Article
JOURNAL OF UNIVERSITY OF BABYLON
For Pure and Applied Sciences (JUBPAS)
Vol. 33 ; No.4 | 2025

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Green Chemistry for Removing Alizarin Red S Dye

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الكيمياء الخضراء لإزالة صبغة أليزارين الحمراء

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Accepted: **20/11/2025** **Published:** **31/12/2025**

ABSTRACT

The current work utilizes the peel and pulp of the Iraqi eggplant to remove Alizarin Red S dye (ARS) from an aqueous solution. The isotherms of adsorption were studied and the factors that the effect them: temperature, the effect of surface nature and effect of ionic strength. The isotherms of adsorption of ARS on the peel were found obey the Freundlich, equation, but the isotherms of adsorption on the pulp were found to obey the Langmuir equation. At different temperatures, the adsorption process was studied, and it was found that when the temperature decreased, the adsorption increased. Based on the data we obtained in practice, the thermodynamic functions (ΔH, ΔG, ΔS) were calculated as the process was exothermic, spontaneous, and more regular. The results showed that the effect of ionic strength (the presence of sodium chloride salt) was positive on the adsorption process for both surfaces. It was found that the nature of the surface has an effect on the adsorption process, as it was found that adsorption on the surface of the peels is more effective than on the surface of the pulp.

Keywords: Alizarin Red S dye, Eggplant, Removal, Adsorption

INTRODUCTION

The biggest challenge to water quality is the discharge of harmful waste from diverse sources into aquatic processing, which then accumulates in the environment. The exhaled organic pollutant effluents from industries like leather production, paint manufacturing, textiles, and paper play a significant role in water pollution by contaminating it with biological and chemical pollutants [1,2], leading to significant amounts of water pollution. Each year, approximately 80,000 tons of dyes from different sources are used annually because they are inexpensive and available in a range of colors [3]. The commonly utilized dye is the (ARS) as an anionic dye. Dyes are thrown into surface waters due to the separation of their molecules in water with negative charges, which can endanger the health of the marine habitat and local inhabitants. Depriving aquatic plants of the necessary sunlight for photosynthesis through tunneling is done [4-6]. The compound's aromatic ring structure (AR) makes it extremely resistant to dissolution, parsing a dangerous impact on the environment and the possibility of jeopardizing human health because of its elevated toxicity. Research has shown that it can cause skin disorders, allergies, vision trouble, and mutagenic effects [7]. There are many researches and studies in Iraq that have worked on removing dyes using different surfaces [8-14].

The peel and pulp of eggplant are considered an effective surface for many removal operations, such as oil [15,16], lead ions (II) [17]. Also used as a low-cost surface to remove ions from aqueous solution under various experimental conditions [18].

In the present work, we will use the peel and pulp of Iraqi eggplant as a novel low-cost biomass sorbent to remove Alizarin Red S dye, which is considered a contaminating dye that causes malignant disorders in the lungs and respiratory system [19].

MATERIALS AND METHODS

Materials

Alizarin Red S (ARS), peel and pulp eggplant, NaCl salt and distilled water.

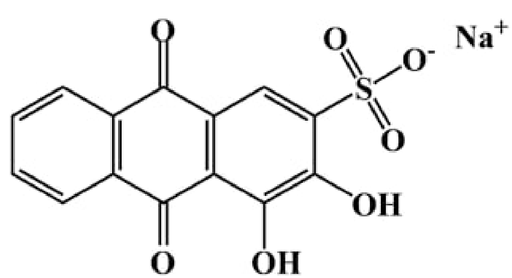

Figure 1. ARS structure [20].

Methods

1-Consider absorbance as a function of concentration by using the UV-Vis technique. The absorption wavelength for ARS was (425) nm.

2-To calculate the equilibrium time between the adsorbate and the adsorbent, we mixed (0.1g) of peel the eggplant once and pulp again with (50ml) from the maximum concentration of (ARS) in six round flasks and then put them in a water bath at (20°C).

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We took one flask every time at appropriate times to determine the change in concentration, we found that the equilibrium time occurs quickly.

3- Adsorption isotherms: to measure the adsorption isotherms for (ARS) Solution, we weighed (0.1g) of the surface with (50ml) from dye solution in different concentration in six round Flasks and put them in a water bath Shaker water bath at (20°C) for (30minutes) then put the mixture in the centrifuge for (10 minutes) to separate. After that we calculate the absorbance by the UV-Vis technique. We repeated the process at various temperatures to study the effect of temperature change on adsorption.

