

Synthetic Textile Red Dye Removal From Aqueous Solution by Adsorption onto Pomegranate Peel

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Abstract

This study is conducted to evaluate the ability of using pomegranate peel as low cost material for adsorption one of synthetic textile dye (C.I.Direct Red 89 dye). The removal of dye from aqueous solution is done by using pomegranate peel with two forms, as raw pomegranate peel (RPP) and activated carbon prepared from pomegranate peel(ACPP). Some operational factors like contact time, pH, adsorbent dosage , and temperature were investigated in experimental work. Also the thermodynamic parameters ΔH , ΔG , and ΔS were calculated, the result shows that the adsorption process of dye onto two forms of adsorbents was spontaneous and endothermic in nature. Finally, the adsorption isotherm of experimental data we refitted for the Langmuir, and Freundlich equations.

Key Words: Adsorption, pomegranate peel, Langmuir isotherm, Freundlich isotherm.

الخلاصة

تهتم هذه الدراسة بتقدير قابلية قشور الرمان كمادة رخيصة الثمن لامتنزاز إحدى صبغات النسيج الصناعية (C.I.DirectRed 89 dye). وقد استخدمت قشور الرمان في ازالة الصبغة من محلولها المائي بشكلين ، بشكلها الخام (RPP) وكفحم منشط محضر من قشور الرمان (ACPP). وقد تم دراسة بعض العوامل المؤثرة على عملية الامتنزاز مثل زمن الاتزان، وتأثير الدالة الحامضية، تأثير وزن المادة المازة، كما تم دراسة تأثير درجة الحرارة على عملية الامتنزاز واستخراج قيم الدوال الترموديناميكية ΔH ، ΔG و ΔS وقد اظهرت النتائج ان عملية امتزاز الصبغة باستخدام قشور الرمان كانت تلقائية وان التفاعل ماص للحرارة. أخيرا تم دراسة ايزوثيرم الامتنزاز بتطبيق نموذج لانكماير وفرندلخ على بيانات الامتنزاز. الكلمات المفتاحية : الامتنزاز، قشور الرمان، ايزوثيرم لانكماير، ايزوثيرم فرندلخ.

Introduction

Textile industry wastewaters are highly colored and their discharge to the rivers makes water ineligible for any use (Baughman & Perenich ,1988). The textile wastewater contain large amount of dyes and other contaminant.

Dye contains pollutant including acids, dissolved solids, toxic impurities, and color, many dyes are poisonous to some living organism and may cause actual destruction of their motivational capabilities. Therefore, we need to get rid of color from the influent wastewater before disposal it to the river stream (Chu, 2001).

There are several treatment technologies used to de-colorization dye from textile waste water .The adsorption , oxidation , and biological methods present the most important of these technologies (Bousher *et.al.*,1997).

Adsorption applications have developed due to sharp rising of environmental and quality requirements. It is often used as a method for purification solution from dissolved pollutant organic compounds, which are highly toxic (Frimmel, 200).

Recently many local cheap materials were studied as new adsorbents to remove pollutant and dye from water. The aim of this work is to evaluate the ability of pomegranate peel as cost-effective and practical adsorbent to rid off the C.I.Direct Red 89 dye from aqueous solution.

Material and methods

A-Adsorbent material

Pomegranate peel was obtained from kitchen waste. It is used to remove synthetic dye as two forms:-

First: as raw material (RPP), pomegranate peel was washed to remove dust, dried and grounded , then the grounded pomegranate peel was washed several times with distilled water til no color was observed. Then it dried in an electrical oven for

ten hours at 50°. Then the dried pomegranate peel was sieved to particle size 75-250 µm and stored for future use. The effective particle size gives higher percentage removal of red dye was 75µm, therefore this size was used in experimental data.

Second: as activated carbon prepared from pomegranate peel (ACPP). The dried pomegranate peels were grounded and sieved to a particle size 1-2 mm. Then it was activated at 500°C in a furnace for (60min) in the absence of air. After activation, it is immersed with HCl solution (0.1 M) to remove ash. In addition, it is washed several times with distilled water, then dried in electrical oven at 50° for ten hours and stored for future use. The batch study is carried out by using particle size 1mm, which is given the maximum adsorption rate.

B- Adsorbate dye

The C.I. Direct Red 89 dye used in the present study was obtained from Al-Hilla textile factory. Table (1) lists some of its properties.

