Application of Surfactant for Enhancing the Adsorption of Azo Dye Onto Buckthorn Tree Wood Surface

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Abstract

   Cetyl trimethyl ammonium bromide (CTAB), was used as surfactant to enhance the removal of Congo- red (C-R) dye from its solution by employing a wood of buckthorn tree as a low cost and eco-friendly adsorbent. Different factors affecting the sorption process like, time of adsorption, wood dose, initial (C-R) concentration and hydrogen ion concentration have been studied for both adsorbent wood (W) and modified wood (MW). The suitability of the two isotherm models Langmuir and frundlich to the equilibrium results was mentioned for the adsorption of (C-R) on both wood and modified wood. From the value of correlation - factor, frundlich model give a better fit than Langmuir isotherm model. Thermodynamic function such as the changes in enthalpy $\Delta H°$, entropy ΔS^o and Gibes free energy ΔG^o for the adsorption process was guessed. These values illustrate that physi-sorption take place .The negative values of ΔH^o shows that the adsorption process accompany with heat releasing with decreasing the randomness of the (solid-solution) interface. Furthermore the negative values of $\Delta G°$ indicated that adsorption of (C-R) dye onto the wood and modified wood occurs spontaneously.

Keywords: adsorption, dye, buckthorn tree, isotherm.

استخدام المنشط لتحسين امتزاز صبغة الازو على سطح خشب شجرة السدرة

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الخلاصة

استخدم سيتايل ثلاثي مثيل امونيوم برومايد (CTAB) كمنشط للسطح لزيادة كفاءة صبغة الـ Congo– red من محاليلها المائية باستخدام خشب شجرة السدرة كمادة رخيصة وصديقة للبيئة.

تم دراسة مختلف العوامل المؤثرة على عملية الامتزاز مثل زمن التماس و وزن المادة المازة والتركيز الابتدائي لصبغة Congo red وتركيز ايون الهيدروجين على سطح كل من الخشب والخشب المحور.

تم بحث ملائمة نوعين من انماط متساويات درجة الحرارة لنكماير وفرندلش لامتزاز الـ (C–R)على سطح الخشب والخشب المحور.

لوحظ من خلال قيم معامل تصحيح R ان ايزوثيرم فرندلش يعطي تطابق جيد من نموذج ايزوثيرم لنكماير.

تم تقدير الدوال الثرموديناميكية مثل التغير في الانثالبي ΔH^o و الانتروبي ΔS^o و طاقة كبس الحرة ΔG^o لعملية الامتزازوقد اشارت هذه القيم الى حدوث امتزاز فيزيائي. القيمة السالبة لـ ΔH^o تبين ان عملية

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الامتزاز مصحوبة بانبعاث حرارة وهناك نقصان في العشوائية على السطح البيني بين الصلب والمحلول،

اضافة الى ذلك فأن القيمة السالبة لـ ΔG^o تشير الى امتزاز   (C−R)على سطح الخشب والخشب المحور

تحدث تلقائيا.

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Introduction

   Some industries often use dye for coloring their products such as textile, paper, plastics and dyestuffs industries [1]. Wastewater from dying in the textile industry are generally high in both color and organic content [2]. Color removal from textile effluents has been taking a great attention in the last few years due to its visibility problems [3]. Different techniques have been submitted to remove of dyes from polluted water, these processes are (precipitation) (coagulation), (chemical oxidation), (sedimentation), (filtration), (osmosis), (ion exchange) and physical adsorption   [4].

   Physical adsorption is one of the most effective and low- cost process for the wastewater treatment. It's used for removal such toxic inorganic and organic compounds to both humans and aquatic life [5]. Therefore finding alternative low-cost materials which have high capacity is important. Many low-cost Materials such as: (natural clay), (sawdust), (maize cob), (wood), (flay ash), (peat) and (waste materials) which are available as solid –waste from other industries have been studied as adsorbent [6]. The adsorbent use may vary due to change in adsorption medium according to the source of compounds that caused the pollution. The properties affecting the extent of an adsorbent are large roughness of surface and porosity, well defined structural properties, adsorption selectivity, easy to purify, regeneration, and thermal stability [7].

   Surface properties of the adsorbent can be modified by addition of surface active agents to the adsorbents, such as increase the removal efficiency of bentonite clay by addition of (HDMAB) hexadecyltrimethylammonium [8]. (C-R) is one of synthetic dyes that is difficult to biodegrade due to their aromatic complex structures, which provide them physical/chemical, optical and thermal stability [9].

