1)$$

Also the removal of dye percentage was calculated by Eq. (2)

$$R_{\%} = \frac{C_0 - C_e}{C_0} x100 \qquad (2$$

where C_0 and Ce (mg/L) are the liquid-phase concentration of RBBR at initial and at equilibrium, respectively. V (L) is the volume of the solution and w (g) is the mass of dry activated carbon.

Results and Discussion:

Effect of initial solution pH on adsorption of RBBR dye

The ionic forms of the dye in solution and the surface electrical charge of the carbon depend on the solution pH. Therefore, the interaction between the dye and adsorbent is mainly affected by ionization states of the functional groups on both dye molecule and adsorbent surface [9, 20]

The effect of solution pH on the RBBR removal was studied at initial pH values of 2–12. As shown in Fig. 2, the percentage removal of RBBR was high at pH 2, then decreased slightly, and after this increased again at pH 6.7, then dropped very high with increasing pH.

The high percentage removal of the RBBR solution at acidic pH could be attributed to the electrostatic interactions between the positively charged adsorbent and the negatively charged RBBR dye anions. The surface charge of adsorbent has become generally positive charge in acidic medium and the negative charge in basic medium. Therefore, the removal of anionic dye by AC was high at lower pH, and will be very high at pH 6.7, this is may be attributed to effect of point of zero charge for the adsorbent surface. The adsorbent surface would attract the negatively charged functional groups located on the RBBR dye and hence increase the adsorption capacity. [21, 22]

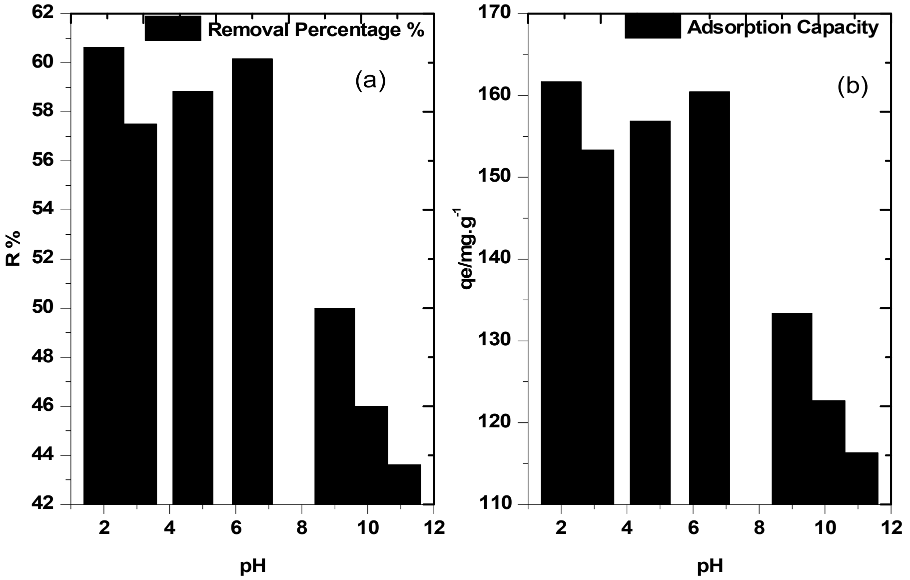

Figure 2: Effect of solution pH on a) removal percentage, b) adsorption capacity of RBBR on ACs.

Effect of initial dye concentration on adsorption of RBB dye

The effect of initial dye concentration can be carried out by prepare adsorbent–adsorbate solution with a fixed adsorbent dose and different initial dye concentration. The percentage removal and adsorption capacity of dye is highly dependent on the initial amount of dye concentration, results shown in Fig. 3.

