Adsorption of Textile Dyes on Willow Tree Pollen: Determination of Equilibrium, Kinetics, and Thermodynamic

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ABSTRACT: *In this study, the characterization and adsorption properties of Brilliant Cresyl Blue (BCB- ALD) and Acid Blue-25 (AB-25) dyes were investigated using willow tree pollen, a low-cost natural adsorbent. All adsorption tests were performed in consideration to contact time, adsorbent concentration, adsorbent dosage, and temperature functions. Equilibrium isotherms were explained in terms of the Langmuir, Freundlich, Temkin, and Dubinin Radushkevich (D-R) linear adsorption equations. It was found that adsorption complied with the Langmuir equation. Moreover, pseudo-first order, pseudo-second order, and intraparticle diffusion models were used to determine kinetic data. Experimental data showed a match with the pseudo-second-order kinetic model. Thermodynamic parameters such as enthalpy, Gibbs free energy, and entropy were examined for willow tree pollen samples. The data obtained led us to the conclusion that adsorption is a spontaneous process. On the other hand, positive enthalpy indicates that adsorption is endothermic. Positive entropy values are a result of changes on the adsorbent surface. Characteristic results and dimensionless separation factors (RL) indicate that pollen can be used as an alternative to commercial adsorbents to remove BCB- ALD and AB-25 from aqueous solution and wastewater.*

KEYWORDS: *Adsorption; Willow tree pollen; Kinetics equilibrium; Thermodynamic; Brilliant cresyl blue- ALD; Acid Blue-25.*

INTRODUCTION

In our age, pollution of the environment is one of the most important problems affecting human health. Pollutants from industrial processes become increasingly more complex and threaten human health. Water is without a doubt indispensable for life in all generations. However, wastewater as a product of industrial manufacturing processes is an important issue today [1]. Especially in the textile industry, dyes wastewater causes harm to various organisms with their chemical content, not to mention the ugly dirty view they create coloring the waters.

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Environmental pollution gets worse day by day with industrial development. Textile manufacturing is one of the leading industries worldwide. Wastewater containing high amounts of dyestuff (coloring agents) is at the root of serious problems in the long run [2-5].

The use of suitable adsorbents in the removal of colored and colorless organic pollutants in industrial wastewater gain recognition as an important application of the adsorption process. Today, adsorption is important in many natural, physical, chemical, and biological processes [6, 7]. Even though activated carbon and resins appear as the best adsorbent for removing chemical wastes from concentrated wastewater, their high costs and the requirements of backwash are considerable setbacks. Adsorbent concentration is the amount per unit surface. However, the adsorbent dosage is a maximum and minimum effective amount [8, 9].

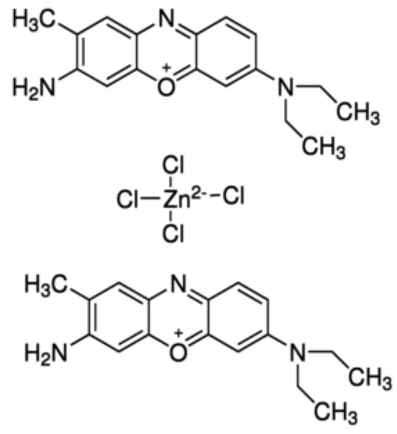
However, studies were performed using more economical adsorbents. These include sugar canes, reactive dyes based on vinyl sulfone and chlorotriazine, natural clay, basic and acidic dyes, sunflower, sepiolite, fly ash, azo dye, montmorillonite, and natural zeolite [10, 11]. BCB-ALD and AB-25 dyes provide many advantages compared to the other dyes. Pollen is a low-cost adsorbent, suitable and economical. It was used as an adsorbent in the treatment of textiles and wastewater. And also it seeks an answer to the problem of removing waste water dyes.

The aim of this study was to eliminate the dyestuff pollution caused by industrial wastewater using the adsorption method. Willow tree pollen was used as an adsorbent in the adsorption process. Dyestuff was removed with the aid of pollen. For this purpose, BCB-ALD and AB-25 were used as the dyestuff solvents. Accordingly, the effects of contact time, dyestuff concentration, and temperature on adsorption were investigated. Moreover, this adsorbent is intended for use in the removal of dyestuff and is an easily available alternative adsorbent.

EXPERIMENTAL SECTION

The willow tree pollen used in this study was obtained from the province of Van, Turkey. Tests were conducted using Sigma Aldrich brand BCB-ALD and AB-25 dyestuffs.

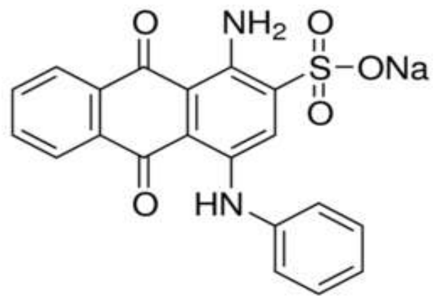
The molecular structure of this BCB-ALD is shown in the following sentences.



dye name: Brilliant Cresyl Blue ALD
molecular formula: $C_{17}H_{20}ClN_3$ 0,5$ZnCl_2$
molecular weight,g.mol^{-1}: 385,96
λ max. (nm): 622

BCB- ALD is mainly used for the selection of oocytes. It helps in determining the activity of glucose-6-phosphate dehydrogenase (G6PD). This enzyme is generated in growing oocytes. However, oocytes that complete their growth have low levels of G6PD. Low G6PD activity results in blue coloration of the cytoplasm because brilliant cresyl blue is not reduced to a colorless compound. It is also used for staining in reticulocytes, where the dye stains reticulin.