   In this paper, we showed that the uptake of (C-R) as anionic dye from water increased when the wood was modified with cetyl trimethyl ammonium bromide (CTAB) as cationic surfactant. The effect of many factors such as wood dose, the time of adsorption, initial (C-R) concentration and hydrogen ion concentration using wood and modified wood were investigated.

Experimental part

   Adsorbate: (C-R) dye used in this study is water soluble dye $(25g.L^{-1})$ with C.I. number (22120), its chemical formula $[C_{32}H_{22}N_6O_6S_2Na_2]$, IUPAC name is [1-Naphthalene sulfonic acid, 3,3-(1,1-bi.phenyldiyl bis (azo) bis (4-amino disodium salt)], molar mass (696.67 g/mol) and (λmax =497nm). Chemical structure of (C-R) dye is shown in Figure -1.
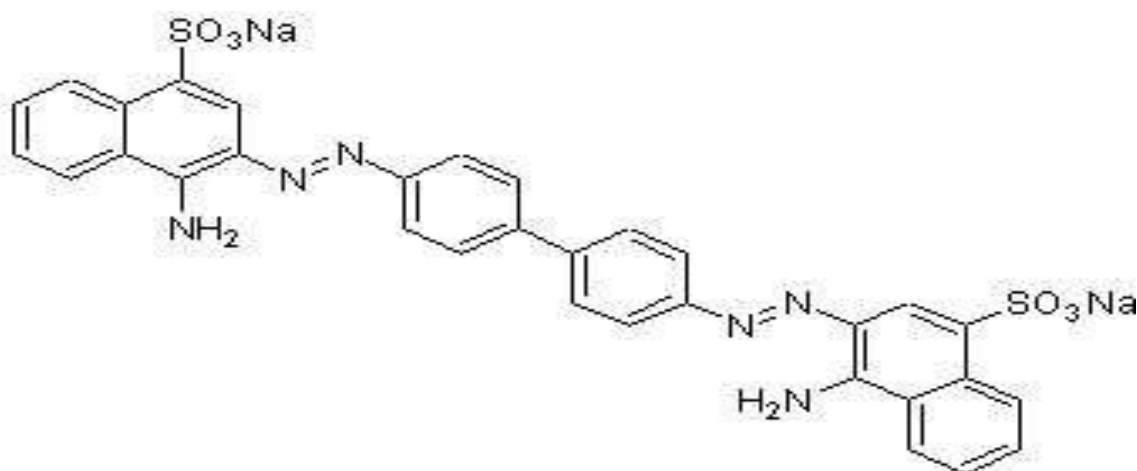

Figure 1- Chemical structure for Congo red(C-R) dye

1gm of (C-R) dye dissolved in 1L of distilled water. Different concentrations from (C-R) dye involving (100, 80, 60, 40 ppm) are prepared.

Adsorbent

The wood of the buckthorn tree was cut into fine pieces then blended using a (food-processing) blendery for several time, the powder was dried at 100 C° for one day in oven and the dry wood was kept in dry place.