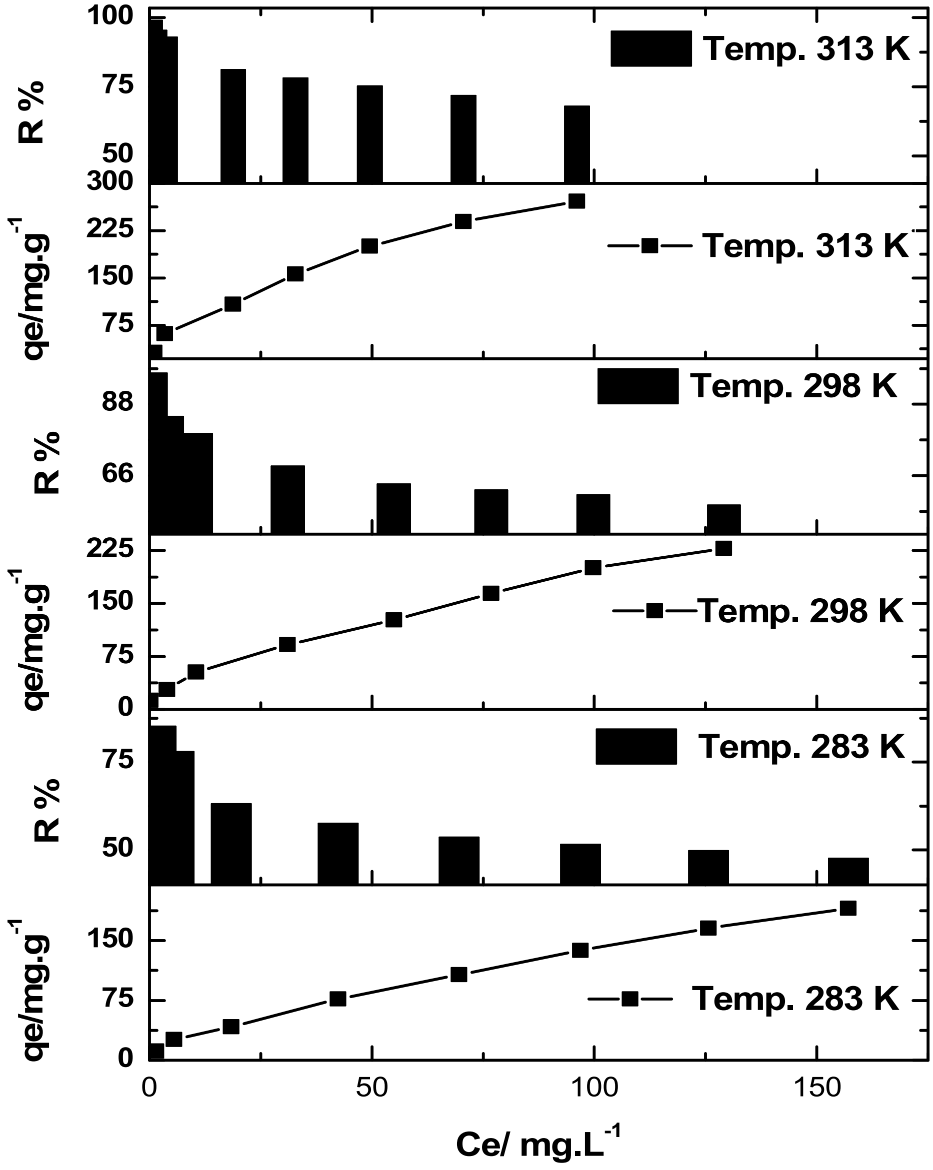

Figure 3: Effect of dye concentration on the adsorption and removal percentage at different temperatures.

The effect of the initial of dye concentration factor depends on the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface[23]. Generally the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface[24]. The suggested mechanism for adsorption behavior of RBBR dye shows in Fig.4.

