High-efficiency of Peanut Shell Biosorbents in Cationic Dye Removal for Water Pollution Treatment

Aziz El Badraoui¹,², *, Loubna Nahali¹, Youssef Miyah¹,³, Fatin Tagnaouti Moumnani¹, Ouissal Assila¹, Hanane Souhassou¹, Farid Zerrouq¹, Bouchta El Khazzan⁴

¹ Laboratory of Materials, Processes, Catalysis, and Environment, University Sidi Mohamed Ben Abdellah, Higher School of Technology, P.O. Box: 2427 Fez, Morocco.
² Urban Studies Team, Faculty of Letters and Human Sciences Dhar El Mehraz, Sidi Mohammed Ben Abdellah University, Morocco.
³ Ministry of Health and Social Protection, Higher Institute of Nursing Professions and Health Techniques, Fez/Meknes, Morocco.

*Corresponding author, Email address: zerrouq1959@gmail.com and youssef.miyah@gmail.com

Received 30 Oct 2023, Revised 11 Dec 2023, Accepted 17 Dec 2023


Abstract: One of the most serious environmental issues in emerging nations is the widespread use of organic dyes in textile production. This study investigates the adsorption of Acid Fuchsin (AF) dye on the peanut shells (PS) surface. The PS material was characterized using Fourier transform infrared (FTIR) and scanning electron microscopy-energy dispersive X-ray (SEM-EDX) studies, which identified fibrous cellulose compounds that allow an understanding of the mechanism and the interactions between the surface functions and solution ions. Multiple adsorption parameters, such as pH, temperature, adsorbent dose, initial dye concentration, kinetics, isotherm, and thermodynamics, were analyzed. As per the results, the adsorption of AF onto the PS surface followed the pseudo-second-order with Langmuir isotherm models and an adsorption capacity of 111.11 mg g⁻¹. These findings reveal that the interactions in the biomaterials surface are monolayer. The thermodynamic study revealed the exothermic and non-spontaneous nature of the retention process of AF dye molecules on the PS surface with reduced randomness as indicated by the energies ΔG°, ΔH°, and ΔS°. Moreover, it demonstrates that PS adsorbent effectively eliminates cationic dyes from aqueous solutions. In addition, the dye (AF) adsorption using this material presents an ecologically advantageous aspect for the treatment of water contaminated by textile dyes.

Keywords: Adsorption; Bio-adsorbent; Characterization; Equilibrium; Kinetics.

1. Introduction

Water pollution has become a major concern due to the unlimited discharge of deadly substances from various activities, mainly anthropogenic activities such as those carried out in industries and their discharge of waste effluents (Mani et al., 2019; Alaqarbah et al., 2022). Large amounts of water are needed to convert raw materials into finished goods, and after processing, this water is released with variable degrees of contamination into seas and rivers. In particular, water contaminated with synthetic dyes. Organic dyes are contaminants of concern in wastewater, and the principal industries that produce dyes are those in the textile, printing, paint, leather, agriculture and cosmetics sectors (Akartasse et al.,...
Anions, cations, and non-ions are the three categories into which dyes are classified; each category includes a sizable number of dyes. Dyes toxicity is an environmental issue due to its low biodegradability, toxicity, and high organic loads (Jaafar et al., 2016; Laskar and Kumar, 2018). The aesthetic quality is diminished by the dark color of dyes and pigments, which also inhibits light from penetrating the water and slows the rate of photosynthesis in aquatic plants. The variations in the biochemical oxygen demand, chemical oxygen demand, pH, and salinity of the water are caused by these harmful effluents (Azeez et al., 2020). It is therefore necessary to remove dyes and other pollutants from wastewater before it is discharged into natural water bodies.

Therefore, appropriate treatment of textile waste is necessary to maintain the water quality, the environment security, and human health. The most frequently used methods for removing polluted water discharged from industries comprise coagulation, precipitation, filtration, reverse osmosis, oxidation, adsorption, advanced oxidation, and chemical oxidation (El-habacha et al., 2023; Loubna et al., 2019). Among the available treatments, the adsorption process using low-cost adsorbents is considered one of the most advantageous methods to remove dyes compared to the rest of the conventional techniques in economic and environmental terms due to its high efficiency, its ease of operation and its sensitivity to toxic substances (Bhatnagar and Minocha, 2006; Miyah et al., 2021, 2019). In recent years, focus has been placed on the low cost of agro-industrial, forestry, and industrial wastes due to their frequent disposal and the minimal treatment they need, making them appealing for such applications (Bhattacharjee et al., 2020; Mane and Babu, 2013; Ssouni et al., 2023).

