# Removal of dye from Water Using raw Pomegranate Peels: Isotherm and Thermodynamic study

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**Abstract.** This study investigates untreated Tunisian pomegranate peels (PGP) as a low-cost and eco-friendly biosorbent for the removal of Methylene Blue (MB) from wastewater. The material was characterized by $N_2$ adsorption–desorption (BET), FTIR spectroscopy, Boehm titration, and point of zero charge ($pH_{pzc}$), revealing abundant functional groups suitable for dye binding. Adsorption isotherms were determined at three temperatures (30, 40, and 50 °C) and analyzed using the usual Langmuir and Freundlich models. The Langmuir model provided the best fit, with a maximum adsorption capacity of 101 mg/g at 30 °C. Thermodynamic analysis revealed negative ΔG°, ΔH°, and ΔS° values, indicating a spontaneous, exothermic process driven mainly by physical adsorption. These results demonstrate that raw PGP is an effective and sustainable biosorbent for dye removal, contributing to the valorization of agricultural waste.

## 1 Introduction

Dyes widely used in textiles, paints, plastics, and pharmaceuticals, are persistent and toxic [1]. Adsorption stands out among removal methods for its simplicity, low secondary pollution, and use of agricultural waste as adsorbents [2]. Pomegranate peels, a by-product of juice, wine, or tannery industries which is very abundant in Tunisia [3, 4], become a promising biosorbent due to its abundance, low cost, and rich surface chemistry [5].

Despite, recent studies highlight its potential for dyes removal [6, 7], most reported works rely on chemical modification or high-temperature thermal activation to enhance adsorption performance [8, 9]. Despite these advances, adsorption performance of untreated Tunisian pomegranate peels, particularly under mild and environmentally sustainable conditions, has not been thoroughly investigated, particularly for Methylene Blue removal. Higher adsorption capacity does not necessarily imply higher sustainability or practical feasibility, especially when extensive pre-treatments are required.

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Accordingly, this study adopts a sustainability-oriented approach to remove Methylene Blue from aqueous solutions using untreated Tunisian pomegranate peels as an efficient biosorbent. The adsorption properties of pomegranate peels (PGP) were investigated without any chemical or thermal pre-treatment. The effect of temperature of Methylene Blue (MB) biosorption were investigated. Adsorption isotherms models and thermodynamic parameters were determined to investigate the adsorption mechanism and assess process feasibility.

# 2 Materials and Methods

## 2.1 Adsorbate

Methylene Blue (MB) was utilized as a model cationic dye. MB has the molecular formula $C_{16}H_{18}ClN_3S$ and was of analytical grade and supplied by Labosi with a purity of 99.99%. Mother solutions (1 g/L) of MB were prepared by dissolving the necessary amounts in one liter of deionized water and working solutions were obtained by dilution to the desired concentrations. The pH of the solutions was adjusted using 0.01 M NaOH or HCl. The concentrations were determined using a PerkinElmer UV–Visible spectrophotometer.

## 2.2 Adsorbent preparation and characterization

Pomegranate peels (PGP) collected from Gabès, Tunisia, were washed, dried, ground, and sieved prior to use without any chemical pretreatment. Elemental composition (CHNS–O), moisture, and ash contents were determined. The pH at equilibrium and the point of zero charge ($pH_{pzc}$) were measured to evaluate surface charge properties. Surface functional groups were analyzed by FTIR and Boehm titration, while textural properties were determined using BET analysis from $N_2$ adsorption-desorption isotherms.

## 2.3 Experimental approach

### *2.3.1 Experiments batch*

Batch experiments were conducted to evaluate the adsorption of MB onto PGP. The effect of temperature (30-50 °C) was studied. In each test, 200 mL of each dye solution was mixed with a fixed weight of PGP and shaken at 300 rpm for 200 min. After centrifugation, the residual dye concentration was measured at the maximum absorbance wavelengths (665 nm) using a UV-Vis spectrophotometer. Adsorption capacity was calculated using standard Eq. (1)

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

In this expression, $q_e$ denotes the quantity of dye adsorbed per gram of PGP at equilibrium (mg/g). $C_0$ and $C_e$ represent the initial and equilibrium concentrations of MB in solution (mg/L), respectively. m is the mass of the adsorbent used (g) and V is the solution volume (L).