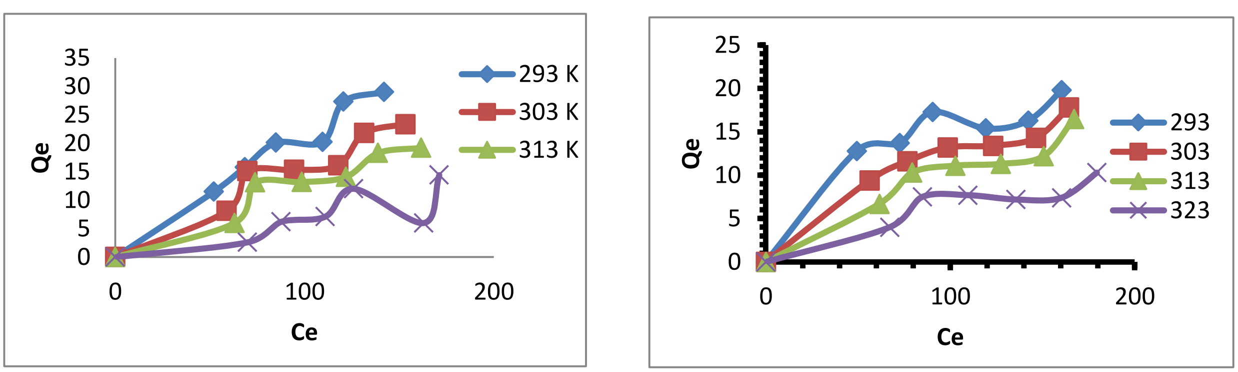
To calculate the adsorption quantities, we follow the equation [21].

$$Qe = \frac{(C_o - C_e)V}{m} \quad \text{.........} \ (1)$$

Qe =the adsorbate quantity (mg/g).
Co =initial concentration (mg/L).
Ce =equilibrium concentration (mg/L).
V =solution volume (L).
m= the surface mass (g).

RESULTS AND DISCUSSION

Adsorption isothermsA graph was plotted between the concentration at equilibrium versus the quantity adsorbed at different temperatures to obtain the adsorption isotherms as shown in Figure (2).



(a) (b)

Figure 2. Adsorption isotherms of ARS on the peel (a), and pulp (b) at different temperatures.

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The total scheme of the adsorption isotherms of ARS on the peel and pulp of the eggplant explains these shapes belong to the S3 class according to Giles' classification system. Isotherms of this type are typically associated with cooperative adsorption, where the binding of initial molecules enhances the affinity of neighboring sites for further adsorption. This behavior is often linked to the presence of weak initial interactions followed by a progressive increase in adsorbent–adsorbate attraction as surface coverage rises. Such a trend implies that the ARS molecules tend to aggregate or cluster on the adsorbent surface, creating a progressively steeper adsorption slope indicative of multilayer formation. Similar S-type isotherms have been reported for dyes interacting with plant-based biosorbents, reflecting the role of surface heterogeneity, natural polymeric structures, and functional groups in governing adsorption behavior [22].

In addition, the adsorption process on the eggplant peel was found to fit the Freundlich adsorption model in its linear form, as shown in Figure (3) and Table (1). The Freundlich model, which assumes heterogeneous surface energies and non-uniform distribution of adsorption sites, is commonly used to describe multilayer adsorption mechanisms. The strong linearity of the plot (ln Qe vs. ln Ce) suggests that the peel contains a diverse set of active sites capable of binding ARS molecules with varying strengths. The value of 1/n, a key indicator of adsorption intensity, further supports the presence of favorable multilayer adsorption on the peel's surface. This aligns with previous studies where agricultural wastes rich in lignocellulosic structures exhibited Freundlich-type adsorption behavior due to their irregular porous matrices and abundant functional groups such as hydroxyl, carboxyl, and phenolic moieties.

Overall, the combination of an S3-type isotherm and good conformity with the Freundlich model strongly indicates that the adsorption of ARS on eggplant peel is governed by surface heterogeneity, cooperative interactions, and multilayer formation rather than simple monolayer adsorption. These findings underscore the potential effectiveness of the eggplant peel as a low-cost, lignocellulosic biosorbent for dye removal from aqueous solutions.