The main contribution of this work is the evaluation of acid fuchsin (AF) dye adsorption using adhering peanut shells (PS) as adsorbent. Acid fuchsin is a triphenylmethane dye, its toxicity is related to its basic character, as well as its release into the natural environment is not only dangerous for aquatic life but also carcinogenic for living species, for this reason, the elimination of fuchsin basic is a great challenge for the purification and conservation of water. The different parameters affecting the adsorption efficiency including dye type, initial concentration, pH, equilibrium time, adsorbent dose, and temperature were evaluated. In addition, adsorption isotherms, kinetic studies, and recycling capacity have been described.

Scheme 1. Molecular structure of acid fuchsin (AF)

2. Materials and methods
2.1 Materials
Acid fuchsin, with a chemical formula of C_{20}H_{17}N_{3}Na_{2}S_{3} and a molecular weight of 585.54 g mol⁻¹, served as the chosen anionic dye model for our experiments. Analytical-grade acid fuchsin, NaOH, and HCl were used without additional purification.
2.2 Adsorbent Preparation
Peanut shells were soaked in distilled water for 3 days to remove the coloring extracts from the peanut fiber until colorless water was obtained. The peanut shells were dried in an oven at 60°C/24h. Then crushed and sieved to obtain a fraction of 63 µm then kept in a desiccator.

2.3 Adsorption procedure
For adsorption experiments, a 100 mg L⁻¹ stock solution was prepared by adding an appropriate amount of AF dye to 1 L of distilled water taken from a flask. After that, to maintain the stock solution's homogeneity, it was kept at ambient temperature and in a dark area. For the 100 ml of AF solution of different concentrations (20, 30 and 40 mg L⁻¹), 1-5 g L⁻¹ of the adsorbent PS was added, and the experiments were carried out by varying the temperatures (20-60°C) using a contact time (60 min), and at different pH ranges (2, 4, 6, 8, 10 and 12). The magnetic stirrer was used to agitate the dye solutions, and a 150-rpm speed was maintained throughout the experimentation. After every 5 min, the sample was removed and filtered, and the concentrations of the dye solution were checked by a UV-vis spectrophotometer. The concentration of residual AF dyes was measured using a UV-visible spectrophotometer (Selecta Vr-2000 spectrophotometer) at λmax = 545 nm. For temperature-dependent experiments, the desired temperature was maintained using a water bath.

Eq.1 was used to calculate the quantity of AF that had been absorbed at time t (mg g⁻¹).

\[ Q_t = \frac{(C_i - C_t)}{m} \times V \]  \hspace{1cm} (1)

The removal rate (R%) of the dye was calculated using the following Eq.2:

\[ R\% = \frac{(C_i - C_t)}{C_i} \times 100 \]  \hspace{1cm} (2)

Where \( C_i \) is the initial concentration of AF in mg L⁻¹, \( C_e \) is the equilibrium concentration of AF in mg L⁻¹, \( C_t \) is the concentration of AF in mg L⁻¹ at time t, \( V \) is the volume of AF in L, and \( m \) is the mass (g) of the adsorbent PS.

2.3 Characterization
The functional group analysis of the samples was conducted through FTIR spectroscopy in the 400–4000 cm⁻¹ range, employing a KBr disc. A BRUKER FTIR spectrophotometer model (Vertex 70) was utilized for this purpose. For elemental characterization and surface morphology assessment of the adsorbent, SEM/EDX analysis was performed in collaboration with the EDAX team at the SEM, UATRS Materials platform.

3. Results and Discussion
3.1 Characterization of the adsorbent
The absorption bands present in the spectra reveal the bond characteristics of the PS powder (Figure 1). The peaks at 3340 cm⁻¹ and 2920 cm⁻¹ correspond to O–H stretch-binding vibrations and methyl groups on the surface, respectively (Miyah et al., 2022; Tewatia et al., 2021). The peak at 1731.99 cm⁻¹ is from the C=O group vibrations, while the band at 1625.21 cm⁻¹ shows the presence of aliphatic vibrations of the group C=C (Hasanah et al., 2022; Miyah et al., 2021). The observed peak at 1245.95 cm⁻¹ corresponds to the C–O stretching of phenolic compounds, while the band at 1022 cm⁻¹ could represent the C–O–C of cellulose (Canteri et al., 2019; Fazio et al., 2020; Rodríguez-Arellano et al., 2021). Finally, the band at 530 cm⁻¹ is attributed to the torsion of the ring in the plane.
The morphology of the biosorbent was assessed through examination of scanning electron micrographs, as presented in Figure 2. These findings reveal that the biosorbent exhibits a rough surface characterized by various pore types and irregular shapes. These pores play a crucial role in providing ample accommodation for AF dye molecules, thereby influencing the adsorption process. These results underscore the remarkable adsorption capacity of peanut shells (PS) for the removal of AF dyes from aqueous solutions.

