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Safranin adsorption onto Acasia plant derived activated carbon: Isotherms, thermodynamics and kinetic studies

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ABSTRACT

This study aimed to evaluate the effectiveness of three surfaces derived from the Acasia plant - specifically, dry powder (DAM), hot activated carbon (HAC), and acid activated carbon (AAC) - in removing safranin dye from aqueous solutions. The experiment examined various parameters, including time, pH, adsorbent dose, initial dye concentration, and temperature, to determine their impact on safranin adsorption by the prepared surfaces. Results indicated that adsorption uptake increased with initial concentration but decreased with temperature, while pH remained relatively constant. The experiment data was then analyzed using Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm models, with the Freundlich model proving to be the best fit for the equilibrium data. The pseudo-second-order equation was found applicable, and the negative ΔG values at 25°C suggested the adsorption process was spontaneous and exothermic. The thermodynamic parameters (ΔG, ΔH, and ΔS) were calculated and explained based on the adsorbate's chemical structure.

Capsule Summary: This study investigated the use of three biosorbents for the removal of safranin dye from aqueous solutions. Results indicated that these biosorbents derived from natural sources were effective in adsorbing safranin, with the Freundlich model proving to be the best fit for the equilibrium data.

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INTRODUCTION

Organic chemical compounds known as synthetic dyes are prevalent in almost every aspect of our daily lives. This group of dyestuffs constitutes the largest family, representing more than half of global production. Synthetic dyes find widespread use in various industries, especially textile factories for coloring fabrics, leather goods, stationery products, plastics, and more (Zghal et al., 2023; Paranjape and Sadgir, 2023; Bhatt et al., 2023). Commercial dyes are produced at a rate exceeding 7 x 10^5 tons annually, with two-thirds of this amount being utilized by the textile industry. Based on estimates, around 10-20% of the produced dye is discharged into effluent streams each year (Pathirana et al., 2023; Elsherif et al., 2014a; Elsherif et al., 2017a). Safranin dye is commonly used in the textile industry to dye cotton, wool, and silk fabrics (Karadeniz et al., 2023). However, the discharge of dye-containing wastewater from these industries poses a significant environmental threat. The presence of these dyes in wastewater can cause severe environmental problems, including water pollution, soil

contamination, and toxicity to aquatic life (Elsherif et al., 2018; Elsherif et al., 2014b; Althomalia et al., 2023; Ghafoor et al., 2023; Elsherif et al., 2013).

The literature features an array of techniques for treating dyes that encompass chemical, physical, and biological approaches. These methods include chemical oxidation, coagulation, photodegradation, biodegradation, adsorption, and membrane separation (Ahamad and Nasar, 2023; Ayodhya and Veerabhadram, 2018; Elsherif and Yaghi, 2014; Elsherif et al., 2019; Adetunji and Olaniran, 2021; Alkherraz et al., 2022; Sun et al., 2020; Elsherif et al., 2021a; Ahmad and Riaz, 2021; Karthikeyan et al., 2022; Elsherif et al., 2016). Physical adsorption methods are a popular choice due to their affordability, ease of use, and durability against environmental factors. Adsorption is a widely used and effective method for the removal of dyes from wastewater. The adsorption process involves the attachment of dye molecules onto the surface of adsorbent materials, which results in the separation of the dye from the wastewater.

Recent research has focused on the study of adsorption of Safranin dye from wastewater using various adsorbent materials. A study by Khalid et al. (2021) (Khalid et al., 2021) investigated the adsorption of Safranin dye on a low-cost adsorbent material derived from olive stones. The study found that the olive stone-based adsorbent material was an effective and low-cost adsorbent for the removal of Safranin dye from wastewater. Another study by Oguz et al. (2021) (Oguz et al., 2021) investigated the adsorption of Safranin dye from aqueous solution using a waste material derived from corn cobs. The study found that the corn cob-based adsorbent material was an effective adsorbent for the removal of Safranin dye from wastewater. Furthermore, a study by Kumar et al. (2021) (Kumar et al., 2021) investigated the adsorption of Safranin dye from wastewater using a biochar derived from rice husk. The study found that the rice husk-based biochar was an effective adsorbent for the removal of Safranin dye from wastewater.

In conclusion, the adsorption process using various low-cost and sustainable adsorbent materials has shown great potential for the removal of Safranin dye from wastewater. These studies highlight the importance of using eco-friendly and cost-effective adsorbent materials for the removal of dyes from wastewater to reduce the environmental impact of textile industries, which is a one of major environmental issues.

Based on aforementioned facts, the focus is on the development of economical and efficient adsorbents using biomass obtained from *Carpobrotus edulis*. These adsorbents were then employed to remove dyes from wastewater, with Safranin dye serving as a representative model dye. Additionally, the study examined the impact of several factors, such as thermodynamics, equilibrium, and kinetics, on the adsorption process.

MATERIAL AND METHODS

Reagent and chemicals

Merck's Safranin-T dye ($C_{16}H_{11}N_2O_4SNa$) was used in the study without any additional purification. A 1000 ppm stock solution was created by dissolving the dye in double-distilled water. To achieve the necessary concentrations for the experiments, the stock solution was diluted using double-distilled water. Merck also supplied the sodium hydroxide, hydrochloric acid, and phosphoric acid used in the study.