The molecular structure of this Acid Blue-25 is shown on the next line.



dye name: Acid Blue- 25
molecular formula: $C_{20}H_{13}N_2O_5S$
molecular weight,g.mol^{-1}: 416,38
λ max. (nm): 600

Properties and Applications: Blue powder. The little blue is soluble in water, but soluble in acetone, and ethanol, slightly soluble in benzene, four hydrogen naphthalene, and insoluble in nitrobenzene and xylene. Meet strong sulfuric acid as dark, after diluted blue precipitation. Mainly used for dyeing nylon and polyamide for supporting the dye. Can also be used for wool, silk, and blended fabric dyeing and printing directly. Can also be used in leather, electrical-controlled aluminum soap, and color.

Preparation of the dyestuff solution

Stock solutions of 500-1000 mg/L (ppm) were prepared for the dyestuff solutions. Then it was used with dilutions at the desired concentrations (C_0) (25, 50, 75 mg/L). pH of dye solutions was adjusted using 0.1N NaOH (Merk) and 0.1N HCl (Merk) solutions (Series ISOLAB, Laborgerate GmbH).

Absorption experiments

10 mL aliquot of the stock solution (25, 50, 75 mg/mL) of BCB-ALD and AB-25 was transferred into a 20 mL volumetric flask, and then an appropriate amount of 0.02g willow tree pollen was added at different temperatures (25^0C, 45^0C, 65^0C). The mixture was diluted to final volume with deionized water and shaken vigorously. The UV–Vis spectra were measured against a corresponding reagent blank.

Adsorption experiments

Adsorption tests were conducted in a temperature-controlled shaking water bath at 110 rpm with the addition of 10 mL dye solutions on 0.02 g of pollen (Nuve ST 30). Tests were studied at the respective K temperatures of 298, 318, and 338 at 1, 5, 10, 15, 20, 30, 60, 90, and 120 minutes. Samples were centrifuged at 3500 rpm for 5 minutes (Shimadzu UV-180). The maximum absorbance of these samples was measured at 622 nm for BCB- ALD and 600 nm for AB-25 at the maximum wavelength on the UV-Visible spectrometer device. Parameters affecting adsorption were examined, including concentration, temperature, and contact time. The effect of concentration on adsorption was tested using dyestuff solutions of 25, 50, and 75 mg/L. Dyestuffs were tested at temperatures of 25^0C, 45^0C, and 65^0C.

In the calculation of the amount of dyestuff removed from the solution medium, the equation,

$$q_e = (C_0 - C_e).V/W \quad (1)$$

was used. Where q_e*:* the amount of colorant adsorbed per unit weight of the adsorbent (mg/g), C_0: is the initial concentration of dye in the solution, C_e: is the dye concentration in the solution after adsorption (mg/L), *V*: the volume of the solution used (L), W: the amount of the adsorbent used (g).

The dye removal percentage can be calculated as follows:

$$\text{dye removal}(\%) = ((C_0 - C_e)/C_0).100 \quad (2)$$

Where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of the dye in the solution.

Adsorption isotherm models

The adsorption equilibrium data on the pollen of the dye were fitted to the Freundlich, Langmuir, Temkin, and Dubinin-Radushkevich(D-R) isotherms used commonly.

Freundlich isotherm

The Freundlich isotherm is used to describe the adsorption of various adsorbent molecules from the solution phase. The linear form of Freundlich isotherm is represented by the equation

$$q_e = K_F.\,C_e^{1/n} \quad (3)$$

to explain the adsorption from the solution [12].

Where C_e: is the concentration of the substance remaining in solution after adsorption (mg/L), q_e: is the amount of substance adsorbed on the unit adsorbent (mg/g), K_F: is the adsorption capacity, and *n*: is the adsorption density.

In the Freundlich isotherm equation, the expression

$$\log q_e = \log K_F + 1/n \log C_e \quad (4)$$

is obtained with the logarithm of both sides of the equation.

Freundlich's model expresses adsorption on heterogeneous surfaces, with the amount of adsorbed in equilibrium increasing as the pollutant concentration increases [13].

Langmuir isotherm

In the Langmuir model, the adsorbed molecules form a single layer on the surface of the adsorbent. In maximum adsorption, molecules attached to the adsorbent surface do not move and form a saturated layer. In this isotherm, the adsorbate increases linearly with the initial concentration. Langmuir model is expressed by the following equation:

$$1/q_e = 1/K_L.Q_M.1/C_e + 1/Q_M \quad (5)$$

The constant of dimensionless separation, R_L, defined by Webber and Chakkraverti to find the suitability of adsorption is calculated with the equation,

$$R_L : 1/1+K_L.C_o \quad (6)$$

This constant is expected to have values between 0 and 1. C_0 is the initial concentration of the substance in the solution [14].

Temkin isotherm

This isotherm takes into account the interactions between adsorbed substances. It was developed with consideration of the adsorbed heat of all molecules in the solution [15].

Temkin model

$$q_e = RT/b.\,Ln\,a_T + RT/b.\,C_e \quad (7)$$

$RT/b = K_T$ the equation

$$q_e = K_T lna_T + K_T C_e \text{ is obtained} \quad (8)$$

a_T: Toth constant (L/g), T: temperature (K), R: gas constant (J/molK). If q_e values are plotted against lnC_e, a_T and K_T constants are found directly.

Dubinin-Radushkevich equation

The characteristic D-R curve assumes the Gauss curve, which shows the volume distribution of micropores [16]. This isotherm is not based on a homogeneous surface or a constant absorption potential. It is used to describe the absorption processes in the same type of porous structures. In mathematical terms:

$$Lnq_e = lnQ'_M - k\varepsilon^2 \quad (9)$$

$$\varepsilon = RT.\,Ln\left(1+1/C_e\right) \quad (10)$$

Where C_e: concentration of the substance remaining in solution after adsorption (mg/L), q_e: the amount of substance adsorbed on the unit adsorbent (mg/g), ε: polany potential, k: DR isotherm constant, R: universal gas constant, and T: temperature (K). Ln q_e is plotted against ε, and the values k and Q_M are found.

Adsorption kinetic models

Different kinetic models determine the mechanism of adsorption and are used to determine which mechanism follows the adsorption of the dyestuff to the adsorbent surface. These fall into three categories: pseudo-first-order kinetic model, pseudo-second-order kinetic model, and intraparticle diffusion model.