Figure 2. Peanut shells powder FTIR

Figure 3. SEM microscopy (a,b) coupled by EDX (c) for PS
To determine the elemental composition, expressed as weight percentages (%), we conducted Energy Dispersive X-ray (EDX) analyses. As depicted in Figure 2, the surface of PS primarily consists of carbon (56.53% by weight) and oxygen (40.37% by weight), making them the predominant elements.

3.2. Effect of initial concentration and contact time

The adsorption of AF (20.40 and 60 mg L⁻¹) on PS at a temperature of 303 K and an adsorbent dose of 1 g L⁻¹ was studied as a function of time to identify the process' equilibrium stage. As shown, the adsorption rate of AF on PS increased rapidly after the first few minutes of contact; however, as the contact time increased, we noted a slow increase. Maximum adsorption was found at 30 min. This may be because the sorption sites are initially open and the acid fuchsin molecules have easy access to them. Furthermore, no such dye removal was observed, which occurred due to the occupation of adsorption sites (Arunarani et al., 2013; Miyah et al., 2023, 2020, 2018; Samant et al., 2017). With an initial concentration increasing from 20 to 60 mg L⁻¹, the elimination rates are of the order of 83.81%, 82.27%, and 77.29%, respectively. This evolution of the rate could be explained by the low dispersion of AF molecules in PS due to the high concentration of AF. Furthermore, the high concentration of AF saturates the material, which reduces the adsorption capacity (Dali Youcef et al., 2019).

3.3. Effect of adsorbent dose

Determining the ideal dose of adsorbent is a crucial element that influences the extent of adsorption. The AF solution's starting concentration was set at 20 mg L⁻¹, and the adsorbent dose was varied between 1 and 5 g L⁻¹ (Figure 4). As the adsorbent dose increased, the removal rates of AF over PS rose to 97.26% because of the rise in the adsorption site number (Okeola et al., 2012).

3.4. Effect of Temperature

Temperature is another important element that affects the adsorption process for dye removal (El-Habacha et al., 2023). At five different temperatures ranging from 20 to 60°C, the impact of temperature on AF adsorption by PS was investigated. Figure 5 shows the impact of temperature on
the adsorption of AF dye at a concentration of 20 mg L\(^{-1}\) on the PS surface with a constant adsorbent dose of 5 g L\(^{-1}\). The results showed that the elimination percentage of AF increased slightly from 83.81 to 96.26% when the temperature was raised from 20 to 60°C, and then it became almost stable. One of the plausible reasons for this observation may be, that a temperature rise could have increased the kinetic energy thus increasing the porosity of the adsorbent. The results showed that the elimination percentage of AF increased slightly from 83.81 to 96.26% when the temperature was raised from 20 to 60°C, and then it became almost stable.

**Figure 5.** Influence of the adsorbent dose on the AF adsorption ([AF]= 20 mg L\(^{-1}\), adsorbent dose = 1-5 g L\(^{-1}\), 20°C, and a stirring duration of 60 minutes).

**Figure 6.** Influence of the solution temperature on the AF adsorption ([AF]= 20 mg L\(^{-1}\), adsorbent dose = 1 g L\(^{-1}\), T=20-60°C, and a stirring duration of 60 minutes).
3.5. Effect of pH
The pH value affects the adsorption process by influencing the degree of ionization/dissociation of metals, the chemical composition of organic dyes, and the characteristics of adsorption sites on the biosorbent particle surface (Caroline Trevisan Weber et al., 2013; Kim et al., 2020). The study investigated the impact of pH on AF adsorption, and the results showed that PS has the potential to be an effective adsorbent for cationic dye removal (Figure 6). Dye adsorption on PS powder increased from 62% to 97% with increasing pH from 2 to 12, primarily due to the functional groups on the adsorbent material's surface undergoing strong protonation at pH 2, resulting in an overall positive charge (Deka et al., 2021).

![Figure 7. Influence of the pH solution (2-12) on the AF adsorption ([AF]= 20 mg L$^{-1}$, adsorbent dose = 1 g L$^{-1}$, 20°C, and a stirring duration of 60 minutes).]

3.6. Kinetic models
This study focuses on the kinetics of adsorption, which is essential for understanding the mechanism and developing an appropriate model.