Preparation of adsorbent

The Acacia plant was sourced from a local agricultural field in Misurata, Libya, and was used to create three adsorbents for the study. To prepare the dry adsorbent material (DAM), the plant was cleaned and washed thoroughly with double distilled water to eliminate any foreign particles from the surface. Subsequently, it was dried in sunlight and then placed in a hot air oven at 70˚C for approximately 24 hours. After drying, the hulls were ground in an electric grinder and then sifted to achieve a particle size of <125 µm. The material was then placed in separate storage containers for future experiments (Elsherif et al., 2022).

To produce the hot and acid-activated carbon (HAC and AAC), the dried material underwent pyrolysis at 550°C in a furnace for a duration of 2 hours (Alkherraz et al., 2022). The resulting biochar was extracted, ground into a fine powder, sifted, washed with double distilled water, and eventually dried at 60°C. This material was designated as the hot activated carbon (HAC). For acid activation, a portion of the carbonized *Carpobrotus edulis* biochar was mixed with 1 M H_3PO_4 and stirred continuously for 1 hour, as described elsewhere (Alkherraz et al., 2022). The solution was diluted with double distilled water and decanted several times. It was then washed with double distilled water until the pH was 7. The acid-activated biochar was dried in an oven at 110°C and reserved for subsequent studies.

Analysis of dye

The molecular absorption spectrophotometer 6305 from JENWAY was used to track the levels of safranin dye both prior to and following the adsorption procedures, with monitoring taking place at λ_{max} = 520 nm. A calibration curve was created using concentrations of safranin ranging from 2-16 ppm, derived from the stock solution. Additionally, the pH of the solution was measured utilizing the pH Meter 3505 from JENWAY.

Batch sorption studies

The adsorption of safranin onto DAM, HAC, and AAC was investigated using a batch extraction method. The adsorption process of safranin was observed while varying parameters such as pH, temperature, amount of adsorbent, concentration and contact time. For each experiment, 0.1 g of safranin was measured into several 150 cm^3 conical flasks and mixed with 50 cm^3 of safranin solution at different concentrations (ranging from 5.0-300.0 mg/L) at a pH of 8.0.

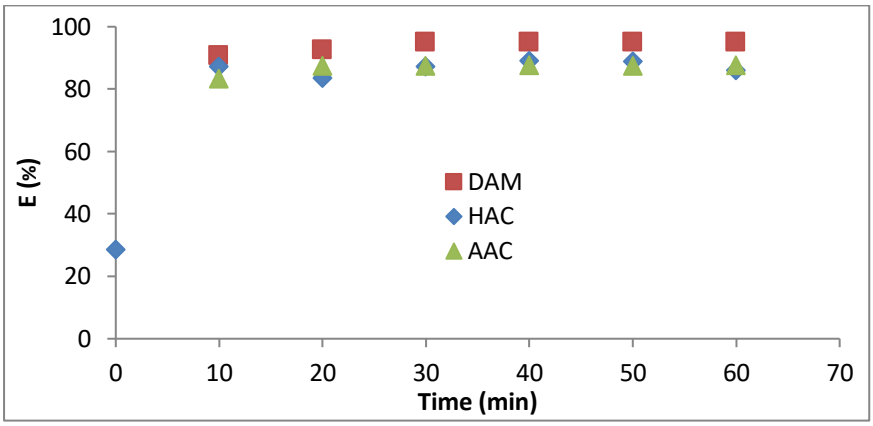

Fig. 1. The impact of time on the adsorption of safranin onto Acasia plant (dry, hot and acid activated materials)

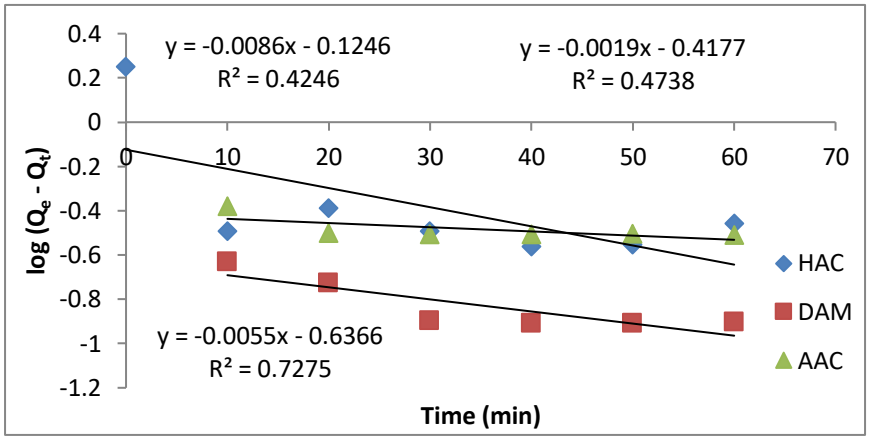

Fig. 2. Pseudo first-order kinetics of safranin adsorption onto Acasia plant (dry, hot and acid activated materials)