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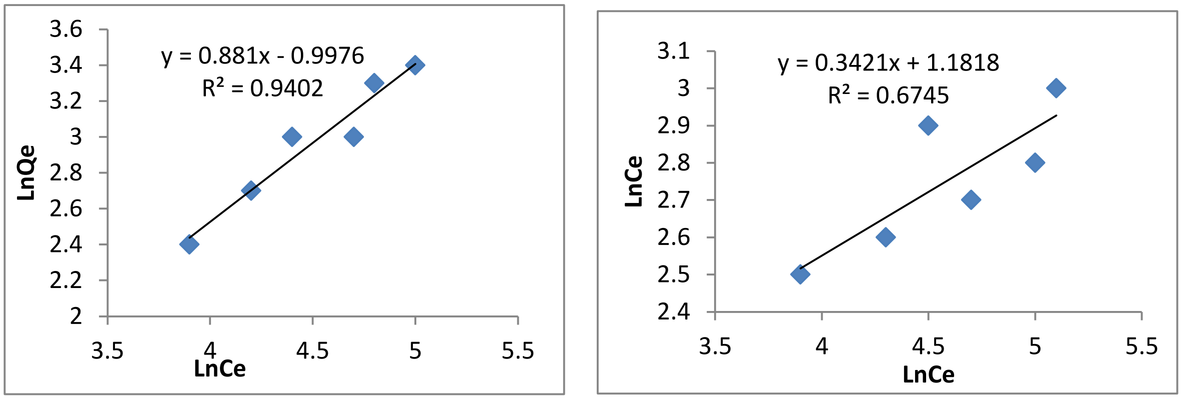


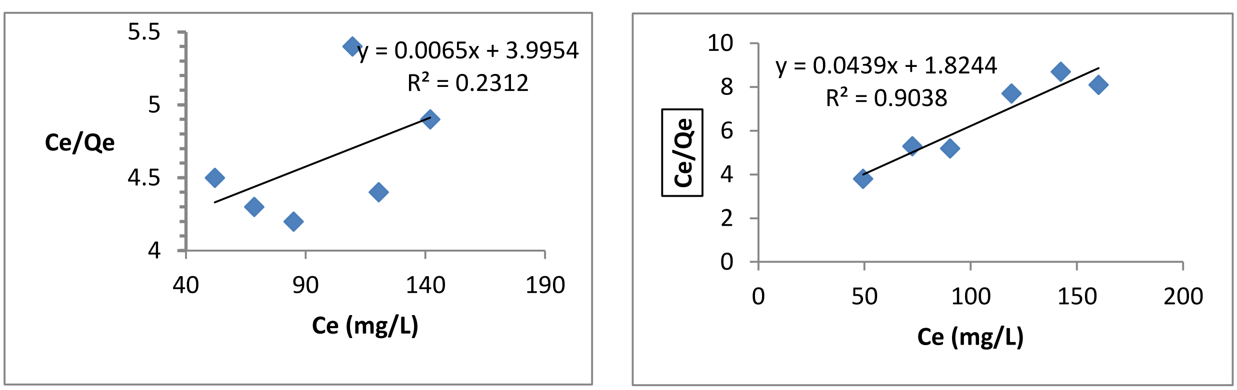
(a) (b)

Figure 3. application of Freundlich equation of ARS on the peel (a) and the pulp (b)

Table 1. Freundlich constants (k_f, n) of ARS adsorption on the peel

Surface	k_f	n	R^2
Peel	0.3687	1.1351	0.9402

While the adsorption followed the linear form of the Langmuir equation (Ce/Qe=1/ak + Ce/a) on the pulp surface as shown in Figure (4) and Table (2).



(a) (b)

Figure 4. application of Langmuir equation of ARS on the peel (a) and the pulp (b).

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Table 2. Langmuir constants for ARS dye dye adsorption on the pulp.

Surface	k	a	R^2
Pulp	0.0240	22.779	0.9038

Effect of temperature

It was found that as the temperature decreased, adsorption increased. Depending on the Vant Hoff-Arrhenius equation to find the ΔH value as shown in the Table (3) and Figure (5)

$$Ln\,Xm = -\frac{\Delta H}{RT} + C \qquad \text{……….} (2)$$

Xm: The maximum amount of adsorbed quantity.
R: Gas constant (8.314J/K.mol)
T: Temperature (K)

able 3. Data to application of the Vant Hoff-Arrhenius equation of ARS on the peel (a) and the pulp (b).