The pseudo-first-order model, proposed by Lagergren, is based on the ability of adsorbents to adsorb dyes. It assumes that uptake at adsorption sites depends on unoccupied adsorption sites and that these phenomena are directly proportional (Ghosh et al., 2021). This kinetic model is described by Eq.3:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t$$

(3)

Where $K_1$ is Lagergren’s first-order constant rate, $q_t$ and $q_e$ are the adsorbent quantities at time $t$ and equilibrium, and $t$ is the contact time.

The pseudo-second-order model is based on chemical adsorption, where the adsorbate creates a covalent chemical bond with the adsorbent surface (Benjelloun et al., 2021). The pseudo-second-order kinetic equation is represented by Eq.4:

$$\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{t}{q_e}$$

(4)

Where $K_2$ is the constant pseudo-second-order rate, $q_e$ is the amount of adsorbate at equilibrium, $q_t$ is the amount of adsorbate at time $t$, and $t$ is the contact time.
The intra-particle diffusion model is often used to study diffusion mechanisms in adsorption. It comprises several stages: adsorbate transfer from solution, film diffusion, intra-particle diffusion in pores and the solid phase, and adsorption onto active sites. This model is described by Eq.5:

\[ q_t = k_p t^{1/2} + I \]  

(5)

Where \( q_t \) is the adsorption capacity at time \( t \), \( k_p \) is the intra-particle velocity constant, \( t \) is time and \( I \) is a constant representing the boundary layer thickness.

With the use of kinetic models, we can determine the most suitable model based on experimental data, providing a better understanding of the adsorption process and predicting its behavior under varying conditions. Figure 7 displays the curves of three different kinetic models, while Table 1 summarizes the kinetic parameters calculated for each model. Based on the regression coefficients (R²), the pseudo-second-order model proved to be in excellent agreement with the experimental data for the sorption of AF on PS, with an R² greater than or equal to 0.99. This indicates that this model accurately fits the process.

Figure 8. Pseudo-first-order (a), pseudo-second-order (b), and intraparticle diffusion (c) of adsorption kinetics models.

However, the graphs in Figure 7c indicated that the intraparticle diffusion model is not the only factor responsible for the rate of dye adsorption onto PS (Mariyam et al., 2021). These graphs suggest that there
are two diffusion stages in the adsorption process: the first stage involves the external diffusion of AF molecules to the PS surface, while the second stage involves intraparticle diffusion, a process delayed due to the low concentration of dye in solution (Nahali et al., 2022).

Table 1. Comparison between the pseudo-first-order, pseudo-second-order, and intraparticle diffusion model adsorption constant rate, calculated and experimental qe values.

<table>
<thead>
<tr>
<th></th>
<th>C0 (mg L(^{-1}))</th>
<th>q_exp (mg g(^{-1}))</th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
<th>Intraparticle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>q (mg g(^{-1}))</td>
<td>K (min(^{-1}))</td>
<td>q(cal) (mg g(^{-1}))</td>
</tr>
<tr>
<td>AF</td>
<td>20</td>
<td>16.762</td>
<td>3.907</td>
<td>0.128</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>32.907</td>
<td>3.884</td>
<td>0.079</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>46.376</td>
<td>4.535</td>
<td>0.038</td>
<td>0.19</td>
</tr>
</tbody>
</table>

3.7. Adsorption isotherms
In this study of adsorption, three isothermal models are used: the Langmuir model, the Freundlich model, and the Temkin model.
The Langmuir model represents adsorption as a function of equilibrium concentration and equilibrium quantity adsorbed (Eq.6) (Ma et al., 2019).

\[
\frac{C_e}{Q_e} = \frac{1}{K_L \cdot Q_{\text{max}}} + \frac{C_e}{Q_{\text{max}}}
\]  
(6)
Where \(C_e\) refers to the equilibrium concentration (mg L\(^{-1}\)); \(Q_e\) is the adsorption capacity (mg g\(^{-1}\)); \(Q_{\text{max}}\) is the maximum adsorbed amount (mg g\(^{-1}\)); and \(K_L\) is the Langmuir equilibrium constant that varies with temperature (L mg\(^{-1}\)).
The Freundlich model is used to study adsorption on heterogeneous surfaces (Eq.7) (You et al., 2021).

\[
\ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e
\]  
(7)
Where the Freundlich constant is represented by \(K_f\), while \(n_f\) is a constant linked to adsorption intensity. Finally, Temkin's model takes into account the effect of sorbate-adsorbate interactions on adsorption and the linear decrease in heat of adsorption (Eq.8) (Chen et al., 2020; Lin et al., 2016).

\[
q_e = B \ln (A_T C_e)
\]  
(8)
Where \(B\) is the Temkin constant, which relates to the heat of adsorption, and \(A_T\) is the Temkin isotherm constant.
The experimental study showed that the Langmuir model was the most suitable to represent acid fuchsin adsorption, with a high coefficient of determination. This suggests monolayer adsorption. Adsorption equilibrium curves for fuchsin acid were obtained for different initial dye concentrations, and adsorption parameters were calculated for each model (Figure 8 and Table 2).