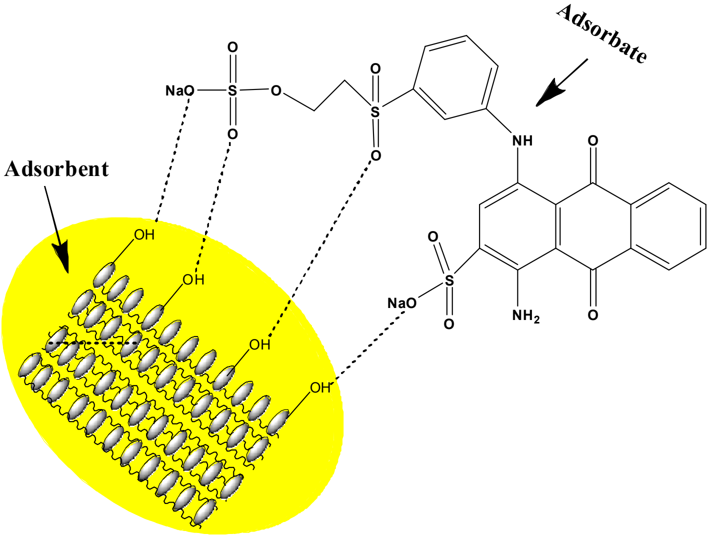

Figure 4: Physical attractive forces between activated carbon surface and functional group in the RBBR dye in aqueous solution.

At a low concentration there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will lack[25].

On the other hand the increase in initial dye concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration[26].

Effect of adsorbent dose

The effect of activated carbon concentration on RBBR adsorption in the first 60min of contact was studied by varying the adsorbent dose from 0.5 to 2.0gL^{-1} in a 200mgL^{-1} RBBR solution. Increasing the adsorbent concentration is seen to enhance the percentage removal of RBBR. Increased adsorbent concentration implies a greater surface area of activated carbon and, consequently, the greater availability of the binding sites on surface area.[27]

The result shown in Fig. 5, that the adsorption of RBBR dye increases upto a certain limit and then it remains constant. An increase in adsorption with adsorbent dosage can be attributed to increased surface area and the availability of more adsorption sites. But the amount adsorbed per unit mass of the adsorbent decreased considerably. The decrease in unit adsorption with increasing dose of adsorbent may be due to the adsorption sites remaining unsaturated during the adsorption process[9, 28]

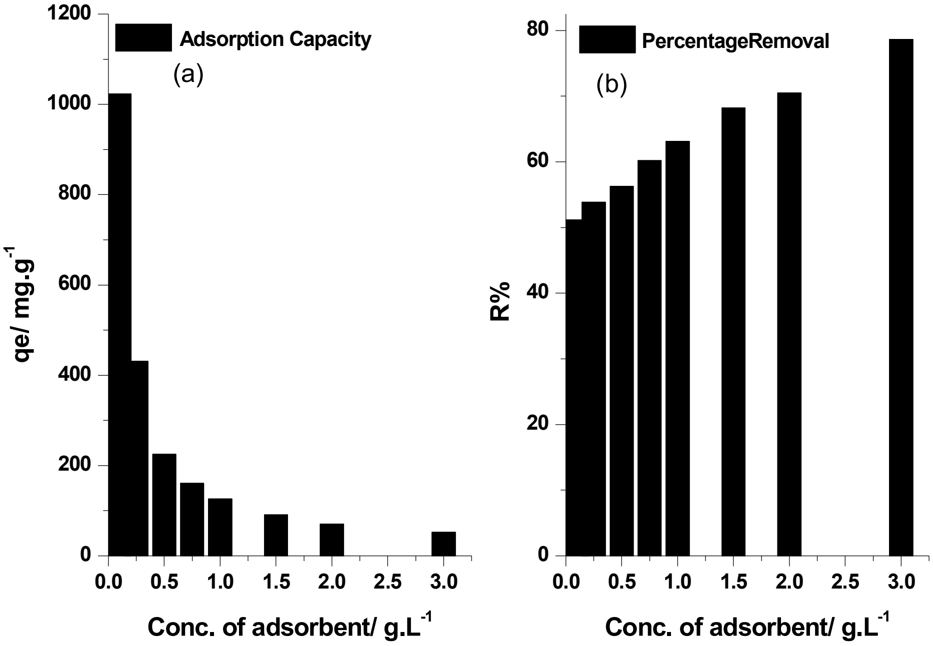

Figure 5: Effect of adsorbent amount on a) adsorption capacity, b) removal percentage.