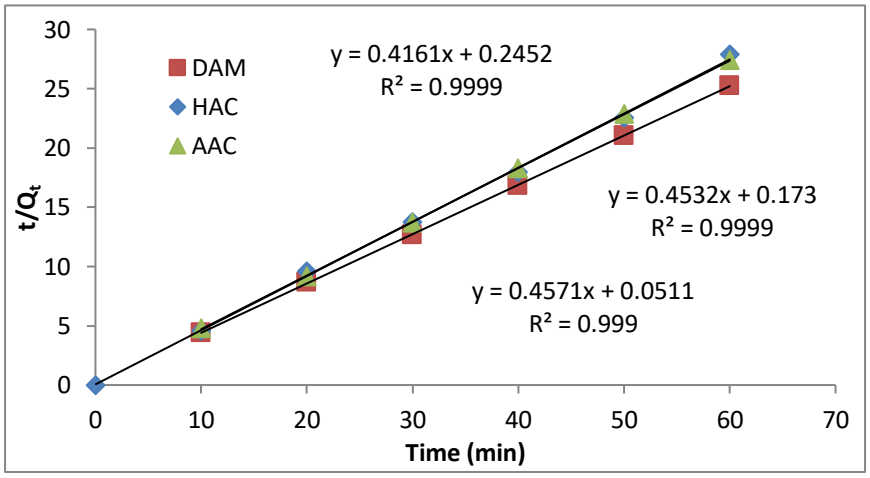

Fig. 3. Pseudo-second-order kinetics of safranin adsorption onto Acasia plant (dry, hot and acid activated materials)

The mixture was then mechanically equilibrated in a shaker at a fixed speed of 150 rpm and 303 K for 30 minutes until equilibrium was reached. At predetermined time intervals, the mixture was removed from the shaker, filtered through Whatman filter paper No. 1, and the concentration of safranin was determined spectrophotometrically at a wavelength of 520 nm. The amount of safranin removed at equilibrium (Q_e) in mg/g was calculated using equation 1, and the percentage of safranin adsorbed (%) was determined using equation 2 (Elsherif et al., 2021a; Alkherraz et al., 2020a; Alkherraz et al., 2020b).

$$Q_e(mg/g) = \frac{(C_o - C_e)x\,V}{M} \quad (1)$$

$$R\,(\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

Table 1. The first and second-order kinetic constants for the adsorption of safranin

First order	Q_e	k_1 (1/min)	R^2
DAM	0.231	0.0055	0.7275
HAC	0.751	0.0086	0.4246
AAC	0.382	0.0019	0.4738
Second order	Q_e	k_2 (g/mg min)	R^2
DAM	Calculated: 2.40 Experimentally: 2.50	0.708	0.9999
HAC	Calculated: 2.19 Experimentally: 2.40	4.080	0.9990
AAC	Calculated: 2.21 Experimentally: 2.40	1.184	0.9999

Table 2. The Langmuir, Freundlich, Temkin, D-R model constants for the adsorption of safranin

Langmuir	Q_m (mg/g)	b (L/mg)	R_L	R^2
DAM	13.35	0.028	0.42	0.2796
HAC	2.47	0.054	0.27	0.9679
AAC	45.66	0.009	0.69	0.0724
Freundlich	K_f (L/mg)	n (g/L)		R^2
DAM	0.356	0.842		0.9667
HAC	0.261	2.348		0.9949
AAC	0.424	1.091		0.9740
Temkin	A (L/mg)	B (J/mol)		R^2
DAM	0.89	5.026		0.7394
HAC	4.47	0.637		0.9967
AAC	0.81	4.702		0.7146
D-R Model	Q_d (mol/g)	β (mol²/J²)	E (KJ/mol)	R^2
DAM	4.65	$3x10^{-6}$	0.408	0.7665
HAC	0.86	$4x10^{-7}$	1.118	0.9524
AAC	3.46	$2x10^{-6}$	0.500	0.8004

Table 3. Thermodynamic properties of safranin dye adsorption on adsorbents at 25 °C

Adsorbed surface	ΔG^o (KJ.mol^{-1})	ΔH^o (KJ.mol^{-1})	ΔS^o (KJ.mol^{-1})	R^2
DAM	-52.40	-28.72	0.079	0.9321
HAC	-56.94	-24.72	0.108	0.9165
AAC	-34.51	-15.94	0.062	0.9174

Where, C_o (mg/L), C_e (mg/L), V (L), and M (g) represents the initial concentration of safranin, equilibrium concentration of safranin, volume of aqueous media, and mass of the dry adsorbent, respectively.

RESULTS AND DISCUSSION

Effect of contact time

Time is considered an important variable in batch adsorption experiments (Ghaedi et al., 2020; Elsherif et al., 2017b), and thus it was studied in the safranin dye adsorption process on dry powder, acid-activated carbon, and heat-activated carbon surfaces. Figure 1 shows that the percentage of safranin adsorption on the studied surfaces increases significantly with time, and it stabilizes at approximately 30 minutes, indicating that these systems reach equilibrium at 30 minutes. Therefore, this time was selected when studying the other variables.

The kinetics of safranin uptake onto (DAM, HAC, AAC) were investigated by fitting experimental data to two kinetic models, namely the pseudo-first-order and pseudo-

second-order models. Lagergren's pseudo-first-order equation (Elsherif et al., 2016; Gupta and Nayak, 2019) is typically formulated as shown in Eq. 3.

$$\frac{dQ_t}{dt} = k_1 (Q_e - Q_t) \quad (3)$$

The sorption capacities at equilibrium and at time t are represented by Q_e and Q_t, respectively, while k_1 denotes the rate constant of pseudo-first order sorption. At boundary conditions, the integrated form of equation (4) is obtained by integrating from $Q_t = 0$ to Q_t and from t = 0 to t, yielding:

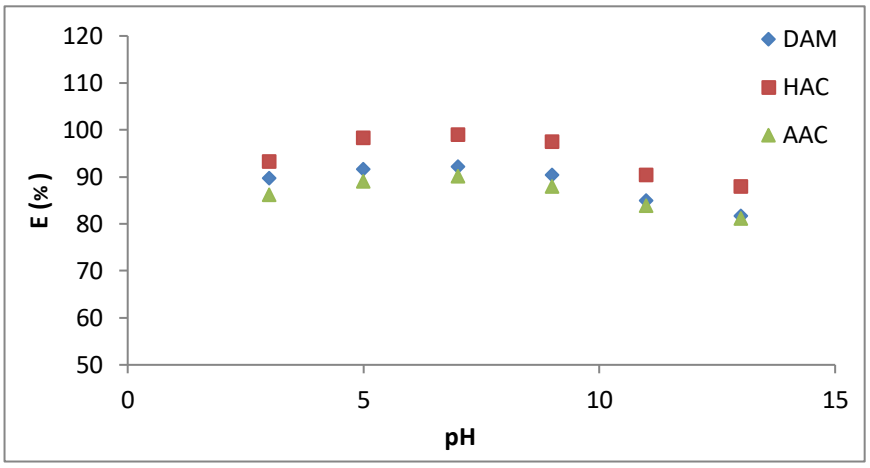

Fig. 4. Impact of pH on the adsorption of safranin onto Acasia plant (DAM, HAC and AAC)

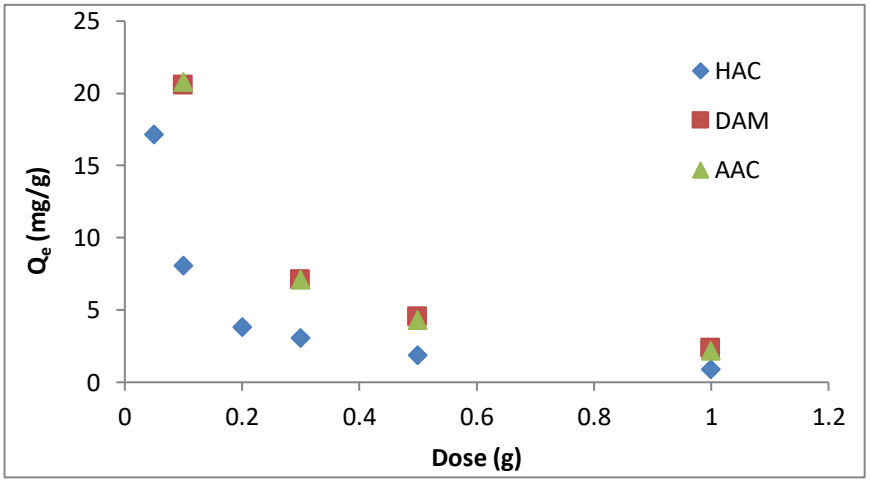

Fig. 5. Impact of adsorbent dosage on the adsorption of safranin onto Acasia plant (DAM, HAC and AAC)

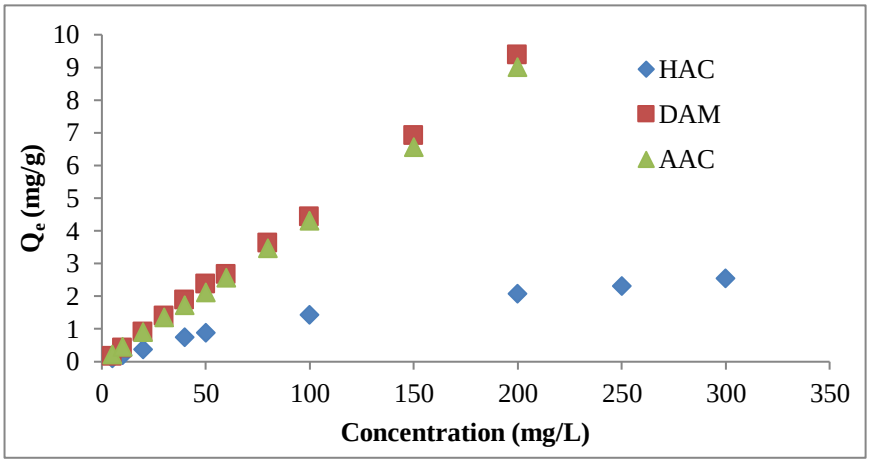

Fig. 6. Initial concentration impact on the adsorption of safranin onto Acasia plant (DAM, HAC and AAC)

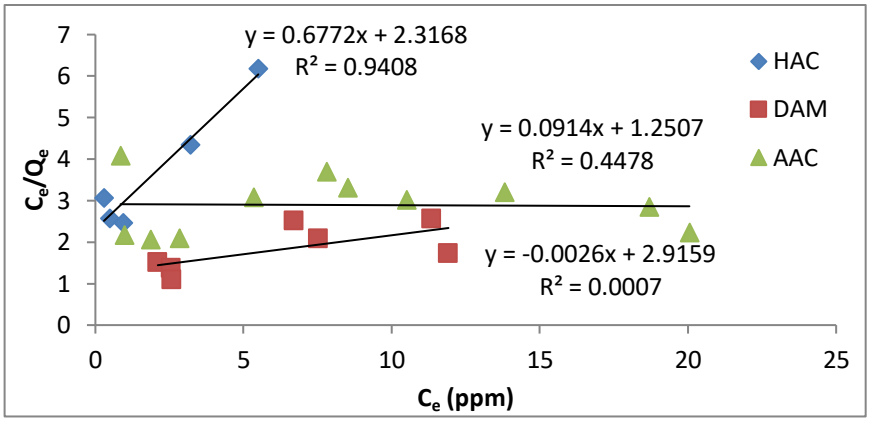

Fig. 7. Langmuir adsorption isotherm for the removal of safranin onto Acasia plant (DAM, HAC and AAC)