(a)

T(K)	1/T	X_m (C_e=142)	Ln X_m
293	0.0034	29	3.37
303	0.0033	23	3.14
313	0.0032	18.7	2.93
323	0.0031	9	2.20

(b)

T(K)	1/T	X_m (C_e=160.3)	Ln X_m
293	0.0034	19.8	2.98
303	0.0033	17	2.83
313	0.0032	14.3	2.66
323	0.0031	7.1	1.96

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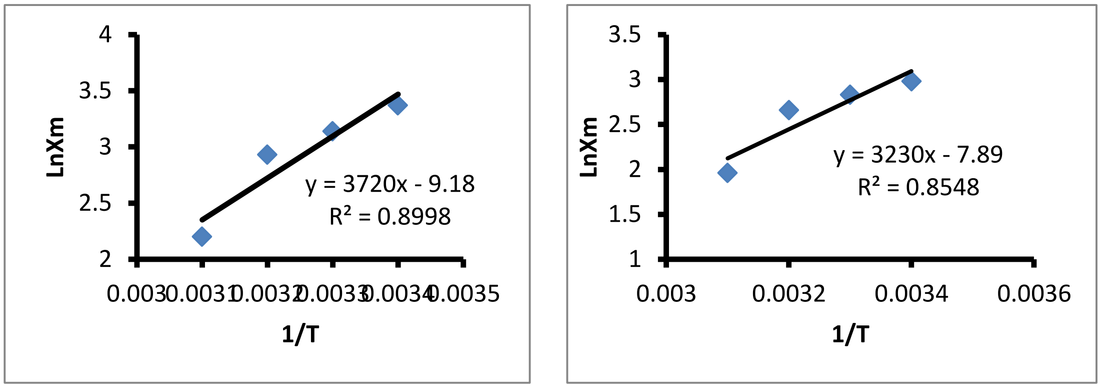

(a) (b)

Figure 5. Application of the Vant Hoff-Arrhenius equation of ARS on the peel (a) and the pulp (b)

We were using the following equations to find the (ΔG and ΔS) values

$\Delta G° = -nRT\ LnQe$ …….(3)

$\Delta G° = \Delta H° - T\Delta S°$……...(4)

Table 4. Thermodynamic functions of ARS adsorption on the peel

SURFACE	T(K)	ΔH KJ/mol	ΔG KJ/mol.K	ΔS J/mol.K
peel	293	-30.928	-8.209	-77.5
	303		-7.910	-75.9
	313		-7.624	-74.4
	323		-5.908	-77.4

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Table 5. Thermodynamic functions of ARS adsorption on the pulp

SURFACE	T(K)	ΔH KJ/mol	ΔG KJ/mol.K	ΔS J/mol.K
Pulp	293	-26.854	-7.259	-66.9
	303		-7.129	-65.1
	313		-6.922	-63.6
	323		-5.263	-66.8

The thermodynamic parameters presented in Tables (4) and (5) provide important insights into the nature of ARS adsorption on both the peel and pulp surfaces. The negative values of the enthalpy change (ΔH) confirm that the adsorption process is exothermic, indicating that heat is released during the interaction between dye molecules and the adsorbent surfaces. This behavior is characteristic of physical adsorption processes in many biosorbent systems, where the binding forces are relatively weak—such as van der Waals interactions or hydrogen bonding—yet sufficiently strong to promote dye uptake.

Furthermore, the negative Gibbs free energy values (ΔG) at all studied temperatures demonstrate that the adsorption is spontaneous, meaning that the process does not require external energy input to proceed. The magnitude of ΔG also provides an indication of the feasibility of adsorption; increasingly negative values typically reflect a more thermodynamically favorable process.

The negative entropy change (ΔS) suggests a decrease in randomness at the solid–solution interface during adsorption. This implies that ARS molecules become more orderly and structured upon binding to the adsorbent surface compared with their more dispersed state in the aqueous phase. Such a decrease in entropy is commonly observed in systems where dye molecules arrange themselves in a more fixed orientation or form organized layers on the adsorbent surface [23].

Overall, the thermodynamic results confirm that ARS adsorption onto eggplant peel and pulp is a spontaneous, exothermic process accompanied by increased molecular ordering, supporting the physical adsorption mechanism proposed in the study.

Effect of ionic strength

The addition of 0.1 g of NaCl to the ARS dye solution for both the peel-based and pulp-based systems resulted in a noticeable increase in the adsorption capacity, as shown in Figure (6) and Table (6). This enhancement in adsorption in the presence of salt can be attributed to several factors related to the behavior of ions in solution and their influence on dye–adsorbent interactions.