Adsorption Isotherm:

In order to describe the uptake of dyes by adsorbent, the isotherms data were analyzed using non-linear theoretical models and non-linear fitting method. The two and three parameters models, namely Langmuir, Freundlich, and Temkin equations were applied to evaluate the fit by isotherm for the adsorption of dyes, results are shown in Fig.6. The general form of the ***Langmuir*** isotherm is[29]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (3)$$

where K_L(L mg^{-1}) is a constant and *Ce* is the equilibrium concentration (mg L^{-1}), *qe* is the amount of dye adsorbed per gram of adsorbent (mg g^{-1}) at equilibrium concentration *Ce*, and *qm* is the maximum amount of solute adsorbed per gram of sorbent (mg g^{-1}), which depends on the number of adsorption sites. The Langmuir isotherm shows that the amount of dye adsorption increases as the concentration increases up to a saturation point [30].

The ***Freundlich*** empirical model is represented by [31]:

$$q_e = K_F\, C_e^{1/n} \qquad (4)$$

where $K_F(\mathrm{mg}^{1-1/n}\,\mathrm{L}^{1/n}\,\mathrm{g}^{-1})$ and n are Freundlich constants depending on the temperature and the given adsorbent–adsorbate couple. The parameter n is related to the adsorption energy distribution, and K_f indicates the adsorption capacity.

The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm is[19]:

$$q_e = \frac{RT}{B}\ln\left(K_T C_e\right) \qquad 5$$

where K_T is the equilibrium binding constant, corresponding to the maximum binding energy, and constant B is related to the heat of adsorption.

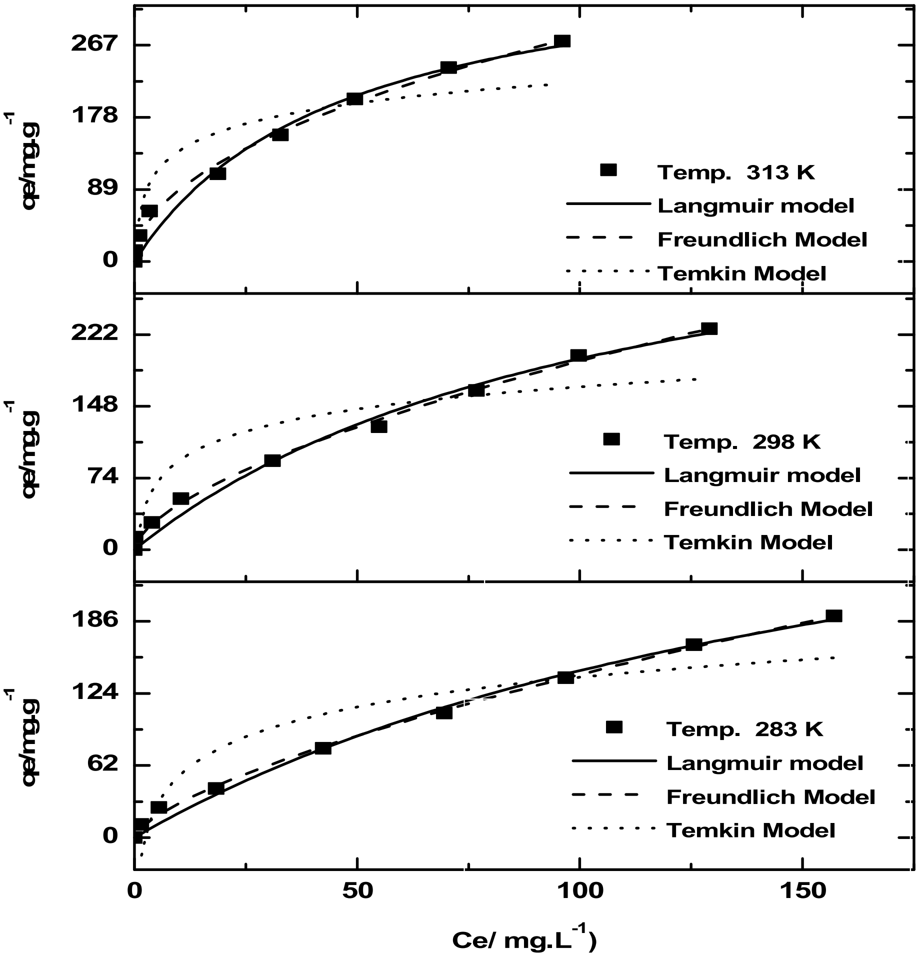

Figure 6: Adsorption isotherm models at different temperatures.