Pseudo-first-degree kinetic model

The first-order kinetic model was developed by Lagergren:

$$Log\,\left(q_e - q_t\right) = log\,q_e - k_1/2.303.t \quad (11)$$

Where q_e (mg/g) is the amount of substance adsorbed at the time of equilibrium and q_t (mg/g) at any time, and k_1 is the adsorption rate constant [17].

Pseudo second-degree kinetic model

A Pseudo second-degree kinetic model was developed by Y. S. Ho:

$$t/q_t = 1/k_2 q_t^2 + 1/q_e t \quad (12)$$

Where k_2: model's rate constant (g/mg.min) for adsorption, q_e: the amount of substance adsorbed per gram (mg/g) at the time of equilibrium, and q_t: the amount of substance adsorbed per gram (mg/g) at any time [18].

Intraparticle diffusion model

It was developed by Weber and Morris and expressed as

$$q_t = k_1.t^{1/2} + C \quad (13)$$

Where k_1: is the intraparticle diffusion rate constant (mg/g.min) and C: is the thickness of the layer formed between the adsorbent and the adsorbate [19].

Adsorption thermodynamics

The enthalpy, entropy, and free energy changes for the adsorption process is determined with the help of the equilibrium constant. Thermodynamic parameters are expressed with the equations,

$$\Delta G^0 = -RTlnK_c \quad (14)$$

$$lnK_c = -\Delta H^0/RT + -\Delta S^0/R \quad (15)$$

Where ΔG^0: standard Gibbs free energy, ΔH^0: standard enthalpy, and ΔS^0: standard entropy. ΔH^0 and ΔS^0 are calculated from the slope and cut point of the 1/T graph against lnK_c, respectively [20].

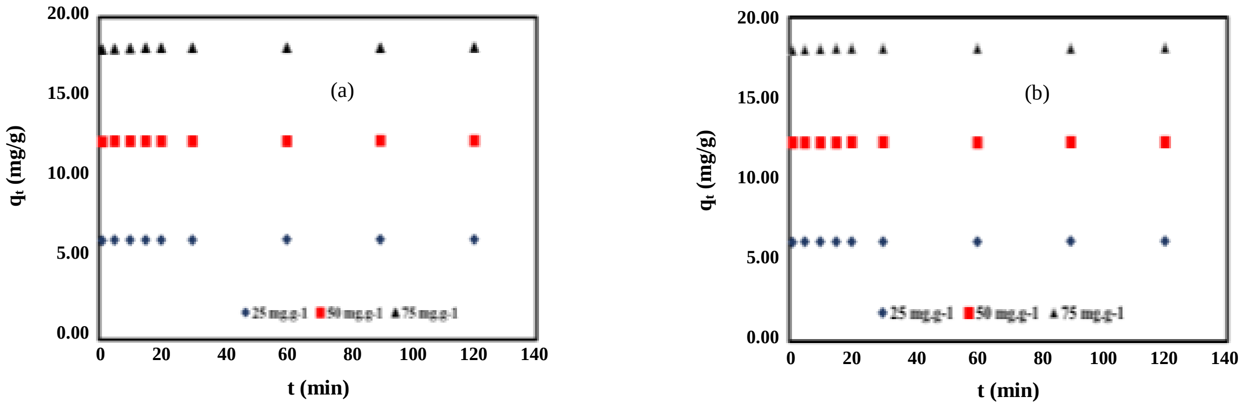


Fig. 1: (a) Effect of initial concentration on adsorption of BCB-ALD on willow tree pollen surface (T:25 ^{0}C, pH=6,46, w/v: 0,02 g (b) Effect of initial concentration on adsorption of AB-25 on willow tree pollen surface (T:25 ^{0}C, pH: 6,64, w/v: 0,02 g).

RESULTS AND DISCUSSION

Effect of contact time on removing dyestuffs from aqueous solution

It is the factor affecting the adsorption rate and amount. An increase in the amount of adsorption is expected as a result of the high surface area that was initially present by considering the relationship between adsorption and contact time. As time progresses, the adsorption rate should fall due to the low amount of adsorbent and the decreasing surface area. Increased contact time cause reduced adsorption The optimal value of contact time was found 90 min for examining pollen on textile dyes.

Effect of initial dye concentration on adsorption

In order to investigate adsorption percent in different conditions using the absorption spectrum of dyes, 25 mg/L of BCB-ALD was determined 89.3%, 90.64%, 97.84% at 25^{0}C, 45^{0}C, 65^{0}C, respectively. 25 mg/L of AB-25 was found 99.08 %, 99.56 %, 99.72 % in different temperatures at 25^{0}C, 45^{0}C, 65^{0}C, respectively. Maximum adsorption of BCB-ALD and AB-25 dyes for all concentrations were determined as 21.9 mg/g, 43.79 mg/g, and 66.50 mg/g at 20 minutes in Fig. 1. (a). In AB-25 dye, the same concentrations were found at 24.75 mg/g, 49.32 mg/g, and 72.55 mg/g at 20 minutes, respectively in Fig. 1 (b). Equilibrium has been achieved as a result of similar properties in adsorption at low concentrations and a high rate of removal in very short times. After these results, there is no significant change in the amount of adsorbed material. Therefore, it has been observed that the adsorption increases with increasing concentration. In the optimization steps of adsorbent concentration, the obtained value was 50 mg/L.

Freundlich Isotherm

The values of Freundlich constants and correlation coefficients (R^2) were given in Table 1. The values of K_F and n changed with the rising in temperature [21].

The correlation coefficient of suitability to Freundlich isotherms was evaluated according to R^2 results. Compliance was known to increase as the correlation coefficient approaches the value of 1 [22].

The value of n>1 represents a favorable adsorption condition or the range of 1 to 10 confirms the favorable condition for adsorption [23].