### *2.3.2 Isotherm modelling*

The values of the adsorption isotherm constants quantify affinity and the surface properties of PGP towards MB [4, 6, 9]. Many isotherm equations are available. Langmuir [6] and Freundlich [6] models were selected and used in their linear form in this study (Eq. (2) and (3)).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (2)$$

$$Lnq_e = LnK_f + \frac{1}{n} LnC_e \quad (3)$$

In this context, $K_L$ (L/mg) corresponds to the Langmuir equilibrium constant, while $q_{max}$ (mg/g) refers to the theoretical maximum adsorption capacity. The Freundlich parameters include n and $K_f$ (mg/g) $(L/g)^n$, associated with adsorption capacity. R (J/mol. K) denotes the universal gas constant, and T (K) represents the absolute temperature.

## 3 Results

### 3.1 Pomegranate preparation and Characterization

Physico-chemical properties of the adsorbent are mentioned in Table 1. Surface functional groups analyzed by FTIR are presented in Table 2.

**Table 1.** Physical and chemical properties of raw PGP

| Parameters | Experimental values |
|---|---|
| C (%) | 43.13 |
| O (%) | 48.15 |
| H (%) | 7.17 |
| S (%) | 0.89 |
| N (%) | 0.66 |
| Total acidic functions | 3.4 |
| Total basic functions | 0.5 |
| pH | 4.16 |
| $pH_{pzc}$ | 4.7 |
| Moisture content (%) | 8.12 |
| Ash content (%) | 9.68 |
| Apparent density ($g/cm^3$) | 0.38 |
| Specific surface area | <1 $m^2/g$ |

The elemental analysis of raw PGP shows high oxygen content (48.15%) and significant carbon content (43.13%), indicating the presence of oxygenated functional groups. Bohem titration reveals a predominance of acidic surface groups over basic ones, which explains the acidic nature of the material (pH = 4.16) and a $pH_{pzc}$ of 4.7. The adsorbent exhibits a an extremely low specific surface area (<1 $m^2/g$), suggesting a non-porous structure, which could influence adsorption mainly through surface functional groups rather than physical porosity.

**Table 2.** Frequencies of different PGP surface functional groups

| **Frequency ($cm^{-1}$)** | **Band** |
|---|---|
| 1020 | (C-O) and C–O–C stretching vibrations of polysaccharides |
| 1227 | C–O stretching vibrations of phenolic, ether, and ester groups |
| 1320 | C–O stretching and O–H bending vibrations of phenolic groups |
| 1446 | Bending vibrations of aliphatic $–CH_2$ and $–CH_3$ groups |
| 1617 | Aromatic C=C stretching vibrations associated with lignin structures |
| 1727 | C=O stretching vibrations of carbonyl groups (carboxylic acids, esters/acetate, ketones, aldehydes) |
| 2935 | Aliphatic C–H stretching vibrations ($–CH_3$ and $–CH_2–$ groups) |
| 3280 | O–H stretching vibrations of hydroxyl groups (phenolic and carboxylic acids) |

The FTIR spectrum (Table 2) reveals bands characteristic of polysaccharides, phenolic, aromatic, and carbonyl groups, confirming the presence of functional groups able to interact with MB molecules**.** These results suggest that adsorption occurs mainly via surface functional groups rather than porosity**.**

## 3.2 Adsorption isotherms

### *3.2.1 Effect of temperature*

Temperature effect of MB adsorption by PGP was studied through isotherms in the range of 30-50 °C. Fig. 1 shows the adsorption capacity of PGP for MB as a function of $C_e$ at different temperatures, providing insight into the thermodynamic behavior of the process.

