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RESEARCH ARTICLE

Adsorption of Acid Blue 25 on peach seed powder: Isotherm, kinetic and thermodynamic studies

Ali Rıza Kul[1], Adnan Aldemir[2,*], Hasan Elik[1]

[1]Van Yüzüncü Yıl University, Faculty of Science, Chemistry Department, 65080, Van, TURKEY
[2]Van Yüzüncü Yıl University, Faculty of Engineering, Chemical Engineering Department, 65080, Van, TURKEY

ABSTRACT

In the present study peach seed powder (PSP) was used as an adsorbent to remove Acid Blue 25 (AB25) a common basic dye, from aqueous solution. The adsorption experiments were carried out in a batch system and the effects of initial concentration, interaction time and temperature were investigated. The Langmuir, Freundlich and Temkin adsorption isotherms were used to model the equilibrium data. The kinetic parameters were determined by the pseudo first order (PFO), pseudo second order (PSO) and intra-particle diffusion (IPD) models. According to the results, the Freundlich isotherm model is a more convenient option compared with the Langmuir and Temkin models. The Freundlich model coefficients increased as the temperature increased, which shows that the adsorption process becomes more favorable with higher temperature. The experimental and calculated q_e values close to one another indicated that this process fits the PSO kinetic model with higher R^2 values than the other two models. Kinetic constants become closer to both the temperatures and initial concentrations and q_e values increases with the increasing concentration of AB25. The initial dye concentration increased from 25 to 150 mg L^{-1}, while the dye adsorption capacity onto PSP increased from 4.80 to 39.01 mg g^{-1}, from 5.57 to 44.27 mg g^{-1} and from 6.80 to 49.22 mg g^{-1} for 298, 308 and 323 K, respectively. The monolayer adsorption capacity (q_m) of PSP was determined to be 56.18, 64.94, 95.24 mg g^{-1} for 298, 308 and 323 K, respectively. Thermodynamic parameters for free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the separation process were determined as -1737,1 J mol^{-1}, 14.776 kJ mol^{-1} and 55,413 J mol^{-1}, respectively. The negative values of ΔG^o showed that this separation process was endothermic and natural. The results of the present study demonstrated that PSP can be used as an alternative material in dye removal.

Keywords: Peach seed powder, dye adsorption, isotherm models, kinetic constants, acid blue 25, thermodynamic parameters

1. INTRODUCTION

Dyes are chemical compounds which bond to surfaces or fabrics to change their colors. As they are complex organic molecules most dyes are resistant to many factors such as the effects of detergents. Dyes can be obtained from different sources and they are commonly used in many sectors [1–6]. These dyes used in ground water tracing for the determination of specific surface area of the activated sludge sewage and wastewater treatment as well [7-9]. The discharge of dyes, especially synthetic dyes into the hydrosphere causes a significant amount of pollution as a result of their recalcitrant nature. Their discharge will also result in an undesirable color in the water body leading to a decrease in sunlight penetration and resisting photochemical and biological attacks to aquatic life [10]. According to up-to-date data, more than 105 commercial dyes are produced at a rate of 7 × 105 tonnes $year^{-1}$ [11]. It is known that more than 10,000 tonnes of dyes used annually worldwide and around 100 tonnes $year^{-1}$ of dyes are released into the environment [12]. However, it is still unknown exactly how much dyes are discharged into the environment as a result of various processes. Nevertheless, the discharge of synthetic dyes has posed many challenges for environmental scientists. It has been reported that synthetic dyes have specifically caused allergies, dermatitis, skin irritations, cancer and mutations in humans [13]. Due to these harmful effects it has

Corresponding Author: adnanaldemir@yyu.edu.tr (Adnan Aldemir)
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become imperative to remove dyes from aqueous solutions.