Finding Freundlich isotherm in region 4 was an indication that adsorption occurred at a low concentration. The increase in the amount of the substance adsorbed by concentration becomes evident at higher concentrations (Fig. 2-3).

Langmuir isotherm

Table 2 shows the correlation values of the lines drawn with dyestuff at different temperatures of the Langmuir constants q_m and *b*.

Since the correlation values for AB-25 were high, they were compatible with the Langmuir adsorption model. For BCB-ALD, it was found to be compatible at 318K in Fig. 4. Accordingly, adsorption for AB-25 occurred in specific homogeneous regions in Figure 5. It was partially realized

Table 1: Freundlich isotherm constant in the adsorption of BCB- ALD and AB- 25 on willow tree pollen at different temperatures.

	BCB-ALD			AB-25		
T(K)	298	318	338	298	318	338
K_F(mg/g)	2.47	3.28	8.34	2.30`	2.80	3.02
n	0.96	1.17	2.18	0.046	0.061	0.071
R^2	0.816	0.8355	0.9903	0.9298	0.9822	0.9695

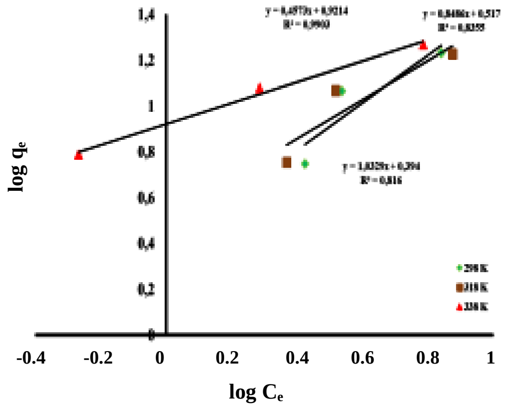


Fig. 2: Freundlich isoterhm of adsorption BCB-ALD of willow tree pollen (pH:6.46, w/v:0,02 g).

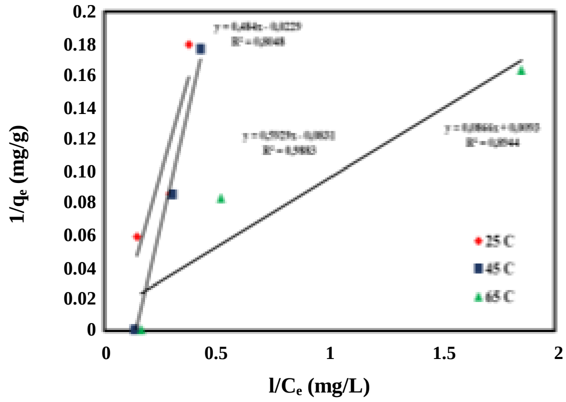


Fig. 4: Langmuir isotherm of adsorption BCB-ALD onto willow tree pollen at varios temperatures (pH:6.46, w/v:0.02 g).

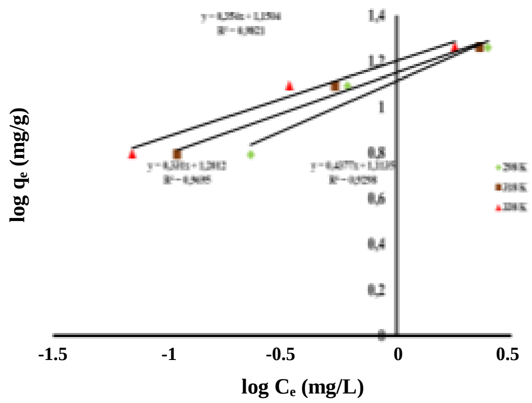


Fig. 3: Freundlich isotherm of adsorption AB-25 of willow tree pollen (pH:6.64, w/v:0,02 g)

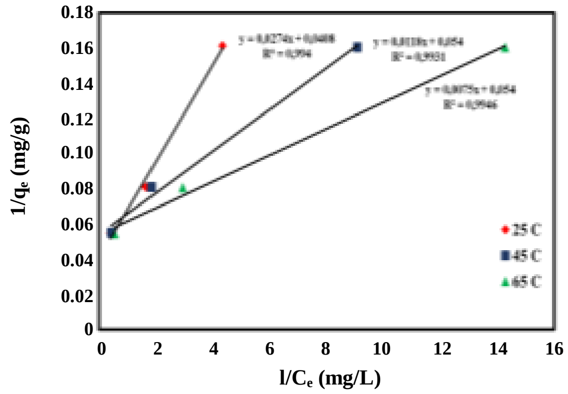


Fig. 5: Langmuir isotherm of adsorption AB-25 onto willow tree pollen at various temperatures (pH:6.64, w/v:0,02 g).

for BCB-ALD. In addition, it can be stated that all dyestuffs were covered in a single layer on the pollen surface [24-26]. The optimum temperature of BCB ALD and AB-25 dyes were found 65 ^{0}C for both of them. The high adsorbent temperature showed that these dyes were more suitable for this studying. It has been observed that the reaction rate increases as the temperature increases.

Temkin isotherm

Correlation values (R^2) with Temkin isotherm equilibrium binding constant A_T and Temkin isotherm constant b_T for both types of dyestuff were shown in Table 3.

Fig. 6 and Fig. 7 results were found compatible with Temkin at all three temperatures of both BCB-ALD and AB-25. Accordingly, it can be argued that the adsorption

Table 2: Langmuir isotherm constants in adsorption on BCB- ALD and AB- 25 on willow tree pollen at different.

	BCB-ALD			AB-25		
T(K)	298	318	338	298	318	338
b	2.06	1.741	1.54	0.671	0.218	0.138
q_m	21.27	7.57	9.34	36.49	84.74	133.3
R_L	0.019	0.052	0.042	0.056	0.1545	0.223
R^2	0.8048	0.9839	0.8944	0.994	0.9931	0.9946

Table 3: Temkin isotherm constant on willow tree pollen of BCB -ALD and AB-25 at different temperatures.