Preparation of the modified wood

To prepare the MW,50gm of the dry wood powder was stirred for 24hour with 100mLof 2M of [CTAB] (Fluka) at room temperature then was filtered and dried at 100C°.The sorption of the dye onto the adsorbent was carried out by batch sorption and the studied variables involved (C-R) concentration, wood dose, contact adsorption time and hydrogen ion concentration .The residual dye was separated using centrifuge and the concentration of the dye was measured using UV - visible spectrophotometer Shimadzo, Japan 160A at λmax =497nm. The spectrum of the initial (C-R) concentration 50 mg/L is shown in Figure -2.
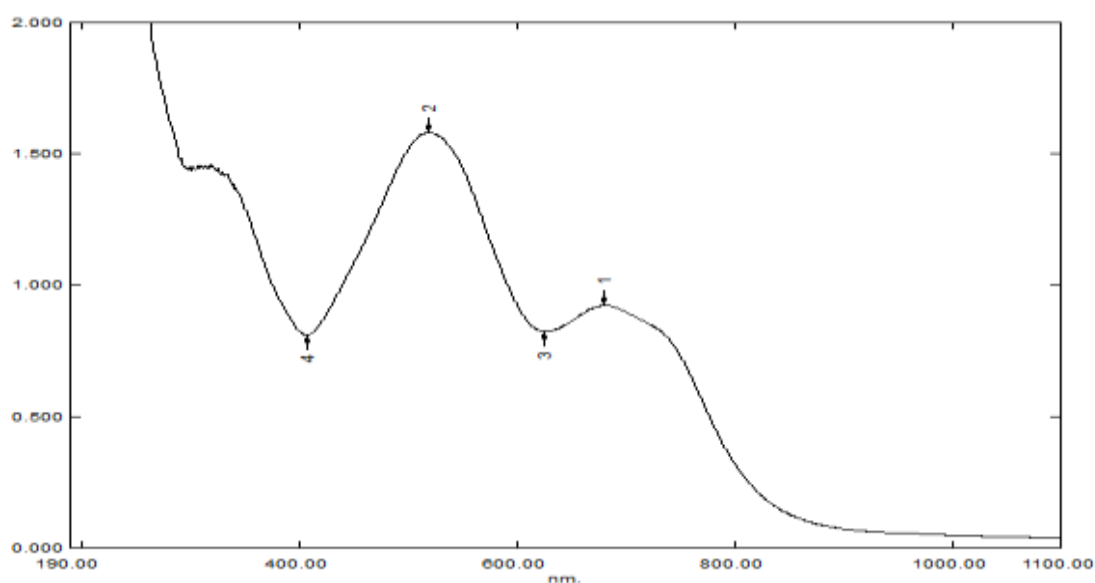

Figure 2- UV. Visible spectrum for (50 mg/L) (C-R) solution.

Characteristic of wood powder was made by FTIR   measurement Figure -3, that carried out using a Shimadzu [FTIR, 8400] as KBr disc in the range of [400-4000] 1/cm.
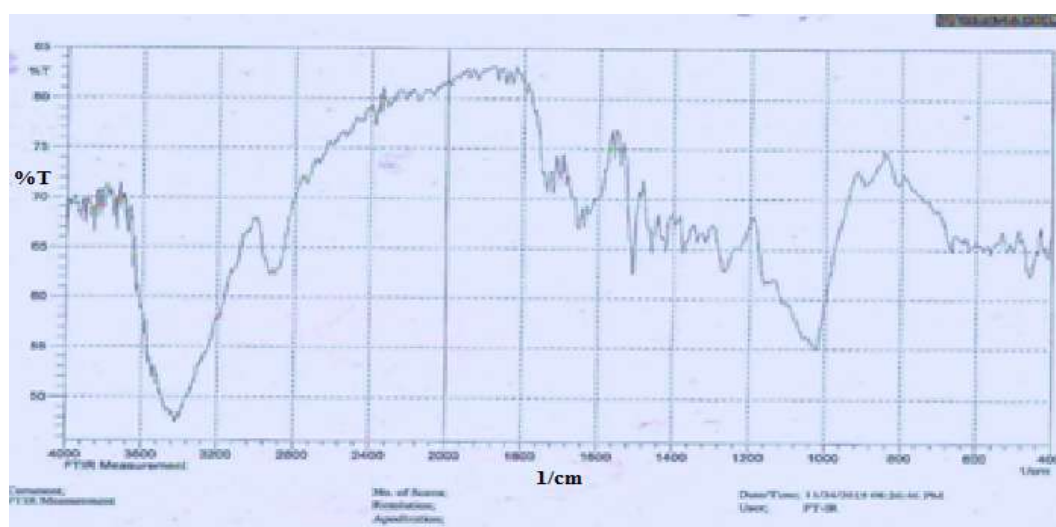

Figure 3- FTIR spectrum for the wood.

The equilibrium amount of adsorbed dye q_e (mg/g) was calculated by using equation-1.

$q_e=\{C_i - C_e\} * V.W^{-1}$ ……………………………………………………………...…..(1)

where **C_i** , **C_e** are initial and equilibrium concentrations in (mg/L) of the (C-R) solution respectively , **V** is the volume of the (C-R) solution (L) and W is the dose of the wood (g).The removal of (C-R) can be estimated using equation-2.