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First, the presence of NaCl increases the ionic strength of the solution, which reduces the electrostatic repulsion between the negatively charged dye molecules and the adsorbent surfaces. As a result, ARS molecules are more easily driven toward the adsorbent interface. This phenomenon, commonly known as the "salting-out" effect, leads to a decrease in the solubility of dye molecules in water, thereby promoting their transfer from the aqueous phase to the solid surface.

Second, sodium ions (Na^+) may shield or neutralize some of the surface charges on the adsorbent, particularly if the surface contains negatively charged functional groups. This partial neutralization enhances the approach and attachment of dye molecules by facilitating closer packing and stronger adsorption.

Additionally, the increased adsorption observed in both the peel and pulp systems suggests that the mechanism is predominantly physical adsorption influenced by ionic-strength effects, rather than chemical or specific binding interactions. The consistency of this trend across both adsorbents reinforces the idea that salt plays a key role in modifying solution properties and surface electrostatic conditions.

Collectively, these results highlight that the presence of NaCl significantly promotes ARS adsorption by enhancing dye affinity for the adsorbent surface and improving the overall efficiency of the biosorption process.

Table 6. Effect of salt on the adsorption of ARS on peel (a) and pulp (b).

(a)

	without NaCl		with NaCl	
C_0	C_e	Q_e	C_e	Q_e
75	52.1	11.5	45.2	14.9
100	68.5	15.8	65.7	17.2
125	84.9	20.1	82.2	21.4
150	109.6	20.2	102.7	23.6
175	120.5	27.3	113.7	30.6
200	142	29	143.8	28.1

(b)

	without NaCl		with NaCl	
C_0	C_e	Q_e	C_e	Q_e
75	49.3	12.8	49.3	12.8
100	72.6	13.7	68.5	15.7
125	90.4	17.3	82.2	21.4
150	119.2	15.4	111	19.5
175	142.4	16.3	124.6	25.2
200	160.3	19.8	138.3	30.8

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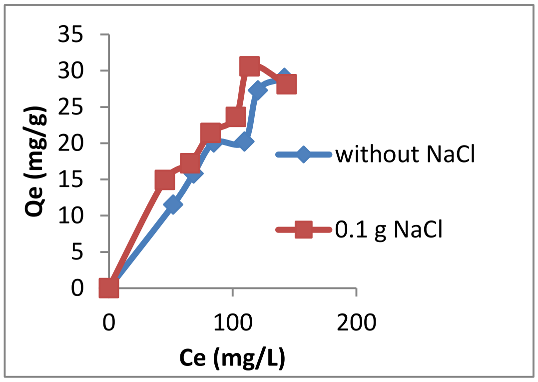

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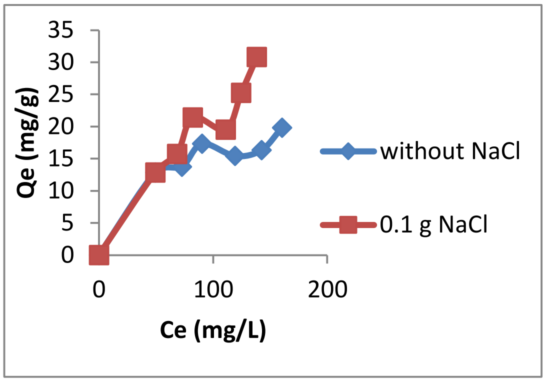


(b)

Figure 6. Effect of salt on the adsorption of ARS on peel (a) and pulp (b).

Isotherm of Desorption

The results showed that it is possible to recover the dye from the surface by the desorption process at (70°C) as shown in Figure (7) and Table (7)

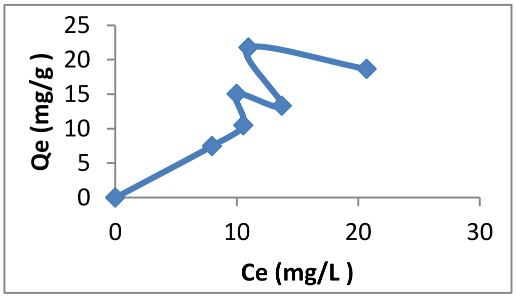
Table 7. the concentration quantity of desorption from (a) peel ,(b) pulp

(a)

C_e	Q_e
7.95	7.48
10.55	10.48
10	15
13.7	13.35
11	21.77
20.7	18.65

(b)