	BCB-ALD			AB-25		
T(K):	298	318	338	298	318	338
AT :	0.705	0.914	1.472	1.035	1.330	1.473
bT :	224	292	756	501	672	756
R2 :	0.9149	0.9268	0.9991	0.9849	0.9999	0.9991

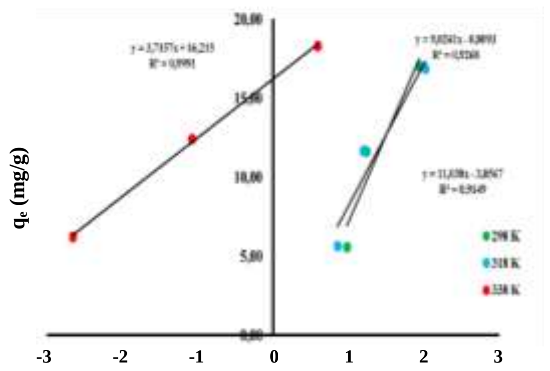


Fig. 6: Temkin isotherm in the adsorption of BCB-ALD onto willow tree pollen (pH:6,46, w/v:0,02 g).

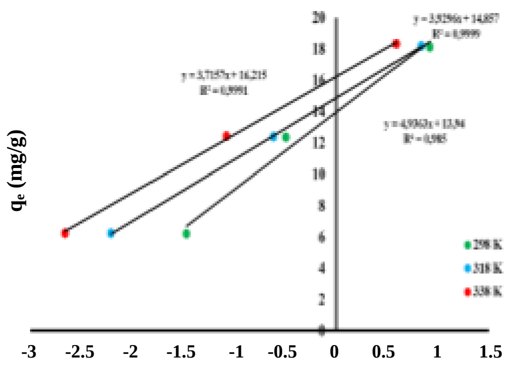


Fig. 7: Temkin isotherm in the adsorption of AB-25 onto willow tree pollen (pH:6,6, w/v:0,02 g).

the heat of all molecules in the layer decreases linearly as the surface is coated due to the interactions of adsorbent and adsorbate for both dyestuff types.

Dubinin-Radushkevich equation

It was found that the adsorption energy obtained from the D-R adsorption isotherm varied within the range of 2.07 kJ/mol (298K), 1.41 kJ/mol (318K), and 1.42 kJ/mol (338K) for BCB-ALD in Fig.8(a). Adsorption energy [ε] values for AB-25, on the other hand, were 3.46 kJ/mol (298K), 2.44 kJ/mol (318K), and 2 kJ/mol (338K) in Fig.8(b). The fact that these values were less than 8 kJ/mol was an indication of the relation between adsorption and physical interactions **[27].**

Kinetic examinations

For the interpretation of the kinetic batch experimental data three different kinetic models were used: (1) the pseudo-first-order kinetic model, (2) the pseudo-second-order kinetic model, and (3) the intraparticle diffusion model.

Table 5 shows that Low correlation values show that adsorption did not comply with the pseudo-first-order kinetic model. The qe values obtained in the equations are needed to be close to each other with the experimental qe values (Fig. 9-10) [28, 29]. qe values of BCB-ALD were calculated 5.58, 11.64 17.01 mg/g in the experimental part for different concentrations (25, 50, 75 mg/L, respectively) in Fig. 9. Fig. 10 showed that qe values were found 6.19,

Table 4: D-R isotherm constant on willow tree pollen of BCB -ALD and AB-25 at different temperatures.

	BCB-ALD				AB-25			
T(K)	K_{ads}(kJ^{-2} mol^{-2})	q_e (mg/g)	E (kJ/mol)	R^2	K_{ads}(kJ^{-2} mol^{-2})	q_e (mg/g)	E (kJ/mol)	R^2
298	2.15	2,83	2.07	0.9436	6.028	1.82	3.46	0.9969
318	1.006	2.45	1.41	0.9998	3.008	12.36	2.44	0.9654
338	1.007	2.48	1.42	0.9309	2.1	18.3	2	0.9436

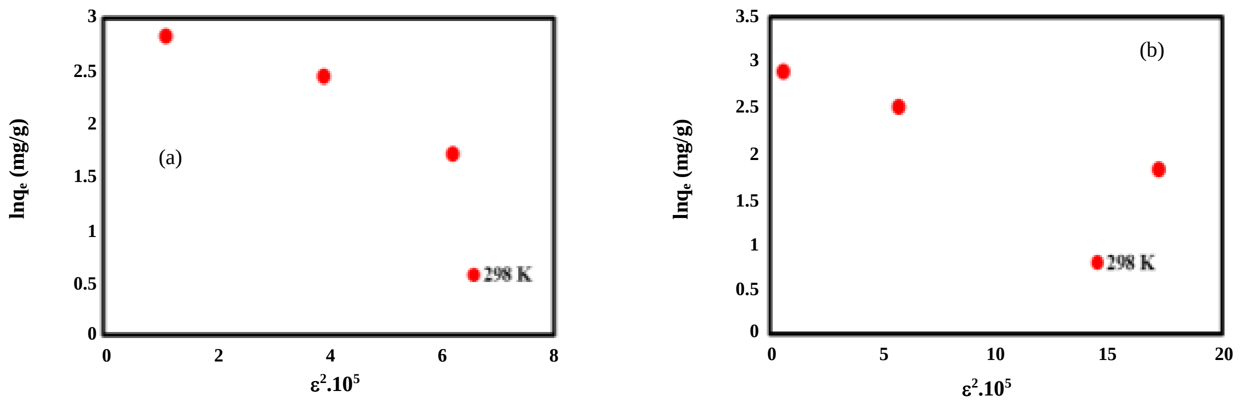


Fig. 8: (a) D-R isotherm for the adsorption BCB-ALD onto willow tree pollen at 298K. (b) D-R isotherm for the adsorption AB-25 onto willow tree pollen at 298K.