Results

1. Effect of adsorption time

Figure -4 showed the effect of adsorption time for the adsorption of (C-R) onto MW and W, the initial of (C-R) dye Ci is 40 mg/L and the optimum value of pH and wood dose is (7) and 0.25 respectively at 25 °C, this figure showed that for both W and MW the percentage of removal for the (C-R) dye increased with increasing adsorption attains equilibrium at two hours after this time the active sites of the surface were saturated with the (C-R) molecules**[10].**

Removal (R) efficiency % = $\{C_i - C_e\} * C_i^{-1} * 100$ …………………………………………..... (2)
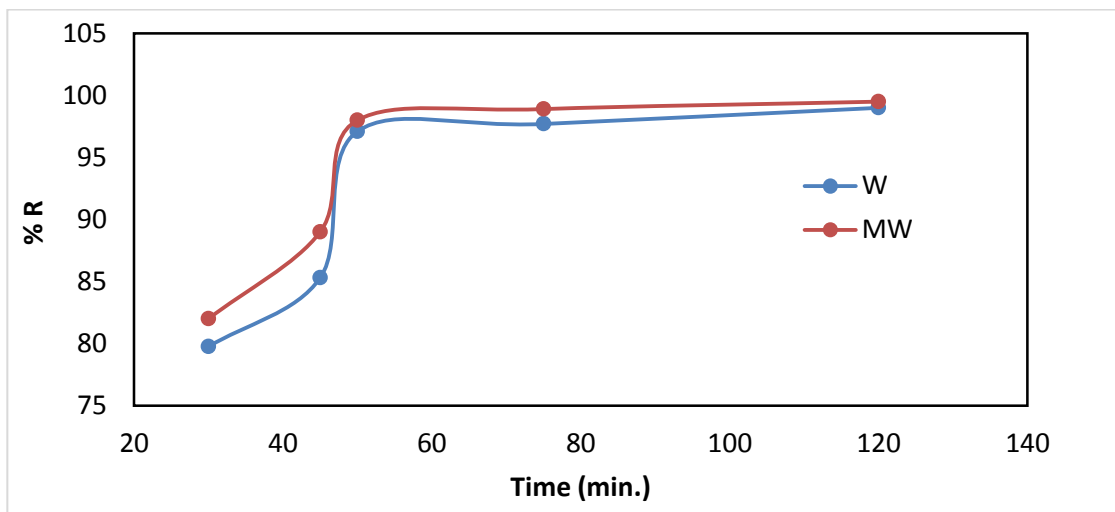

Figure 4- Effect of adsorption time on adsorption of (C-R) dye onto W and MW.

2. Effect of buckthorn wood

Figure -5 showed the effect of the wood dose on the removal of the dye for both W and MW for C_i (80 mg/L) and at constant value of pH (7) and adsorption for 2 hours at 25C°. The percentage removal increased in the parallel with increasing wood dose and reaches maximum removal when the wood dose was 0.25 gm. The increasing in wood dose leads to increase the surface area by the availability of more active adsorption centres **[11].**
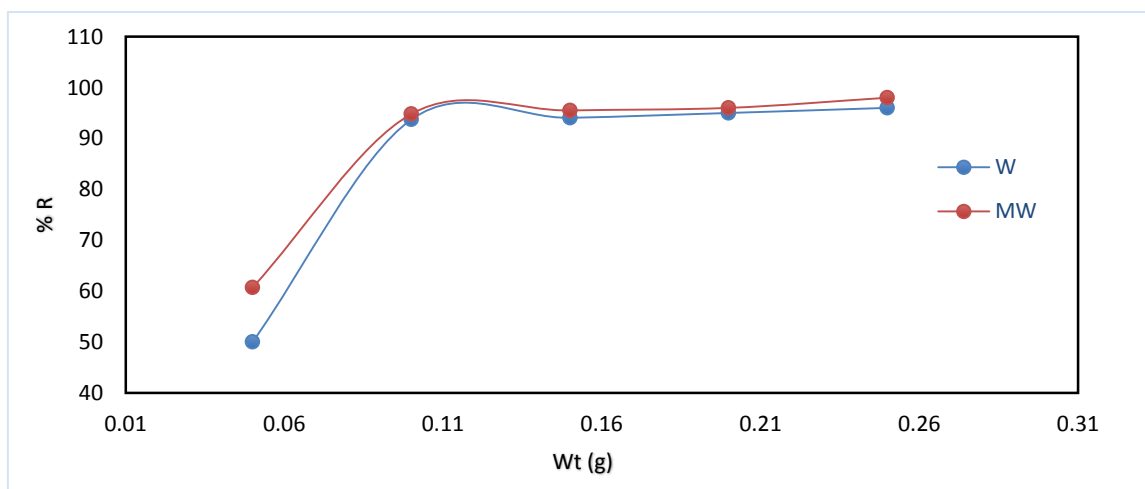

Figure 5- Effect of buckthorn dose on the adsorption of (C-R) onto W and MW.