Table (1) Properties of C.I. Direct Red dye 89 (Al-Hilla textile factory)

Properties	
Name	C.I. Direct Red 89
Molecular Formula	C ₄₄ H ₃₂ N ₁₀ Na ₄ O ₁₆ S ₄
Molecular Weight	1177.0
Cas Registry Number	12217-67-3
Chemical structure	

Batch adsorption experiments

This work is conducted to study the factors effecting adsorption process. These factors included the effect of contact time, solution pH, adsorbent dosage, and temperature. Experimental procedure was done with two forms of adsorbent (RPP) and (ACPP) and compare their adsorption removal efficiencies. Batch experiments were implemented by using knowing weight of both two forms of adsorbents into separate conical flasks with (25ml) of dye solution of (10 ppm) and shaking at 300 rpm at temperature (30°) and pH solution equal to (6.5). The contact time was determined by shaking 0.2 gm from adsorbents with 25ml solution of (10 ppm) of red dye for different time (10,20,30,40,50,60,70,80,90,100,110,120) min. the effect of pH solution was carried out by mixing 0.2 gm of adsorbents and 25ml of dye solution at different values of pH (2,4,6,8,10) for 70 min and 80 min for (RPP) and (ACPP) respectively. Solution pH was modified with 0.1M HCl and 0.2M NaOH. The impact of adsorbent dosage is done by adding desired weights (0.05, 0.1, 0.15, 0.2, 0.25, 0.3) of both forms of adsorbents to the (25ml) of dye solution of (10 ppm) for 70 min and 80 min for (RPP) and (ACPP) respectively. Effect of temperature on adsorption process is implemented at (10, 20,30,40,50 C °). The percentage removal of dye in the solutions before and after adsorption was identified by using UV-visible

spectrophotometer at wavelength (λ max.) for red dye 495nm. The adsorption rate of dye can be describe according to the express below:

$$\% \text{ Adsorption} = \left[\frac{C_0 - C_e}{C_0} \right] \times 100 \quad \dots\dots\dots(1)$$

And the quantity of red dye at equilibrium (Q_e) was computed from the equation below: (Ahmed *et.al.* , 2005)

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad \dots\dots\dots(2)$$

Where:-

C_0 = the initial concentration of dye (mg/L)

C_e = the equilibrium concentrations of dye in solution (mg/L).

V = the volume of solution (L)

m = the weight of adsorbate (gm)

Result and discussion

Effect of contact time

The experimental work shows that the adsorption capacity of two forms of adsorbents increases with increasing contact time till reaches to equilibrium. The contact time stabilizes at 70min for (RPP) and 80 min for (ACPP).

Effect of pH

Five experiments were implemented with different solution pH (2,4,6,8,10) to consideration the effect of pH of the solution on the efficient removal of direct red dye by adsorption onto (RPP) and(ACPP) respectively . Figure (1) shows the effect of pH solution. The result showed that the efficient removal of dye increase with decreasing of pH value in both forms of adsorbents.

The high percentage efficiency removal of the dye at acidic medium may be attributed to the electrostatic reactions between the positively charged adsorbent and the negatively charged dye anions. The surface charge of adsorbent has become positive charge in an acid pH medium (Bello *et.al.*, 200).