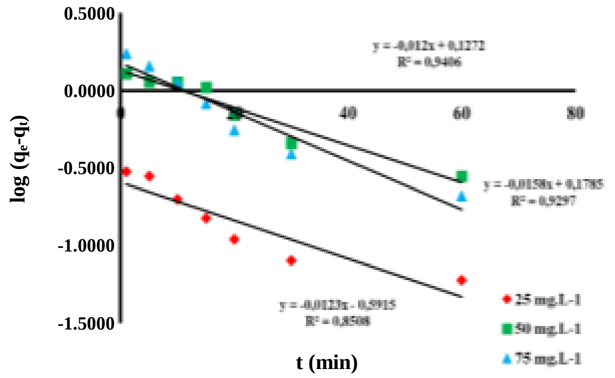


Fig. 9: Pseudo-first orders kinetics of BCB-ALD adsorption on willow tree pollen at different concentrations at 298K.

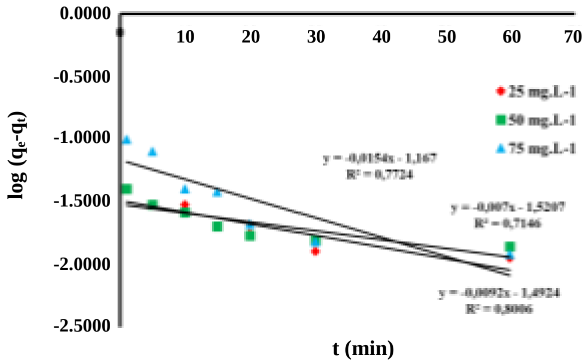


Fig. 10: Pseudo-first order kinetics of AB-25 adsorption on willow tree pollen at different concentrations at 298K.

12.34, 18.12 in experimental results for AB-25 concentrations of 25, 50, 75 mg/L, respectively.

Table 6 shows the kinetic lines and correlation values (R^2: 0.999-1) obtained for BCB-ALD and AB-25. As the qe values obtained in the equations are close to the experimental qe values, it is possible to conclude that the adsorption complied with the pseudo-second-order kinetic model. This indicates that chemical interaction with willow tree pollen is possible for both types of dyestuff [30-32]. The obtained results from the pseudo-second-order adsorption kinetic of BCB-ALD were compared to experimental and calculated results. These results were very close values for this equation. The experimental qe BCB-ALD values were 5.58, 11.64, 17.01, and calculated qe values were 5.62, 12.13, 17.01 in 25, 50, 75 mg/L, respectively in Fig. 11. Pseudo-second order adsorption kinetics of AB-25 were found very suitable results

Table 5: Pseudo-first order kinetic parameters of BCB -ALD adsorption onto willow tree pollen and AB-25 concentrations (T=298 K).

adsorbent	concentration mg.L^{-1}	experimental q_e mg/g	calculated q_e mg/g	k_1	R^2
BCB-ALD pollen	25	5.58	0.256	0.0283	0.9406
	50	11.64	1.340	0.0276	0.9297
	75	17.01	1.50	0.0363	0.8508
AB-25 pollen	25	6.19	0.0211	0.0211	0.8006
	50	12.34	0.0301	0.0161	0.714
	75	18.12	0.0345	0.0345	0.7724

Table-6: Pseudo-second order kinetic parameters of BCB- ALD adsorption onto willow tree pollen and AB-25 concentrations (T=298 K).

	concentration mg/L	experimental q_e	calculated q_e	k_1 (dk^{-1})	R^2
BCB-ALD	25	5.58	5.62	0.5156	0.9997
	50	11.64	12.13	0.0233	0.9997
	75	18.32	17.01	0.0859	0.9999
AB-25	25	6.19	5.92	0.5405	1
	50	12.34	12.36	1.7692	1
	75	18.12	16.89	4.3821	1

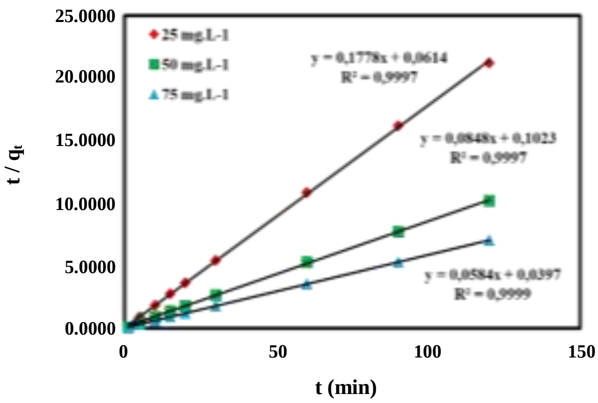


Fig. 11: Pseudo-second order adsorption kinetics of BCB-ALD onto willow tree pollen at different concentrations and at 298K.

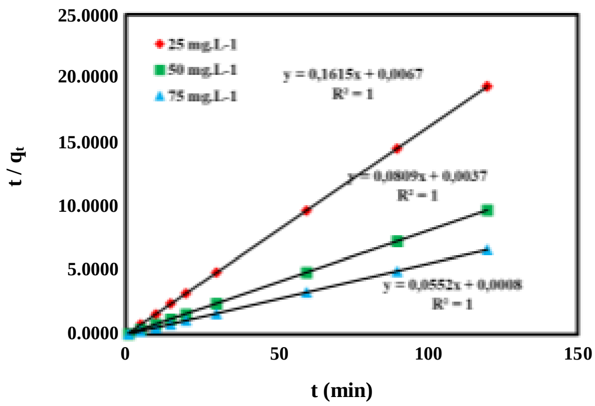


Fig. 12: Pseudo-second order adsorption kinetics of AB-25 onto willow tree pollen at different concentrations at 298 K.

for experimental and calculated qe values. Experimental and calculated qe results were 6.19, 12.34, 18.12 and 5.92, 12.36, 16,89 in different concentrations (in 25, 50, 75 mg/L), respectively in Fig. 12.