3. Effect of initial Congo red dye concentration

Figure -6 showed the effect of (C-R) concentration for the W and MW. The operation conditions are pH (7), temperature (25C°), 2 hour adsorption time, (0.25) gm wood dose and C_o range (0.04-0.1) mg/L. It was detected that for both W and MW the removal percentage decreases with increasing the initial (C-R) concentration. This indicated that for (C-R) dye molecules to accumulate there is a definite value of active sites on the wood surface that was suitable for the adsorption **[12].**
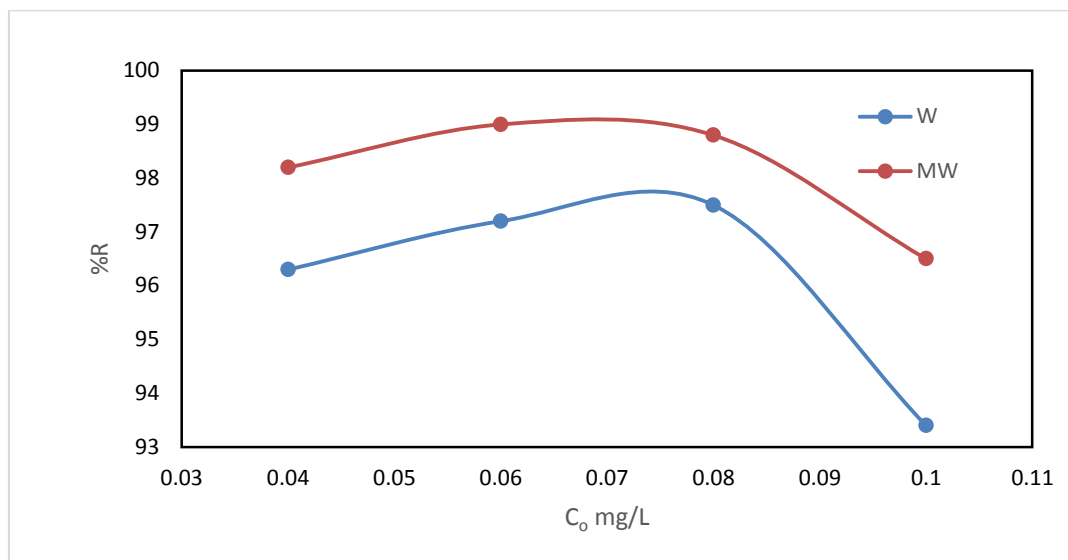

Figure 6- Effect of initial (C-R) concentration.

4. Effect of hydrogen ion concentration

Figure -7 showed the effect of hydrogen ion concentration for adsorption of dye onto W and MW adsorbent. The experiment conditions are (60 mg/L) (C-R) concentration, (25C°) temperature, two hour adsorption time, 0.25gm wood dose and pH range (2-12).
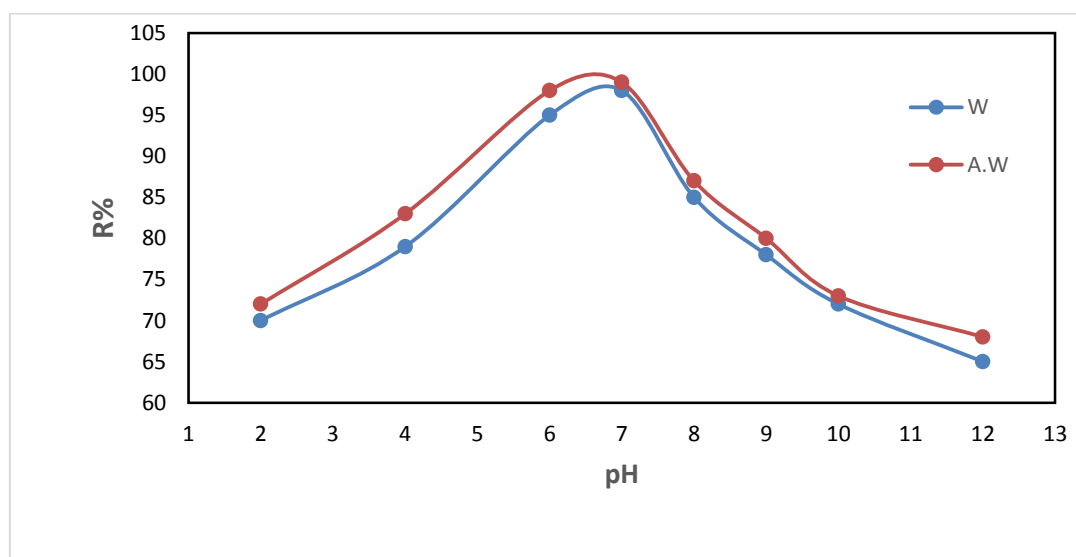

Figure 7- Effect of hydrogen ion concentration value on the adsorption of (C-R) onto W and MW surface.