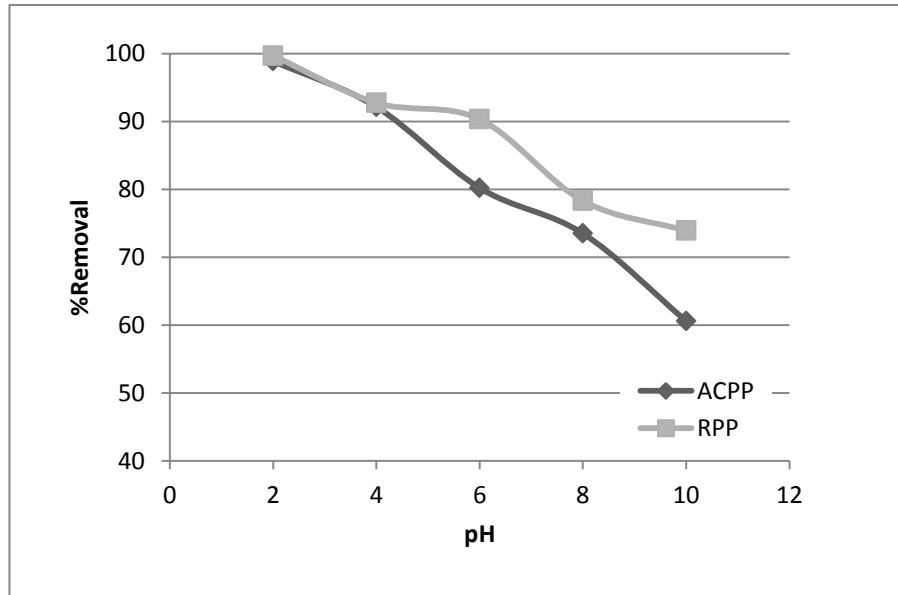


Fig.(1): Effect of pH solution on adsorption red dye.

Effect of adsorbent dosage

The effect of adsorbents dosage is obtained and plotted in fig (2). This figure shows that the efficient removal of dye increase with increasing weight dosage for both form of adsorbents. It is evident that at 0.2 gm of both adsorbents the pomegranate peel started for achieving the higher removal percentages of dye. This is beyond to the at higher dosage of sorbent the surface area of adsorption increases.

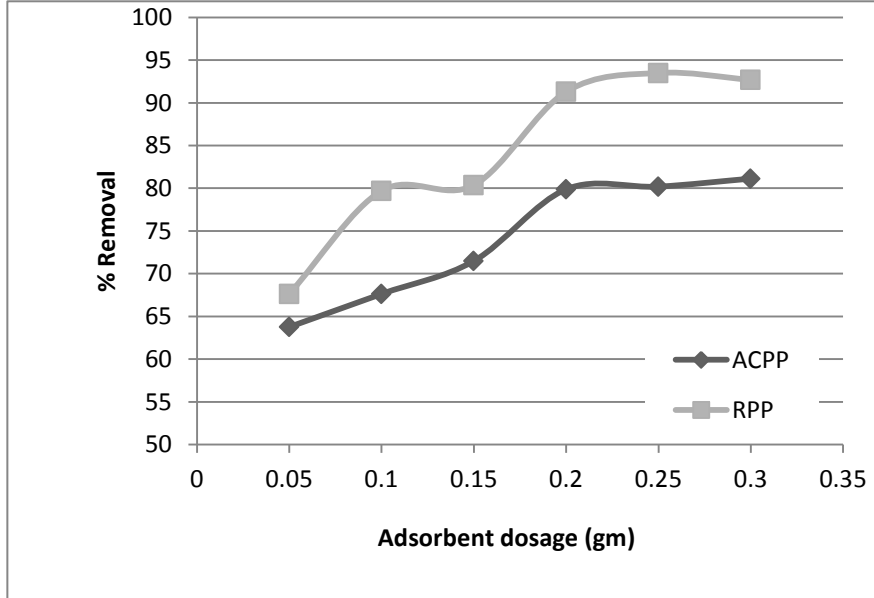


Fig. (2) : Effect of adsorbents dosage on removal rate of dye

Effect of temperature

To study the influence of temperature on the adsorption five different temperature were used (10,20,30,40,50C °) with concentration of (10 ppm) of dye. The results show there is little variation in adsorption efficiency at this range of temperature and adsorption efficiency of dye increases with temperature increase. Thus it indicated that the adsorption process endothermic.

This means the interaction between adsorbents and the dye molecules needs a perceivable energy in order to occur. Endothermic dye uptake may also be returned to the possibility of occurring absorption process by the surface (Saja *et.al.*, 2007).

The study of temperature effect also helps in estimating the basic heat adsorption (ΔH), thermodynamic functions Gibbs energy (ΔG), and the change in entropy (ΔS) of the adsorption process.

The equilibrium constant (K_d) at each temperature is obtained from the equation (3):

$$K_d = \frac{Q_e}{C_e} \times \frac{V}{W} \dots\dots\dots(3)$$

Where

Qe: the magnitude adsorbate in (mg/gm),

Ce: the concentration of the adsorbate at the equilibrium (mg/L).