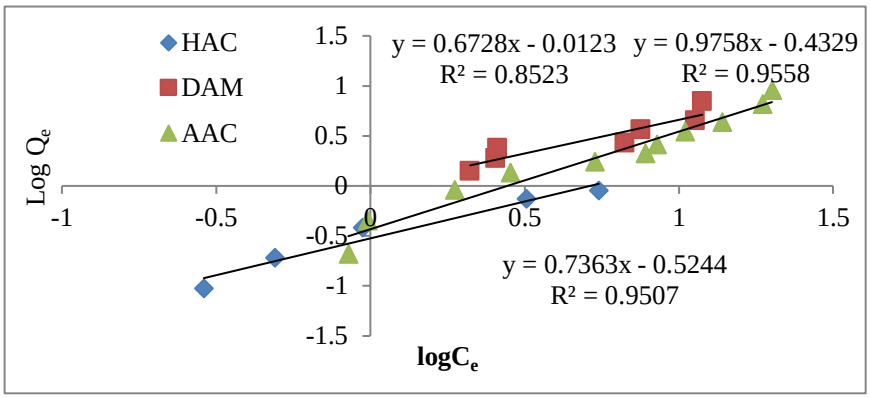

Fig. 8. Freundlich adsorption isotherm for the removal of safranin onto Acasia plant (DAM, HAC and AAC)

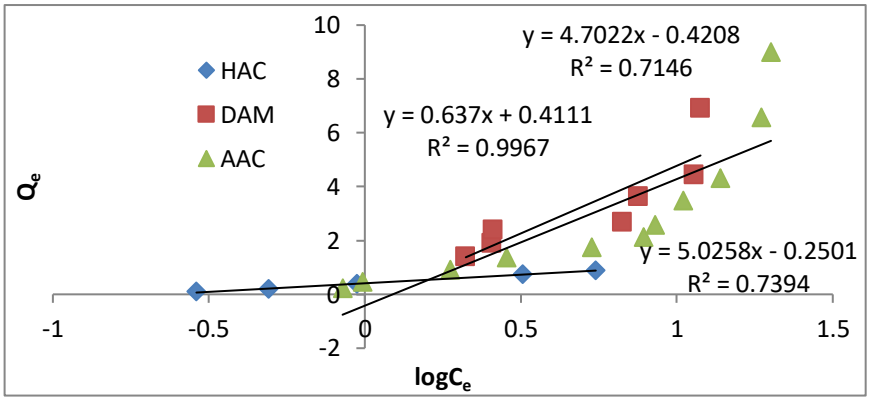

Fig. 9. Temkin adsorption isotherm for the removal of safranin onto Acasia plant (DAM, HAC and AAC)

$$Log(Q_e - Q_t) = LogQ_e - k_1 t \quad (4)$$

To fit the integrated form of the pseudo-first order equation to experimental data, the equilibrium sorption capacity Q_e must be known. However, Q_e must also be treated as an adjustable parameter to be determined since extrapolating the experimental data to t = 0 is necessary. Thus, it is necessary to use trial and error to obtain the equilibrium sorption capacity and analyze the kinetics of the pseudo-first order model. The equation applicable to experimental results differs from a traditional first-order equation in two ways: the terms k_1 and (Q_e - Q_t) do not represent the number of available sites, and the log Q_e is an adjustable parameter that is often not equal to the intercept of a plot of log (Q_e - Q_t) against t, where log Q_e should be equal to the intercept in a true first-order sorption reaction and the rate constant can be obtained from the slope. Figure 2 shows that in most cases in the literature, the amount sorbed is still significantly smaller than the equilibrium amount and the Lagergren equation does not fit well for the whole range of contact time process (Lagergren, 1898). The results and their corresponding linear regression correlation coefficient values are listed in Table 1, where R^2 values were found to be 0.4246, 0.4738, and 0.7275,

indicating that this model cannot be applied to predict the adsorption kinetic model.

The pseudo second-order rate expression, which is commonly used for analyzing sorption kinetics, is represented by the Eq. 5 (Ho and McKay, 1998).

$$\frac{dQ_t}{dt} = k_2 (Q_e - Q_t) \quad (5)$$

The integrated form of the equation is obtained by integrating from $Q_t = 0$ to Q_t and from $t = 0$ to t, as follows for the boundary conditions (Eq. 6).

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (6)$$

The variables used in this context include t, which represents the contact time in minutes, Q_e and Q_t, which denote the amount of solute adsorbed at equilibrium and at any time t in milligrams per gram, respectively, and k_2, which is the rate constant of pseudo-second order sorption expressed in grams per milligram per minute.

When pseudo-second order kinetics is applicable, a linear relationship should be observed in the plot of t/Q_t versus t, as shown in Figure 3. From this plot, Q_e and k_2 can be determined from the intercept and slope, respectively. Table 1 provides the values of the pseudo-second order rate constant k_2, the calculated Q_e value, and the corresponding linear regression correlation coefficient values R^2. The high R^2 values (0.999 and 0.9999) at all initial metal concentrations indicate that the adsorption data are better represented by pseudo-second order kinetics. The calculated Q_e values also agreed with the estimated experimental Q_e values (2.40-2.50, Table 1), further supporting the conclusion that the adsorption of safranin ions follows pseudo-second order kinetics.