There are various methods are used to remove dyes from wastewater [14-15]. Adsorption is an effective wastewater treatment process used to remove hazardous inorganic/organic pollutants that are present in the effluent [16]. Many textile industries utilize commercial activated carbon to treat dye waste. The aim of the present study was to create an alternative to activated carbon as a cost effective but potential adsorbent. Adsorbents obtained from natural materials, agricultural by-products, industrial wastes and biosorbents has been reported as a feasible option by many researchers [17]. These researchers applied types of physical or chemical treatments to various raw biomass adsorbents to improve their adsorption capacity [18].

Dyes can be divided into different groups and classes depending on their source, general structures and fiber type. Synthetic dyes can be categorized as: non-ionic dyes, cationic dyes and anionic dyes [19-20]. Acidic dyes have been commonly utilized for dyeing leather, silk, polyamide, wool, as well as in industries such as cosmetics, paper, food, and ink-jet printing. The main categories of the acidic dyes are anthraquinone, azo dyes, triphenyl methane, azine, xanthene, nitroso and nitro. Due to their fused aromatic rings, anthraquinone dyes are especially resistant to degradation. In addition, more care and attention must be given to their removal process [21]. AB25 an anthraquinone dye is widely used in detergents, wood, fur, wool, ink, silk, nylon, paper, biological stain and cosmetics. AB25 and other anthraquinone based dyes are resistant to degradation and preserves color for a longer period of time [22]. Due to their toxic effects, dyes have raised concerns relating to their use. They have been found to induce chromosomal fractures, carcinogenesis, mutagenesis and respiratory toxicity. In relation with these detrimental effects, it is extremely important to remove AB25 from aqueous solution [23]. Many adsorbents such as, activated carbon and unmodified and modified biosorbent species have been investigated for the adsorption of AB25 from aqueous solutions. However most of them were not found to be enough efficient [24].

Adsorption kinetics, thermodynamic and equilibrium data are required for the development of an effective design model for the removal of pollutants from aqueous solutions. The isotherm model is considered to be efficient as it provides information regarding the theoretical maximum adsorption capacity and possible interactions between the adsorbents and adsorbate. Various isotherm models including the Langmuir, Freundlich and Temkin models have been commonly used [25]. According to the Langmuir isotherm, all binding sites have equal affinity for the sorbate, which results in a monolayer of the adsorbed molecules [26]. Freundlich isotherm mainly describes adsorption onto heterogeneous surfaces which provide the adsorption sites of different affinities [27]. Temkin isotherm indicates the interaction of solute molecules in the aqueous phase with heterogeneous solid surface [25].

Kinetic studies are of great importance for the determination of the optimum conditions in full scale batch adsorption processes. Kinetic modeling provides information regarding adsorption mechanisms and possible rate controlling steps including mass transport or chemical reaction processes [28]. PFO, PSO and IPD models are the most prevalent kinetic models for explaining the adsorption mechanism [29].

Thermodynamic studies are carried out to determine the adsorption spontaneity, the nature of the adsorbent and adsorbate at equilibrium conditions. Through thermodynamics the temperature range in which adsorption will be favorable or unfavorable can be determined. The primary thermodynamic parameters are as follows; adsorption enthalpy (ΔH) and entropy (ΔS), change of Gibbs energy (ΔG). These parameters can be measured by fitting the data obtained by the adsorption experiments at different temperatures [30].

In the present study, the adsorption performance of peach seed powder (PSP) for AB25 was investigated. Various effective parameters including dye concentration and temperature were examined on the removal of AB25. This dye was selected as the adsorbate as it is one of the most widely used dyes. For this aim, kinetic studies using PFO, PSO and IPD models, isotherm studies using Langmuir, Freundlich and Temkin equations and thermodynamic studies were performed for the AB25 adsorption on PSP.

2. MATERIALS AND METHOD

2.1. Adsorbent (Peach seed powder)

The experiments were conducted with peach seed powder (PSP) from Prunus persica grown in the province of Van, in Turkey. The collected peach seeds were washed with deionized water several times and dried at room temperature for 24 h. The seeds were crushed by using a high-speed cutting machine and cut into small pieces in size. The obtained powder was sieved and particles below 150 µm were collected for the adsorption experiments.