V: volume of liquid phase (25ml)

W: weight of adsorbent (0.2gm)

The heat of adsorption (ΔH) calculated from plotted ($\log K_d$) versus ($1/T$) produce straight line with slop ($-\Delta H/ 2.303R$) as shown in figures (3&4) according to the Van't Hoff equation:

$$\text{Log}K_d = -(\Delta H/2.303RT) + \text{constant} \dots\dots\dots(4)$$

The change in the Gibbs energy is determined from the equation (5). :

$$\Delta G = -RT \ln K_d \quad \dots\dots\dots(5)$$

Where R, is the gas constant (8.314 J K⁻¹ mole⁻¹),

T is the absolute temperature in Kelvin.

The change in entropy (ΔS) is calculated from Gibbs-Helmholtz equation

(Ayad, 2007):

$$\Delta G = \Delta H - T\Delta S \quad \dots\dots\dots(6)$$

Table (2) illustrates the thermodynamic parameters values of red dyes on the two forms of pomegranate peel.

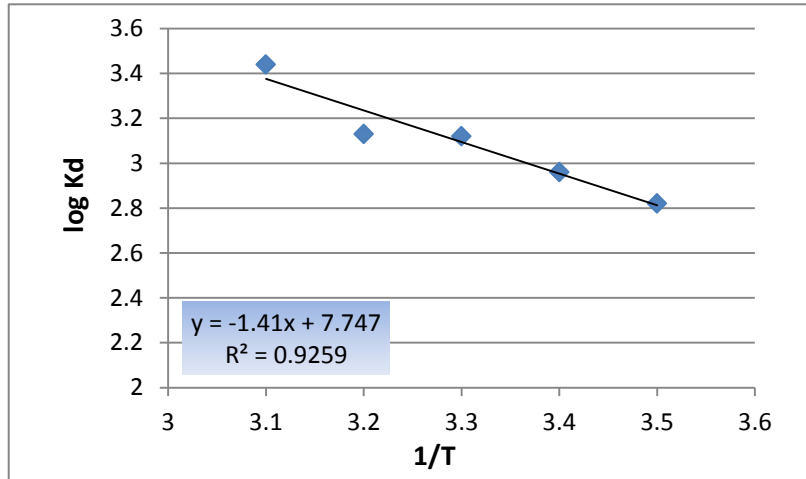


Fig (3): Plot of logK_d versus 1/T for estimation thermodynamic parameters to RPP

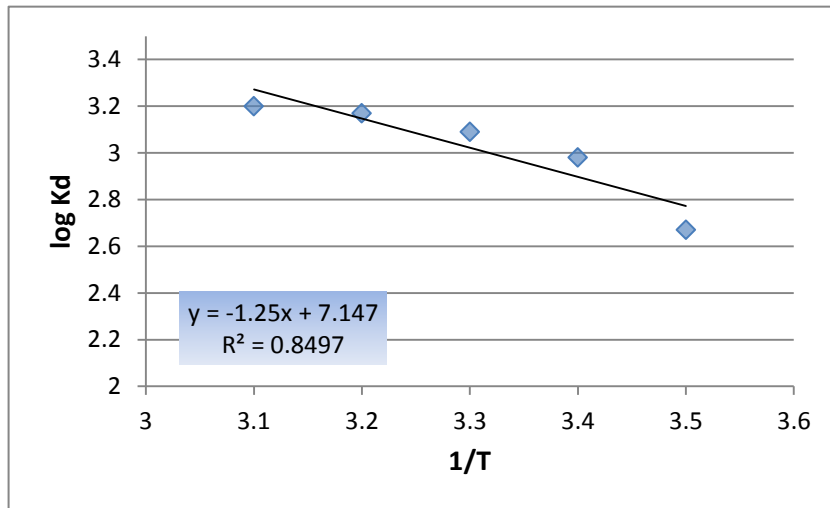


Fig (4): Plot of logK_d versus 1/T for estimation thermodynamic parameters to ACPP

Table (2): Values of thermodynamic parameters' (ΔH , ΔG , ΔS) of red dye solution (10ppm) and PH=6.5.

Pomegranate peel form	T (K)	K_d	ΔH KJ/ mol	ΔG KJ/ mol	ΔS J/ mol.K
RPP	283	661.16	26.99	-15.279	149.36
	293	908.06		-16.875	149.71
	303	1311.78		-18.085	148.76
	313	1397.69		-18.847	146.44
	323	2781.91		-21.297	149.50
ACPP	283	464.03	23.43	-14.446	133.84
	293	953.41		-16.711	137.00
	303	1237.73		-17.938	136.53
	313	1492.56		-19.018	135.62
	323	1601.41		-19.814	133.88

The result shows that the enthalpy change (ΔH) value of two forms of adsorbents positive that indicated the adsorption of dye onto pomegranate peel was endothermic. All adsorption process is considered spontaneous nature according to the negative value of ΔG . The positive value of ΔS is attributed to random of irregularity at the liquid- solid interaction (**Kailas, 2010**).