Intraparticle diffusion model

Graphics showing intraparticle diffusion kinetics drawn for both dyes were provided in Figs. 13 and 14. Correlation values and values calculated from the chart were given in table 7. [33].

Standard Gibbs free energy change ΔG^0 values of the dyestuff types BCB-ALD and AB-25 were found negative. Accordingly, adsorption processes by pollen for both types of dyestuff were considered to be spontaneous processes. As temperature increases, ΔG^0 decreases.

Standard enthalpy (ΔH^0) and standard entropy (ΔS^0)

Table 7: Intra-particle diffusion kinetic parameters of BCB -ALD adsorption onto willow tree pollen and AB-25 concentrations (T=298 K).

	BCB- ALD		AB- 25	
25 mg.L^{-1}	k_i =0,036	R^2 =0,9376	k_i : 0,0041	R^2 : 0,8534
50 mg.L^{-1}	k_i =0,1529	R^2 =0,9565	k_i : 0,0052	R^2 : 0,8293
75 mg.L^{-1}	k_i =0,1778	R^2 =0,8874	kİ : 0,0089	R^2 : 0,5638

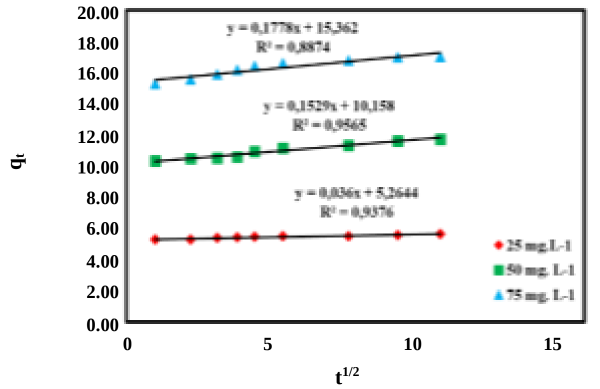


Fig. 13: Intraparticle diffusion drawings for BCB-ALD and willow tree pollen adsorption different concentration at 298 K.

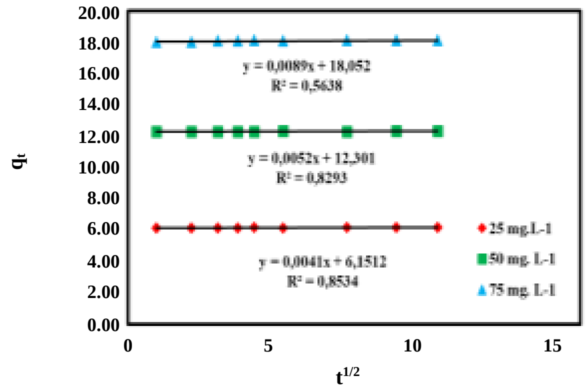


Fig. 14: Intraparticle diffusion drawings of AB-25 and willow tree pollen adsorption different concentration at 298 K.

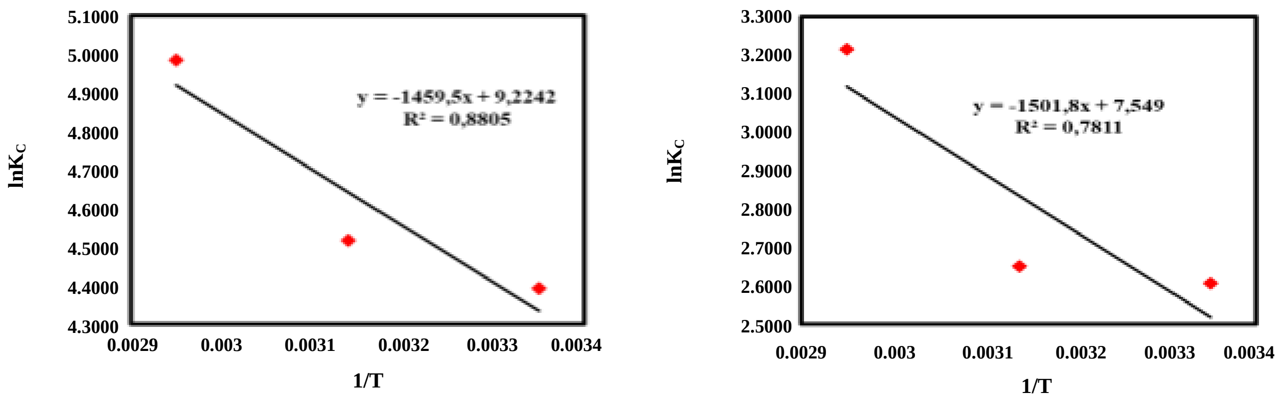


Fig. 15(a): Clausius-Clapeyron equation for the adsorption of BCB-ALD with willow tree pollen (Co: 50mg/L, pH=6.46) and (b). Clausius-Clapeyron equation for AB-25 adsorption with willow tree pollen (Co: 50 mg/L, pH=6.64).

values of the dyestuff BCB-ALD and AB-25 were positive. Positive enthalpy was indicative of endothermic adsorption. A positive ΔS^0 value indicates certain changes in the adsorbent surface [34, 35]. Low values of ΔS^0 for both types of dyestuff indicate a lack of any significant change in entropy.

In this study, we investigated the effect of dyes including BCB-ALD and AB-25 for adsorption on the pollen surface based on sample concentration, contact time, pH, and temperature. In the literature, equilibrium studies have been used for the adsorption of malachite green by Jordanian diatomite ores. In the phase of liquid adsorption, the results of several experimental factors, namely diatomite size of particles, pH, and initial concentration of MG were studied. Various isothermic equilibrium models have been used. Diatomite was observed to have a substantial impact on the adsorption process as a starting MG concentration, pH, and particle size. MG absorption

Table 8: Thermodynamic parameters of BCB-ALD (C0:50 mg/L, pH:6,46) and AB-25 (Co:50 mg/L, pH:6,64) of different temperatures.