Effect of pH

The adsorption of safranin dye from its aqueous solution is influenced by pH, which is one of the most important factors controlling the adsorption process of organic materials. Safranin dye adsorption was monitored on three surfaces over a range of pH values from 3.0 to 13.0, as shown in Figure 4. A slight decrease in the adsorption percentage was observed at acidic pH values (less than 5.0) while it decreased with increasing pH (pH > 9). The maximum removal efficiency of safranin was achieved at 98.98, 90.12, 92.26 % at pH (6-7) in the case of hot activated carbon, acid activated carbon, and dry powder, respectively. Within the pH range of 5.0 to 9.0, the removal efficiency of safranin dye remained almost constant. If electrostatic attraction is the only mechanism responsible for dye adsorption, its removal efficiency is maximized in a relatively weak acidic environment (pH 4-9) (El-Shafey and El-Khodary, 2017; El-Hashani et al., 2018). At these values, the surface of the adsorbent material is negatively charged while the dye is positively charged. In a strong acidic environment (less than 3.0), removal efficiency is expected to decrease due to competition between hydrogen ions and positively charged dye ions for vacant adsorption sites, leading to a decrease in dye adsorption. In a basic environment (greater than 10), the charge of the dye may change, resulting in repulsion between it and the adsorbent surfaces, leading to a decrease in adsorption efficiency (Li et al., 2021; Mohammadi et al., 2021).

Effect of adsorbent dose

The quantity of the adsorbent material is an important variable as it determines the maximum capacity for dye adsorption. The adsorption capacity for safranin molecules was studied as a function of the adsorbent dosage on the three studied surfaces, as shown in Figure 5. It can be observed that the dye adsorption capacity decreases with an increase in the adsorbent dose, and the maximum capacity is obtained using 0.1 g of the adsorbent material. This result can be explained by the fact that the adsorption sites on the adsorbent surfaces are still unsaturated during the adsorption process, while the number of available sites for adsorption increases with an increase in the adsorbent material quantity (Gupta and Nayak, 2021; Alkherraz et al., 2019). In subsequent experiments, it was considered that 0.1 g is the optimal quantity to achieve the maximum adsorption capacity for the dye.

Effect of concentration

The study examined how varying initial concentrations of dye affected the equilibrium of biosorption experiments onto (DAM, HAC, and AAC), with concentrations ranging from 5 to 300 ppm at a pH of 6. Figure 6 displays the relationship between equilibrium uptake (Q_m) in milligrams per gram and initial dye concentration. As depicted in Figure 6, the Q_m of dye gradually increased as the initial concentration of safranin dye increased. At lower concentrations, dye molecule adsorption was still possible; however, as the concentration increased, so did the driving force, which favored adsorption at higher concentrations. The increase in adsorption capacity with increasing dye concentration is likely due to a greater interaction between the safranin ions and biosorbent sequestering sites (Alkherraz et al., 2022; El-Hashani et al., 2018; Rajabi and Tyagi, 2017).

Adsorption isotherms

Four adsorption isotherms were employed to model the biosorption of safranin onto dry powder, hot activated carbon, and acid activated carbon (DAM, HAC, AAC), which characterizes the partitioning of sorbate molecules between the liquid and solid phases at equilibrium.

Langmuir isotherm

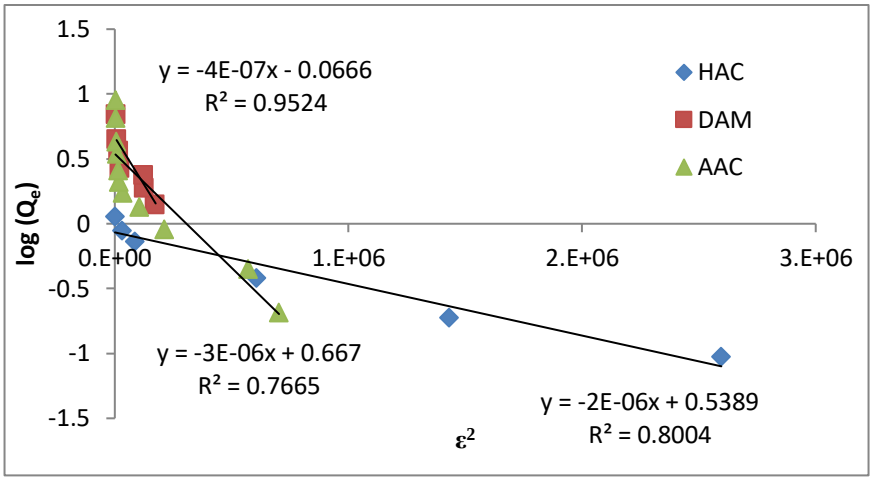

Fig. 10. D-R model adsorption isotherm for the removal of safranin onto Acasia plant (DAM, HAC and AAC)