Adsorption isotherm

The study Adsorption isotherms are essential for the description of how adsorbant will interact with an adsorbent surface and are important to optimize the use of adsorbent. Thus, isotherm is important parameter to evaluate the sorption mechanism (**Safanah & Ddoosh,2013**). The analysis of isotherm information's is important to achieve an equation which exactly represents the results and which could be applied for design purposes (**McKay, 1985**).

Many isotherm equations are available, the two significant Langmuir and Freundlich models are employed in this study.

The form of the Langmuir model can be written as

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \dots\dots\dots(7)$$

Where q_e is the amount of the adsorbed at equilibrium (mg/g), C_e the equilibrium concentration (mg/L), q_{max} the higher adsorption capacity and K_L is the Langmuir constant(**Malik, 2004**).

The linear fitting of C_e/q_e versus C_e give a straight line with slope $1/q_{max}$ and an intercept of $1/K_L q_{max}$.

The major characteristics of the Langmuir isotherm can be described in terms of dimensionless constant separation factor (R_L), which is refer to isotherm shape that is estimated either isotherm is favourable or unfavourable. R_L can be computed from the equation (8). (**Ladhi& Patil, 2014**).

$$R_L = 1 / (1 + K_L C_0) \dots\dots\dots(8)$$

Where: K_L and C_0 are the Langmuir parameter, and the peak initial concentration of adsorbate. Values of (R_L) were computed and listed in table (3).

The Freundlich isotherm model form is expressed according to the equation (9). (**Weber , 1972**):

$$q_e = \frac{X}{M} = K_F C_e^{1/n} \dots\dots\dots(9)$$

Where.

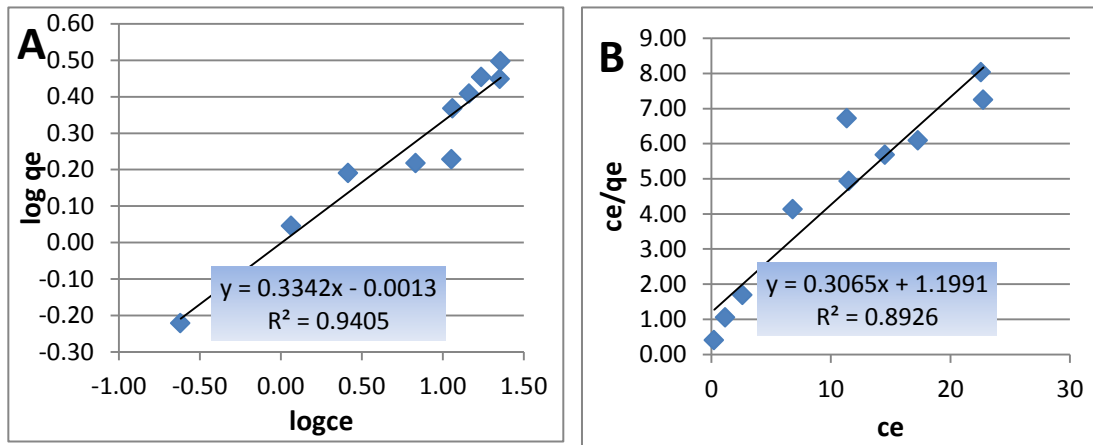
x : mass of the adsorbate. (mg)
 m : mass of the adsorbent. (mg)
 C_e : equilibrium concentration. (mg/L)
 K_F and n : the Freundlich constants.