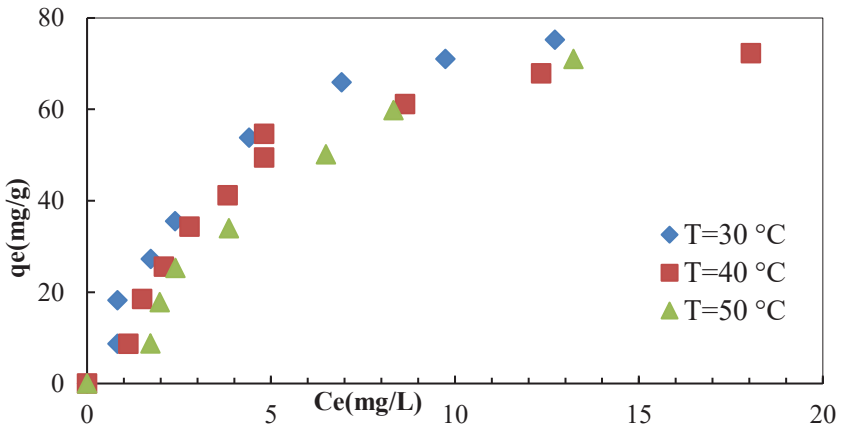


**Fig 1.** Experimental isotherms of MB adsorption on PGP adsorbent (pH=5.8, adsorbent mass=0.15g).

The increase in temperature reduced the adsorption capacity, indicating the exothermic nature of the process. Elevated temperatures may weaken adsorbent dye interactions, modify the pomegranate peel structure, and decrease the number of available active sites, thereby lowering adsorption efficiency. This behavior is further confirmed by thermodynamic analysis of MB adsorption. [4, 6, 9].

### *3.2.2 Isotherm modelling*

Adsorption isotherms of MB on PGP were evaluated using two models (Langmuir and Freundlich) under optimal conditions (0.15 g/L, 200 min, pH 5.8, 300 rpm). Calculated parameters are showing in Table 3. These optimal conditions were determined based on prior investigations currently under publication, which guided the selection of experimental settings for the present study.

The adsorption data show that Langmuir model provides a better fit than the Freundlich model, as evidenced by the higher correlation coefficients close to the unity. This suggests that the adsorption process predominantly follows a monolayer mechanism on a relatively homogeneous surface. The maximum adsorption capacity ($q_{max}$) decreased with temperature, suggesting an exothermic process [6, 7].

**Table 3.** Langmuir and Freundlich isotherm parameters for MB adsorption onto raw PGP

| | **Langmuir model** | | | **Freundlich model** | | |
|---|---|---|---|---|---|---|
| **T (°C)** | $q_{max}$ (mg/g) | $K_L$ | $R^2$ | $K_f$ | 1/n | $R^2$ |
| 30 | 101.01 | 0.242 | 0.993 | 11.80 | 0.648 | 0.975 |
| 40 | 97.74 | 0.225 | 0.987 | 15.92 | 0.614 | 0.90 |
| 50 | 76.92 | 0.245 | 0.971 | 21.24 | 0.543 | 0.88 |

## 3.3 Thermodynamic study

The thermodynamic behavior of MB adsorption was evaluated through ΔG°, ΔH°, and ΔS° (Table 4), reflecting spontaneity, interaction energy and system disorder. The equilibrium constant $K_C$ was derived from the Langmuir constant $K_L$ after converting it to a dimensionless form and ΔG° was calculated from $K_C$.

$$\Delta G° = -RTLnK_c \quad (4)$$

Where T is the temperature, R is the universal gas constant and. The relationship between ΔG°, ΔH°, and ΔS° is given by Eq. (5):

$$\Delta G° = \Delta H° - T\Delta S° \quad (5)$$

**Table 4.** Thermodynamic characteristics of MB adsorption onto raw PGP

| **T (K)** | **ΔG° (kJ/mol)** | **ΔH° (kJ/mol)** | **ΔS° (J/mol. K)** |
|---|---|---|---|
| 303 | -37,15 | - 45,64 | -28,97 |
| 313 | -36,86 | | |
| 323 | -36,57 | | |

Based on the results of Table 4, the adsorption of MB onto PGP was found to be spontaneous and thermodynamically favorable, as indicated by the negative ΔG° values at all temperatures studied [4, 9]. The negative ΔH° values confirm that the process is exothermic, while the negative ΔS° values reflect a reduction in randomness at the solid–liquid interface, likely due to the structured arrangement of MB molecules on the PGP surface.

## 4 Conclusions

This work demonstrates that untreated Tunisian pomegranate peels (PGP) are an effective, low-cost, and sustainable biosorbent for the removal of Methylene Blue. The adsorption process follows the Langmuir isotherm, indicating monolayer coverage on a relatively homogeneous surface. Thermodynamic analysis confirms that the process is spontaneous and exothermic. Overall, raw PGP represents a promising material for wastewater treatment, offering an environmentally friendly way to valorize agricultural waste.

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