At low values of pH, anionic ion of the (C-R) dye compete with hydrogen ions for the active sites on the wood surface. As the pH of (C-R) dye reaches maximum a proportional decrease in removal watch due to the deprotonation of positive charged group on the both W and MW **[13].** MW showed higher removal percentage (%) than that of W because CTAB molecule has a head

group with a positive charge that leads to point of this groups towards the bulk of the solution causes the potential of the surface to be positive.

5.   Adsorption isotherm

The degree of adsorption on a surface, usually depends on the types of the adsorbent and the molecular of the adsorbate. The description of the equilibrium adsorption data for the adsorption of (C-R) on the wood surface occurs by employing two adsorption isotherm models.

Langmuir adsorption isotherm

This type of isotherm based on the adsorption of molecules is confined to a mono-molecular layer [14]. The Langmuir relation:

$[C_e/q_e] = [C_e/Q_o] + [1/bQ_o]$ …………………………………………………………….... (3)

The Langmuir constants b (L/mg) and Q_o (mg/g) are determined from slope and intercept of the linear plot of $[C_e/q_e]$ [y-axis] versus $[C_e]$ [x-axis] as shown in Figure -8, and their values were shown in Table -1.
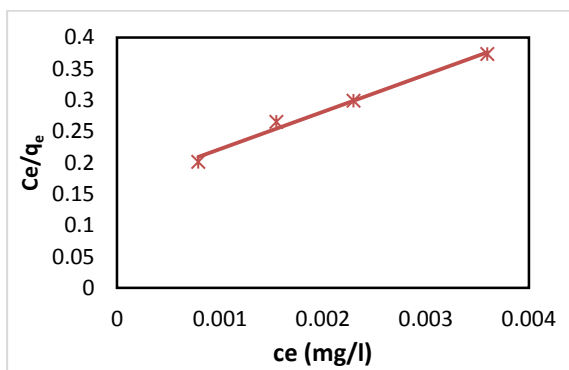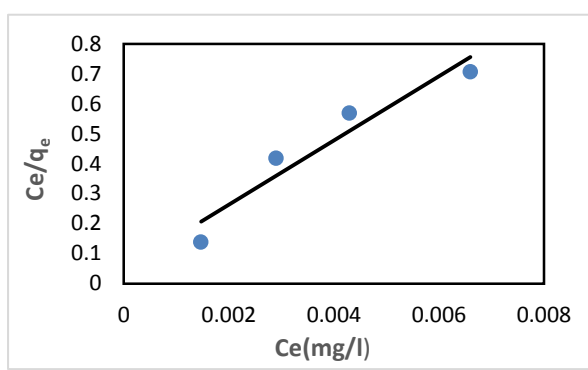

Figure 8-(a)   **Figure 8-(b)**

Figure 8- (a, b) Langmuir adsorption isotherms at 298K for the adsorption of (C-R) on to a: W and b: MW

Frundlich- adsorption- isotherm

Langmuir isotherm described well the homogenous, uniform adsorption, to describe the sorption on the surface that have different values of diffusion energy (heterogeneous surface), frundlich model was used [**15**].

The formula of this model represented by the relation:

$[\ln q_e] = [\ln k_f] + (1/n)[\ln C_e]$…………………………………………………….. …..(4)

Where $[K_f]$, [n] are frundlich constants use for measuring the capacity and intensity of the adsorption process. By plotting $[\ln q_e]$ against $[\ln C_e]$ values straight line obtained, the values of $[K_f]$, [n**]** are calculated from the slope and intercept of the plot Figure -9 and their values are shown in Table -1**.** From the values $R^{2,}$ it can be deduced that frundlich model is well described the sorption data.