BCB-ALD				
Tem.(^{0}C)	Kc	(ΔG^0(j.mol^{-1})	(ΔH^0(jmol^{-1}K^{-1})	(ΔS^0(jmol^{-1}K^{-1})
25	13.59	-6454.2		
45	14.15	-7005.1	12130	76.65
65	24.90	-9054.5		
AB-25				
Tem.(^{0}C)	Kc	(ΔG^0(j.mol^{-1})	(ΔH^0(jmol^{-1}K^{-1})	(ΔS^0(jmol^{-1}K^{-1})
25	80.96	-10886		
45	91.59	-11923	12479,3	62,76
65	146	-13768		

improved over the whole concentration spectrum from 99.3 mg/dm^3 to 898.7 mg/dm^3. The diatomite particle size decreased from 500-710 μm to 125-250 μm, which was accomplished by a high percentage of elimination from MG (99.6 percent). The ideal pH was = 9 for MG elimination [**36]**. Meanwhile, Methylene blue (MEB) removal performance was investigated from aqueous media in various pH conditions, contact time, and initial adsorbate concentrations. Activated Biochar rice husk (ARHB) with BET surface area and XRD have been characterized. The amorphous aspect of the pore size (cm/g) and pore surface area (m^2/g) of the BET surface plane was demonstrated by the XRD diffraction, respectively, by 9,369 and 27,32. The following order was seen as the best-fit model for the equilibrium isotherm dependent on the non-determination factor: Hill > Kiselev > Elovic > Floral-Huggins > Langmuir > Jovanovic > Harkin-Jura > Freundlich > Henry > Redlich Peterson > Durbinin-Kaganer Redushkevich > Hill – de Boer > Fowler – Guggenheim [**37]**. In another, the study of Bark biomass from Gmelina Arborea is a wood industry agricultural waste. Chemically-activated carbon was generated with carbon. Methyl violet was taken out of the watery process by batch adsorption using carbon. The results of the initial pH, the initial solution, or the adsorbent dosage were tested at a concentration of 28 ^{0}C. Experimental results suggest that the potential to adsorb balance improves as the concentration for time and initial solution rises but declines as adsorbent concentrations. For balance adsorption capability and initial solution concentration, adsorbent dose, and pH respectively, the optimum values were 106 mg g, 75 mg/L, 0.04 percent, and 10 for the parameters collected. The pH 8 was added due to its eco-friendly nature. The experimental evidence mainly complemented Dubinin-Radushkevich Isothermal and pseudo-second-order cinemas. The microporous adsorbent was. Both the Pleasant n and E values of Dubinin-Radushkevich indicate that the adsorption during a Temkin B is chemisorption [38]. In another study, Mango seeds (MGA) were used in the processing of activated carbon using a one-stage process with 62.27 % yield, 2.23 % ash content, 819.80 m^2/g The region of the CHN study has been calculated by 762mg / g of iodine, 52,31% C, 3,38% H and 1,02% N. FT-IR showed vibration extending N-H, C-H, C = C, and C-O. The first 15 minutes of agitation saw swift adsorptions of Alizarin and Fluorescein dyes at 86.90 % and 85.75 %, respectively. The adsorption balance was obtained in 90.44 % Alizarin coloring and 91.32 % Fluorescein coloring in 90 minutes of stirring. For pseudo-first order and pseudo-second order, the correlation coefficient, R^2 is 0.938 and 0.999. Data for alizarin and fluorescein dyes adsorbed on MGA equipped very close to unity and maximal adsorption constant qm 1,00 deep into the Langmuir isotherm with correlation coefficient (R^2) [**3]**. The other adsorption of acid black 1 study was examined by utilizing activated carbon prepared from scrap tires. The initial concentration of dye, pH, time of contact, and the adsorbent dosage have been tested. Scanning Electron Microscope (SEM) imagery along with Energy Dispersive Spectrometry (EDS) also studied the chemical composition and stable structure of the activated carbon. Apply Brunauer-Emmett-Teller (BET) isotherm was used for calculating surface areas. The Langmuir model was well-suited for experimental adsorption, and the optimum adsorption capability (Qm). The kinetic experiments have shown that AB1 adsorption is in line with a kinetic pseudo-second-order ($R^2 > 0.9999$) [40]. When the various methods were compared with our developed method, it was seen that The pollen that is used to adsorb BCB-ALD and AB-25 was found to be an effective adsorbent and to be used in the other dyestuff adsorption as an alternative adsorbent. In order to investigate adsorption percent in different conditions using absorption spectrum of dyes, 25 mg/L of BLC-ALD was determined 89.3%, 90.64%, 97.84% at 25 ^{0}C, 45 ^{0}C, 65 ^{0}C, respectively. 25 mg/L of AB-25 was found 99.08 %, 99.56 %, 99.72 % in different temperatures at 25 ^{0}C, 45 ^{0}C, 65 ^{0}C, respectively.

CONCLUSIONS

In this study, the adsorption of BCB-ALD and AB-25 dyes on the pollen surface was investigated. The effects of solution concentration, contact time, pH, and temperature on the removal of both dyestuffs in the aqueous environment were examined. When the effect of temperature on the adsorption of both dyes by pollen was examined, it was observed that the adsorption increased from the beginning and reached the maximum level in 90 minutes.

According to the isotherm examinations, it has been observed that it is suitable for the Frendlich isotherm model for AB-25. It was determined that the langmuir isotherm model for BCB-ALD is also compatible with 318 K and also for AB-25. Correlation values obtained for both dyestuffs were found to be compatible with the Temkin isotherm for AB-25 and partially suitable for BCB-ALD.

According to the kinetic studies, it was determined that the adsorption of BCB-ALD and AB-25 on the pollen surface was found appropriate for the pseudo-second-order kinetic model. Free energy change was found to be negative at all temperatures. Standard enthalpy and entropy were positive values.

As a result, it was deduced that the pollen used for the adsorption of BCB-ALD and AB-25 is a suitable adsorbent and can be used as an alternative adsorbent in the adsorption of other dyestuffs.

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