The logarithms form of Freundlich equation is given as (Saman *et.al.*, 2013):

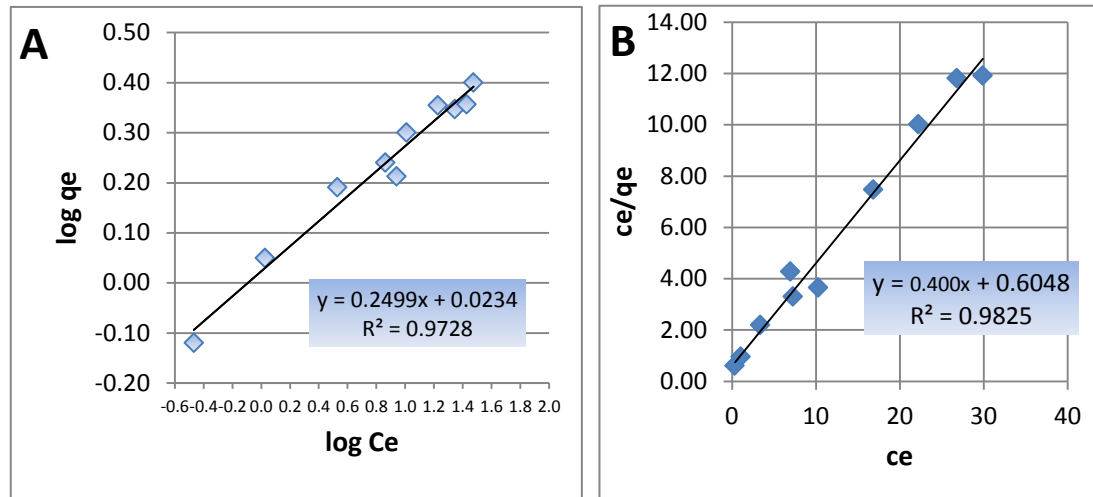
$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \dots\dots\dots(10)$$

plot of $\log q_e$ versus $\log C_e$ afford a straight line with slope and intercept equal to $1/n$ and K_F respectively

The isotherms of Langmuir and Freundlich models of red dye adsorption onto the (RPP) and (ACPP) are given in figs (5&6). The parameters for Langmuir and Freundlich and the correlation coefficient (R^2) were calculated and offered in Table (4).



Fig(5). Plots of (A) Freundlich , (B) Langmuir isotherms of red dye onto RPP



Fig(5). Plots of (A) Freundlich , (B) Langmuir isotherms of red dye onto RPP

Table (3) :Values of R_L for RPP and ACPP at different concentration of red dye

Concentration (ppm)	R_L value	
	RPP	ACPP
5	0.439	0.232
10	0.281	0.131
15	0.207	0.091
20	0.163	0.070
25	0.135	0.057
30	0.115	0.048
35	0.100	0.041
40	0.089	0.036
45	0.080	0.032
50	0.072	0.029

Table (4) : Isotherm parameters for red dye onto RPP and ACPP

adsorbent	Model					
	Langmuir			Freundlich		
	q_{max}	K_L	R^2	1/n	R_F	R^2
RPP	3.268	0.256	0.892	0.334	0.998	0.940
ACPP	2.5	0.662	0.982	0.249	1.054	0.972

The figures (5&6) and the results in tables (3&4) shows obviously that:

Correlation coefficient (R^2) value for RPP was higher for Freundlich (0.940) than Langmuir that indicates that the Freundlich isotherm is clearly the better fitting isotherm to the experimental data, While the value of (R^2) for ACPP was higher for Langmuir (0.982), that means the adsorption isotherm of red dye onto ACPP obeyed Langmuir model.

The value of (R_L) for experimental data was ranged ($0 < R_L < 1$) for (RPP) and (ACPP). This refers to that the favorable for adsorption of red dye onto the two forms of adsorbents is used in the present study.

Conclusions

In this study, the efficiency of using pomegranate peel as local and novel adsorbent was investigated and the following conclusions were obtained:

- pomegranate peel with two forms (RPP and ACPP) gives a good efficiency removal of C.I. Direct Red 89 dye from aquatic solution.
- The efficiency of adsorption process increases with decreasing of pH value in both form of adsorbents, the maximum percentage adsorption was attained at pH 2.
- Both forms of pomegranate peel reflect the same behavior at experimental works , but the raw pomegranate peel of particle size (75 μ m) signs removal rate of dye higher than activated carbon prepared from pomegranate peel of particle size (1mm).
- The adsorption isotherms for the red dye adsorption onto RPP& ACPP were of favorable type and were in good agreement with Langmuir and Freundlich models.
- Thermodynamic parameters calculations showed that the adsorption process of red dye onto RPP and ACPP has endothermic and spontaneous nature.

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