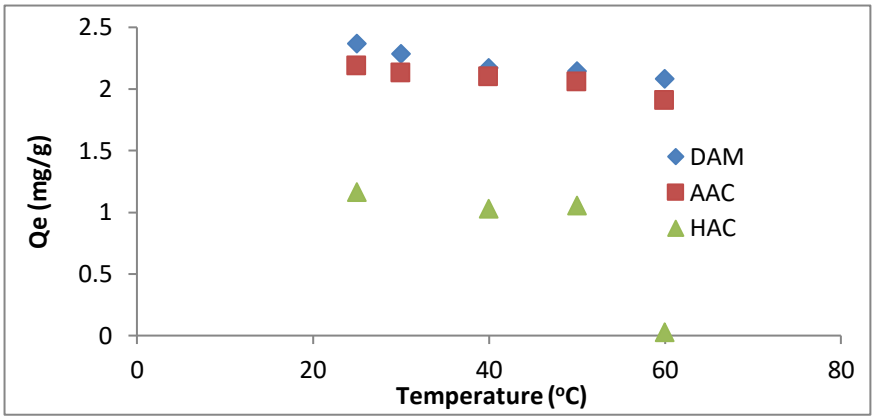

Fig. 11. The impact of temperature on the adsorption of safranin onto Acasia plant (DAM, HAC and AAC)

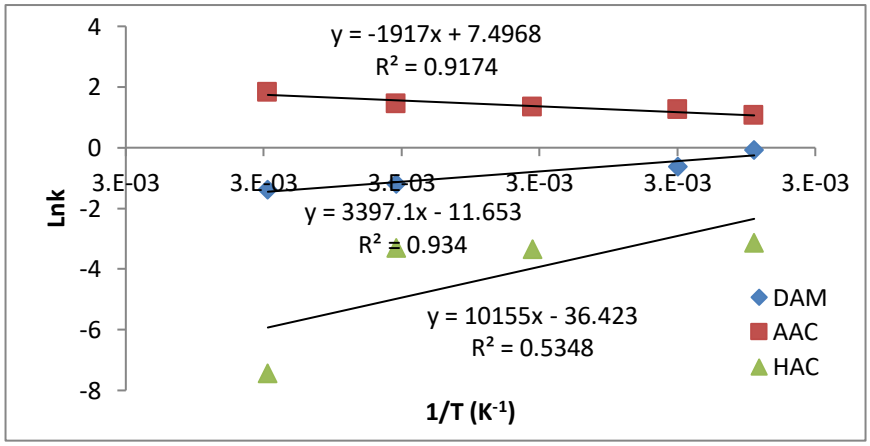

Fig. 12. Thermodynamic study of safranin adsorption onto Acasia plant (DAM, HAC and AAC)

The Langmuir isotherm model assumes that adsorption occurs as a monolayer on a uniform surface with a limited number of adsorption sites. When an adsorption site is occupied, no additional sorption can occur at that site. Consequently, the surface will eventually reach a saturation point where the maximum adsorption capacity is attained. The Langmuir isotherm model is represented in a linear form, which is defined as shown in Eq. 7 (Elsherif et al., 2021b; Alkherraz et al., 2020b).

$$\frac{C_e}{Q_e} = \frac{1}{b\,Q_m} + \frac{C_e}{Q_m} \quad (7)$$

In equation 7, the Langmuir model parameters Q_m, b, and C_e correspond to the maximum adsorption capacity, Langmuir

constant, and equilibrium dye concentration, respectively. Additionally, the Langmuir model parameter R_L can be determined using the relationship shown in Eq. 8.

$$R_L = \frac{1}{1+b\ C_o} \quad (8)$$

The equilibrium parameter R_L is a dimensionless quantity that relates to the Langmuir model. C_o and b represent the equilibrium dye concentrations and Langmuir constant, respectively. The value of R_L determines the type of adsorption: $R_L = 0$ indicates irreversible adsorption, $0 < R_L < 1$ indicates favorable adsorption, and $R_L > 1$ indicates unfavorable adsorption. As shown in Table 2, the R_L values for all adsorption surfaces were less than 1 indicating the favorable adsorption process. The maximum adsorption capacity Q_m and Langmuir constant b were determined from the intercept and slope of the C_e/Q_e versus C_e plot (Figure 7) and depicted in Table 2 (Alkherraz et al., 2022; El-Hashani et al., 2018).

Freundlich isotherm

The Freundlich equation is one of the earliest and most widely-known models for describing the adsorption process. This model is applicable to adsorption on heterogeneous surfaces and takes into account the interaction between adsorbed molecules. It suggests that sorption energy decreases exponentially as the sorption centers of an adsorbent become fully occupied. The Freundlich isotherm is an empirical equation that can be used to describe heterogeneous systems and is expressed in linear form as shown in Eq, 9. (Freundlich, 1906).

$$Log Q_e = Log K_f + \frac{1}{n}\ Log C_e \quad (9)$$

The Freundlich equation includes the Freundlich constant K_f, which is related to the bonding energy, and the heterogeneity factor 1/n, where n (g/L) represents the degree of deviation from linearity in adsorption. The Freundlich equilibrium constants were obtained by plotting $\log Q_e$ versus $\log C_e$, as demonstrated in Figure 8, based on the linearity of the Freundlich equation. The n value indicates the degree of non-linearity between solution concentration and adsorption: if n = 1, adsorption is linear; if n < 1, adsorption is a chemical process; if n > 1, adsorption is a physical process (Foo and Hameed; 2010). The Freundlich equation yielded an n value of 0.842 for dry material indicating a chemical process (Table 2). However, the values of n were 2.348 and 1.091 for hot activated and acid activated carbon; indicating that physical adsorption of safranin ions. However; the adsorption isotherm model that provided the best fit was chosen based on the R^2 values, therefore, the adsorption process of safranin dye was found to be in good agreement with the Freundlich isotherms for all adsorbents tested (DAM, HAC, AAC) as shown in Table 2.