After the equilibrium adsorption data were fitted with different isotherm models, the fitting parameter values are summarized in Table 1. The favorability of the dye adsorption process onto AC was evaluated using a dimensionless parameter (R_L) derived from the Langmuir expression[32]. It is defined as:

$$R_L = \frac{1}{1 + bC_0} \qquad (6)$$

The b parameter is a coefficient related to the energy of adsorption and increases by increasing strength of the adsorption bond. The adsorption process can be defined as irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$) in terms of R_L. The calculated value of R_L for adsorption of different initial concentrations at different temperatures they are shown in Fig.7. that they fall between 0 and 1. The highest correlation factors ($R^2 > 0.99$) of Freundlich model for all dyes indicates that the Freundlich model gives the best fit to the experimental data and so the nature of adsorption of dyes on the adsorbents is more compatible with Freundlich assumptions and imply that adsorption of investigated dyes on the adsorbent is mono-layer and after saturation of this layer no further adsorption took place Fig. 7.

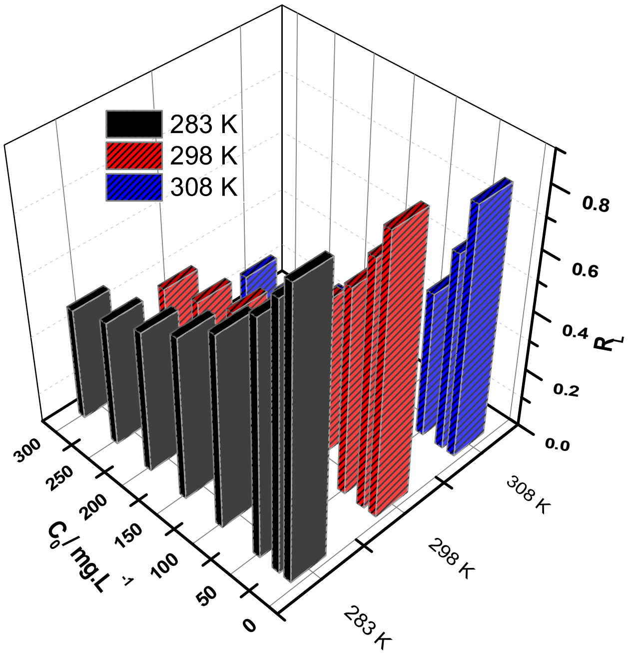

Figure 7: Three dimensional model for effect of initial dye concentration on the R_L values in the presence of different temperatures.

Table 1: Isotherm parameters for various parameters adsorption isotherms for the adsorption of RRBBR dye onto AC at different temperatures.

Isotherm models	***Parameters***	***Temperature***		
		283.15 K	***298.15 K***	***308.15 K***
Langmuir	q_m (mg.g^{-1})	402.87±66.752	414.83±72.562	393.85±59.791
	K_L(L.mg^{-1})	0.005±0.001	0.009±0.002	0.021±0.007
	R^2	0.98759	0.97923	0.96524
	F value	1087.21107	641.0075	375.56949
	prob>F	6.10949E-9	3.82893E-8	2.42886E-7
Freundlich	K_F	6.176±0.637	11.168±1.418	27.896±2.928
	1/n	0.678±0.021	0.620±0.028	0.500±0.025
	R^2	0.99734	0.99499	0.99396
	F value	5083.532	2665.758	2176.766
	prob>F	2.807E-11	2.678E-10	5.433E-10
Temkin	B/J.mole^{-1}	63.743±10.344	74.834±15.407	69.770±11.818
	K_T	0.418±0.203	1.599±1.304	4.105±3.016
	R^2	0.85841	0.79117	0.84645
	F value	70.965	46.601	63.881
	prob>F	6.544E-5	2.471E-4	9.169E-5

Effect of temperature

The effect of temperature on the adsorption process can be carried out by prepare adsorbent–adsorbate solution with different initial dye concentration then shaken together until 60 minutes at 30, 40 and 50 °C. results are shown in Fig. 3.