This model based on that if the (C-R) concentration increased this lead to increase the concentration of the (C-R) on the wood surface also, and corresponding to that sorption energy decreased on completing of the active sites wood.
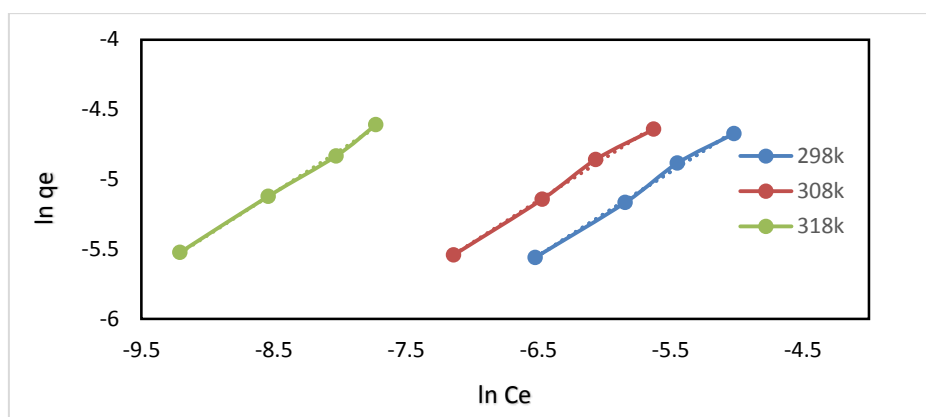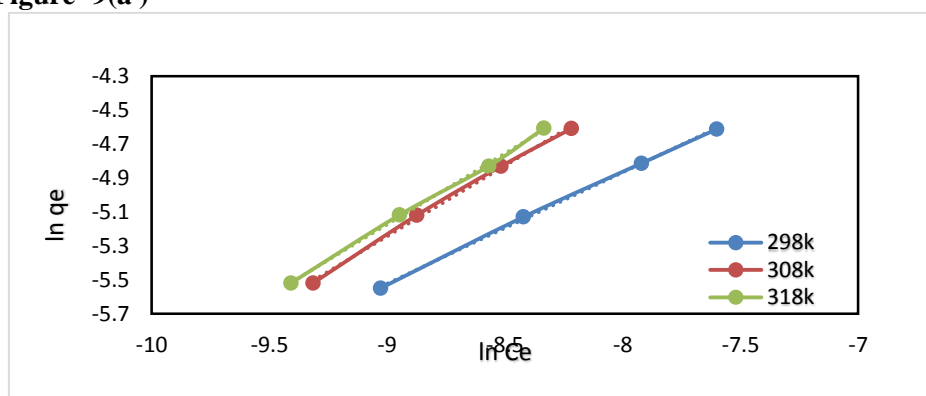
Figure -9(a)

Figure -9(b)

Figure 9- (a, b): Frundlich adsorption isotherm for the adsorption of (C-R) onto a: W b: MW at different temperatures.

Table 1- Langmuir and frundlich isotherm constants for the adsorption of (C-R) onto W and MW.

	Langmuir isotherm					
T\K	**b (mg/g)**		**Q$_o$ (mg/l)**		**R^2**	
	W	**MW**	**W**	**MW**	**W**	**MW**
298	2183	2252	0.00935	0.0185	0.9213	0.9745
308	367.6	1415	0.01683	0.0372	0.988	0.9976
318	2717	1152	0.00176	0.0457	0.947	0.9386
	Frundlich isotherm					
T\K	**K$_f$**		**n**		**R^2**	
	W	**MW**	**W**	**MW**	**W**	**MW**
298	1.075	10.77	1.6446	1.1919	0.9968	0.9994
308	0.2932	12.698	1.656	1.962	0.9969	0.9979
318	0.192	9.384	1.6681	0.1189	0.9982	0.9988

6. Thermodynamic calculations

The thermodynamic functions $\Delta G°$, $\Delta S°$ and $\Delta H°$ were calculated using the following equations [16]:

$$K_d= C_{sd} / C_{ld} \quad …………………………………………………………...…… (5)$$

Where K_d= equilibrium constant,

C_{sd}= solid - phase conc. (mg/L)

C_{ld}= liquid - phase conc. (mg/L).