Temkin isotherm

The Temkin isotherm equation (Temkin and Pyzhev, 1940) proposes that the heat of biosorption for all molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions. It also suggests that the adsorption process is characterized by a uniform distribution of binding energies up to a maximum binding energy. The Temkin isotherm is typically expressed in a linear form, which is given in Eq. 10.

$$Q_e = B\ LogA + B\ Log C_e \quad (10)$$

By plotting Q_e versus $\log C_e$, the isotherm constants B and A can be determined from the slope and intercept, as shown in Figure 9. The equilibrium binding constant A (L/mg) corresponds to the maximum binding energy, while the constant B is related to the heat of biosorption, as listed in Table 2.

Dubinin-Radushkevich (D-R) model

The experimental data was also tested using the Dubinin-Radushkevich (D-R) model (Eq. 11), which does not assume a homogeneous surface or a constant biosorption potential as the Langmuir model. (Gupta and Ali, 2004).

$$Log Q_e = Log Q_d + \beta\varepsilon^2 \quad (11)$$

The value of ε can be related to C_e (mg/L) using the relation shown in Eq. 12.

$$\varepsilon = RT\ Log\ (1 + \frac{1}{C_e}) \quad (12)$$

The Dubinin-Radushkevich (D-R) isotherm parameters β and Q_d can be obtained from the slope and intercept of the plot of $\log Q_e$ versus ε^2, as shown in Figure 10, where R represents the universal gas constant (8.314 J/mol K) and T is the absolute temperature (K). The calculated values for β and Q_d are listed in Table 2. The correlation coefficient values were found to be lower compared to those obtained for the Freundlich isotherm.

The mean free energy of biosorption (E), which is defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the solid, can be calculated from the β value using Eq. 13 (Dubinin, 1960).

$$E = \frac{1}{\sqrt{2\beta}} \quad (13)$$

If the value of E falls within the range of 8 to 16 KJ/mol, it is considered as an indication of chemisorption, while a value less than 8 kJ/mol suggests physical adsorption (Gupta and Rastogi, 2008). For the biosorption of safranin ions by dry powder, hot activated, and acid activated carbon, the values of E were calculated from equation (13) as 0.408, 1.118,

0.500 KJ/mol, indicating that the biosorption process is of physical nature

Effect of temperature

The effect of temperature on safranin adsorption was studied in the range of 25-60°C while keeping other parameters constant. The results are displayed in Figure 11, which indicate that the adsorption capacity of the dye decreased with increasing temperature. Specifically, for all adsorbents (DAM, AAC, and HAC), the dye adsorption capacity decreased from 2.37 to 2.08, 2.19 to 1.91, and 1.17 to 0.03 mg/g, respectively, as the temperature was increased from 30 to 65°C. These results suggest that the adsorption process is exothermic in nature (Yahya et al., 2015).

Thermodynamic studies

The thermodynamic parameters, including Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS), were determined for the safranin adsorption process on all three adsorbents using Eqs. 14-15 (Anwar et al., 2010).

$$\Delta G = \Delta H - T\,\Delta S \quad (14)$$

$$\Delta G = -\,RT\,\mathrm{Ln}\,K_d \quad (15)$$

The thermodynamic equilibrium constant K_d was calculated using R (8.314 J/mol K) and the absolute temperature T (K), while the values of ΔH and ΔS were determined from the slope and intercept of the plot of Ln K_d vs. 1/T using the van't Hoff equation (Eq. 16) (Siddiqui et al., 2017).

$$LnK_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (16)$$

The thermodynamic parameters for safranin adsorption on all adsorbent surfaces were calculated and are presented in Table 3. The negative values of ΔH indicate that the adsorption process is exothermic, while the positive values of ΔS suggest that the process becomes more random. The negative values of ΔG indicate that the adsorption process is spontaneous at all temperatures (Chen et al., 2018; Mao et al., 2016).

CONCLUSION

Three natural source materials (DAM, HAC, and AAC) have been used for the adsorption of safranin dye from aqueous solution. The removal effectiveness of these surfaces as adsorbents for safranin from aqueous solution, as well as cationic dyes, was described in this study, which aimed to limit the environmental effect of synthetic product dyes in water and wastewater. The optimization of the adsorption process depends on large parameters (time, pH, adsorbent dose, temperature, and the concentration of the pollutant and the nature of the adsorbent), which govern its effectiveness. In such a way, by keeping the pH constant at 6.0 and varying the solution temperatures at 20,30, 40, 50, and 60°C, one could find a significant influence on the adsorption process for safranin dye. The best safranin dye removal effectiveness was found in dry material (96%), which took place within 30 min The equilibrium adsorption data fitted well to the Freundlich adsorption isotherm, better than the Langmuir isotherm. The pseudo-second-order kinetics model was observed to fit the adsorption data. At 25°C temperature, negative standard Gibbs free energy change values (ΔG) indicated that the adsorption process was endothermic, spontaneous, and practicable. The negative values of standard enthalpy change (ΔH) indicated that the adsorption process is exothermic sorption.

DECLARATION OF COMPETING INTEREST

The authors declare no competing financial interest.

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