Temperature is an indicator of the adsorption nature whether it is an exothermic or endothermic process. If the adsorption capacity increases with increasing temperature then the adsorption is an endothermic process. This may be due to increasing the mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature[33, 34]. This effect depends mainly on the movement of dye molecules of each dye class. The decrease of adsorption capacity with increasing temperature indicates that the adsorption is an exothermic process[35]. The increase in the adsorption capacity at higher temperatures is due the mobility of dye molecules, which facilities their penetration and accessibility to active sites in the porous structure of the solid and is reflected in a higher retention of anionic dye on the ACs. This effect suppresses the activation energy barrier and increases the rate of intraparticle diffusion[33]. Gibbs free energy ($\Delta G°$) was exothermic in nature, suggesting that the adsorption process is spontaneous and more favored at higher temperatures. The change in total enthalpy was endothermic, suggesting that the process is endothermic in nature. Thus, the equilibrium adsorption capacity was clearly affected by temperature, demonstrating that higher temperatures favor the interaction between the dye and ACs. The positive entropy variation ($\Delta S°$) suggested that the process was governed by entropic effects corresponding to an increased degree of freedom in the system during the adsorption of the dye molecules onto the solid.[33]

Adsorption thermodynamic

It is well known that thermodynamic parameters can evaluate the orientation and feasibility of the physiochemical adsorptive reaction. Three thermodynamic parameters that being considered are standard enthalpy ($\Delta H°$), standard free energy ($\Delta G°$) and standard entropy ($\Delta S°$). The value of $\Delta H°$ and $\Delta S°$ can be obtained from the following equation:

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (7)$$

where R (8.314 J/mol K) is the universal gas constant, T (K) is the absolute solution temperature and K_L(l/mg) is the Langmuir isotherm constant. The values of $\Delta H°$ and $\Delta S°$ can be calculated, respectively from the slope and intercept of ln K_L versus $1/T$ plot (Figure not shown). $\Delta G°$ can then be calculated using the relation below:

$$\Delta G^0 = -\mathrm{RT}\ln K_L \qquad (8)$$

The calculated values of $\Delta H°$, $\Delta S°$, and $\Delta G°$ for adsorption of RBBR on AC are shown in Table 2. The important thermodynamic function $\Delta H°$ is very useful whenever a differential change occurs in the system[36]. The positive $\Delta H°$ value indicated that the adsorption process was endothermic in nature which is consistent with the results obtained earlier when the RBBR uptake increases with increasing solution temperature. In addition, the $\Delta G°$ values for all temperatures were negative, which reflect the spontaneous nature of the adsorption processes[21]. The positive values of $\Delta S°$ showed the affinity of the adsorbent for adsorbate and the increasing randomness at the solid–solution interface with some structural changes in the adsorbates and adsorbents during the adsorption process[22, 36].

Table 2: Thermodynamics parameters for adsorption of RBBR dye on the surface of ACs.

Temp./K	ΔH^0/ kJ.mole^{-1}	ΔS^0/J.K^{-1}.mole^{-1}	ΔG^0/ kJ.mole^{-1}
283	33.50625	131.9681	-4.01104
298			-5.44378
313			-8.00803

Conclusion

1. The results show that the adsorption behavior of RRB dye by AC could be described by Langmuir, Freundlich and Temkin models.

2. The removals of RBBR increase parallel with the increase of the adsorbent dose, and temperature. The efficiency was increased at pH 2 and 6.7, whereas it was diminished at pH 12.

3. The adsorption was highly dependent on initial dye concentration, temperature, adsorbent dose and pH.

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