3.8. Thermodynamic studies
The study employed a series of five temperature settings (20, 30, 40, 50, and 60°C) to investigate the Gibbs free energy (\(\Delta G^0\)), entropy (\(\Delta S^0\)), and enthalpy (\(\Delta H^0\)). The determination of these parameters was achieved through the utilization of the Van't Hoff expression (Eq.9, Eq.10, and Eq.11) (Ho et al., 2000):

\[
K_d = \frac{Q_e}{C_e}
\]  
(9)
\[
\Delta G^\circ = -RT \ln K_d
\]

(10)

\[
\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T}
\]

(11)

With \( R \) is the ideal gas constant \((R = 8.314 \text{ J mol}^{-1} \cdot \text{K}^{-1})\), \( T \) is the absolute temperature of the solution \((\text{K})\), \( K_d \) is the partition coefficient, \( Q_e \) is the amount of adsorbate in the adsorbent at equilibrium \((\text{mg g}^{-1})\), and \( C_e \) is the Equilibrium concentration of the adsorbate \((\text{mg L}^{-1})\).

**Figure 9.** Isotherm of Langmuir (a), Freundlich (b), and Temkin (c) of AF adsorption

**Table 2.** Isotherm constants for dye adsorption

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( Q_{max} ) (mg.g(^{-1}))</td>
<td>( K_l ) (L.mg(^{-1}))</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>AF</td>
<td>111.111</td>
<td>0.056</td>
<td>0.99</td>
</tr>
</tbody>
</table>

The determination of \( \Delta H^\circ \) and \( \Delta S^\circ \) involved analyzing the linear plots between \( \ln K_d \) and \( 1/T \), as depicted in **Figure 9.** Based on the results presented in **Table 3**, we can conclude that the \( \Delta H^\circ \) value
was negative, indicating exothermic adsorption of cationic dye AF onto adsorbent PS (Singha and Das, 2011). Furthermore, the negative $\Delta S^\circ$ value suggests that there was reduced randomness in the adsorption of dye particles at the solid/liquid interface (Benjelloun et al., 2022; Hadi et al., 2010). In addition, the positive values of $\Delta G^\circ$ imply that the adsorption process of AF on PS was not spontaneous.

![Figure 10. The plot of Ln(K_d) as a function of 1/T](image)

**Table 3.** Equilibrium constant and thermodynamic parameters for the adsorption of AF onto PS biosorbent

<table>
<thead>
<tr>
<th>$\Delta H^\circ$</th>
<th>$\Delta S^\circ$</th>
<th>$\Delta G^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-54.355</td>
<td>-191.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>20°C 30°C 40°C 50°C 60°C</td>
</tr>
<tr>
<td></td>
<td>0.085 5.182 6.402 7.329 8.285</td>
<td></td>
</tr>
</tbody>
</table>

**Conclusion**

This study involved the use of peanut shells (PS) as a low-cost abundantly available adsorbent to remove acidic fuchsin (AF) dye from its aqueous solution. The remarkable adsorption capacity of this bio-adsorbent for the cationic dye serves as a promising foundation for potential applications in the removal of other cationic pollutants from the environment. The adsorption capacity for acidic fuchsin reached 111.11 mg g$^{-1}$. The adsorption behavior of AF on peanut shell-derived bio-adsorbent could be accurately described by the Langmuir model, indicating monolayer adsorption, with the process following pseudo-second-order kinetics. Additionally, the calculation of Gibbs free energy suggests that the AF adsorption process is non-spontaneous, while the negative value of $\Delta H$ indicates that the AF adsorption process is exothermic. This study underscores the promising potential of PS in the treatment of wastewater containing AF and its effectiveness in removing organic pollutants.

**Disclosure statement:** *Conflict of Interest:* The authors declare that there are no conflicts of interest. *Compliance with Ethical Standards:* This article does not contain any studies involving human or animal subjects.
References


(2024); https://revues.imist.ma/index.php/morjchem/index