$$\Delta G°= -8.314 * T * \ln (K_d)……………………………………………….. … (6)$$

$$\ln K_d= \Delta S°/8.314 - \Delta H°/8.314 *(T^{-1}) ……………………………………………..(7)$$

The values of $\Delta S°$ and $\Delta H°$ were calculated from the slop and intercept from the plot between (ln K_d) and (T^{-1}) Figure -10.
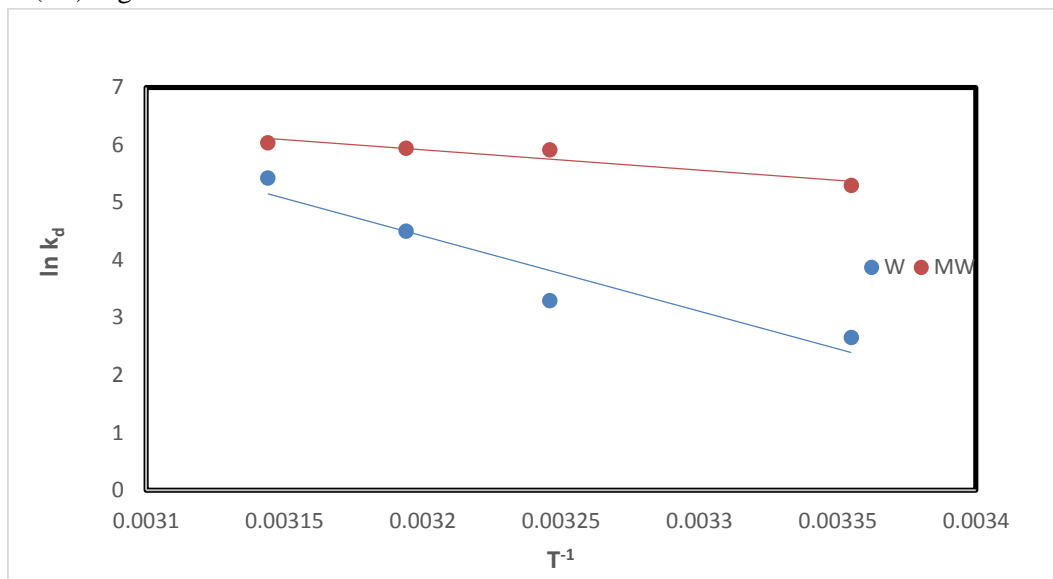

Figure 10- Plot of (ln K_d) vs (T^{-1}) for the adsorption of (C-R) onto W and MW for C_i = 100 (mg/L)

The results are shown in the Table -2. The values of $\Delta H°$ for MW indicate that physi-sorption for the dye molecules onto the solid surface was taken place, furthermore the adsorption of (C-R) dye onto both W and MW adsorbent exothermic accompany with release of heating.

The values of $\Delta S°$ reflect the decrease on the randomness and disorder of the system during the adsorption process, while the negative value of $\Delta G°$ confirms that the adsorption process, occurs spontaneously.

Table 2-Thermodynamic functions for the adsorption of (C-R) dye onto W and MW at different temperatures

Ci PPM	W					MW			
	T(K)	K_d	$-\Delta H$ J.mol^{-1}	$-\Delta S$ J.mol^{-1}	$-\Delta G$ KJ.mol^{-1}	K_d	$-\Delta H$ J.mol^{-1}	$-\Delta S$ J.mol^{-1}	$-\Delta G$ KJ.mol^{-1}
100	298	14.151			6.565	189.939			13.113
	308	26.789			8.419	369.444			15.138
	313	89.657	108.539	384.065	11.749	378.418	29.242	142.75	15.536
	318	226.331			14.334	415.673			15.942
80	298	17.605	103.085	367.895	7.106	215.293	26.471	133.93	13.309

	308	35.304			9.126	361.405			15.338
	313	121.629			11.792	419.893			15.600
	318	244.447			14.538	458.567			15.988
60	298	19.687	107.682	383.990	7.383	271.782	20.923	116.479	13.874
	308	37.712			9.292	427.519			15.512
	313	169.414			12.074	460.355			15.845
	318	307.969			15.149	488.332			16.212
40	298	38.861	106.660	382.95	8.091	332.287	14.430	96.940	14.384
	308	49.650			10.012	443.634			15.607
	313	190.571			12.874	478.186			15.958
	318	399.414			15.836	503.432			16.312

Conclusion

In present work we can predict that:

1- The wood of buckthorn tree is a good adsorbent for (C-R) removal.

2- The addition of CTAB to the wood improved the surface properties that leads to increasing removal percentage for (C-R) dye.

3- From the correlation-factor (R) values for both (Langmuir and frundlich) models, it can be deduced that the data follows frundlich model.

4- The thermodynamic calculation showed that the adsorption of (C-R) onto the W and MW was companioned with release of heating, decreasing in randomness and occurs spontaneously.

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