C_e	Q_e
6.71	9.49
8.35	9.52
11.92	11.34
11.37	9.72
17.81	7.39
16.3	11.7



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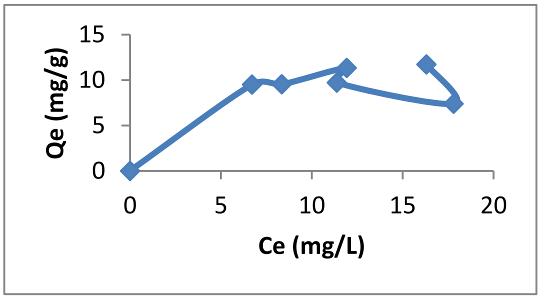
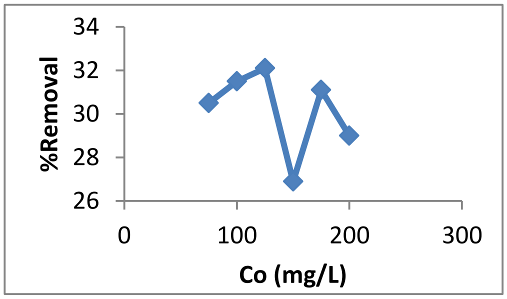


(b)

Figure 7. Isotherms of desorption dye at (70°C) (a)peel and (b) pulp

Removal Percentage

By using the following law: $\%Removal = \frac{Co-Ce}{Co} X\ 100\%$



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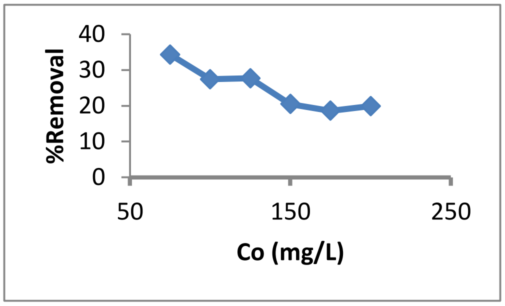

(b)

Figure 8. The percentage of removal at 20°C (a) peel (b) pulp.

Effect of surface nature

The results show that eggplant peels are more effective in removing ARS than eggplant pulp, Figure (9)

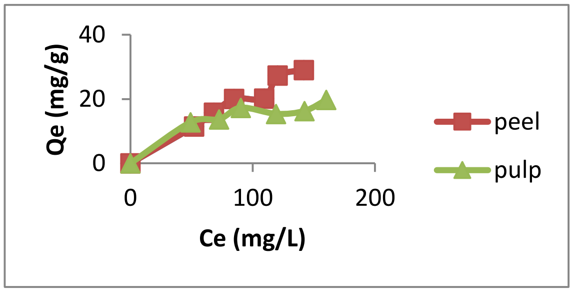

Figure 9. Effect of surface nature

CONCLUSION

The results showed that it is possible to remove the blue pearlescent dye using eggplant pulp and peel, and that the adsorption process is a physical process. The results also showed that it is possible to recover the dye from the surface at high temperatures

Acknowledgments

The researchers extend their sincere thanks and appreciation to all those who contributed to the completion of this research, especially their colleagues in the Department of Chemistry for their scientific and technical support.

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Conflict of Interests.

The authors declare that there is no conflict of interest regarding the publication of this paper.

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ISSN: 2312-8135 | Print ISSN: 1992-0652
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ISSN: 2312-8135 | Print ISSN: 1992-0652

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الخلاصة

يتناول العمل الحالي استخدام قشور ولب الباذنجان العراقي في إزالة صبغة أليزارين الحمراء (ARS) من محلولها مائي. تمت دراسة ايزوثيرمات الامتزاز والعوامل المؤثرة فيها مثل درجة الحرارة، وطبيعة السطح، وقوة الأيونية. وُجد أن ايزوثيرمات الامتزاز للصبغة ARS على القشور تتبع معادلة فريندلش، بينما تتبع على اللب معادلة لانغموير. وقد تمت دراسة عملية الامتزاز عند درجات حرارة مختلفة، وظهر أن الامتزاز يزداد عند انخفاض درجة الحرارة. وبناءً على البيانات العملية، تم حساب الدوال الثرموديناميكيةΔH ، ΔG، ΔS، حيث تبين أن العملية طاردة للحرارة، تلقائية، وأكثر انتظامًا. أظهرت النتائج أن تأثير القوة الأيونية (وجود ملح كلوريد الصوديوم) كان إيجابيًا على عملية الامتزاز لكلا السطحين. كما تبين أن طبيعة السطح لها تأثير على عملية الامتزاز، حيث كانت القشور أكثر فاعلية في الامتزاز مقارنةً باللب.

الكلمات المفتاحية: صبغة اليزارين الحمراء، الباذنجان، الازالة، الامتزاز