2.2. Adsorbate (Acid Blue 25)

AB25 an acidic dye, was used as the adsorbate in this study. The formula of AB25 is $C_{20}H_{13}N_2NaO_5S$ and it has a molecular weight of 416.38 g mol^{-1}. The powdered dye was purchased from Merck Chemicals, dark blue in color and it was used without further purification. The required concentration of the solutions used in the adsorption process was prepared to the stock solution of AB25 with deionized water to obtain the suitable solution concentrations.

Sulfuric acid (H_2SO_4) 95-97%, A.R grade, sodium hydroxide (NaOH) pallets 98.5% A.R grade were purchased from Merck Chemicals. The other reagents were A.R. grade and used as received.

2.3. Adsorption experiments

In the batch experiments conducted in a temperature controlled water bath, 2 g PSP was treated with 500 mL of the dye solution. Different initial AB25

concentrations (25, 50, 75, 100, 125 and 150 mg L^{-1}) were used for 200 min while the pH was adjusted by adding H_2SO_4 or NaOH solutions (0.1 M). All experiments were conducted in triplicate under the same conditions which were applied for the 298, 308 and 323 K temperatures and the average values were taken to represent the result with all data being considered.

The concentration of MB in solution at a maximum absorption wavelength of 660 nm was evaluated by using UV/VIS spectrophotometer (PG Instruments Ltd, T80 model). A calibration curve was obtained by plotting among absorbance and certain concentrations of the solution. Unknown MB concentration was measured using a calibration curve. The dye adsorption capacity on the adsorbent was analyzed as:

$$q_e = \frac{C_0 - C_e}{W} V \quad (1)$$

where V is the solution volume (L), C_0 and C_e are initial and the equilibrium concentration of the dye (mg L^{-1}) respectively and W is the adsorbent mass (g). Finally, the data obtained from this study were confirmed by fitting in the isotherm, kinetic and thermodynamic relationships for the AB25 dye removal using PSP.

3. RESULTS & DISCUSSION

3.1. Effect of interaction time and initial dye concentrations on adsorption

Contact time is an important physical parameter used for plan and operating wastewater treatment plants. As seen in Fig 1-3, the removal of AB25 from the solutions was rapid at the initial period and the velocity at the final period that near the reach of the balance decreased. The surface of the adsorption process was large in the beginning, and thus the adsorption on this surface was fast. In the dye adsorption, the equilibrium time was determined as 120 min for AB25 removal from the solutions.

It can be seen from Fig 6-8 that the rise at the initial concentration of AB25 caused an increase in adsorption capacity for three temperatures, respectively. As the initial dye concentration increased from 25 to 150 mg L^{-1}, the adsorption capacity of the dye onto PSP increased from 4.80 to 39.01 mg g^{-1}, 5.57 to 44.27 mg g^{-1} and 6.80 to 49.22 mg g^{-1}, respectively. These results show that the initial concentration is an important parameter in the dye adsorption capacity and provides a driving force for the interaction between the PSP and AB25. Furthermore, an increase in the initial concentration induces an increase in the removal amount of the dye. Based on the experimental results the maximum dye adsorption rate was obtained with 150 mg L^{-1} initial dye concentration. In the present study, AB25 adsorption on PSP has similarity. Previously reported results from various researchers were available for AB25 adsorption on different adsorbents and biosorbents such as; rubber leaf powder [2], sepiolite [3], lychee peel waste [5], activated carbon [14], diatomite [16], cempedak peel [28], soya bean waste [29], tarap peel and water lettuce [30]. As a result of the comparison of the results of the present study with other studies in literature, the dye adsorption capacity of PSP was found to be good and PSP may be a novel material to be used as an inexpensive adsorbent for dye removal.

3.2. Adsorption isotherm studies

Various models were used to identify the dye adsorption on solid surfaces in this study. For the interaction between the adsorbate molecules and adsorbent surface investigations, three isotherm models (Freundlich, Langmuir and Temkin) were chosen to endeavor to simplify the interactions between dye and adsorbent in the present study. Three models were applicable for the descriptions of the experimental results obtained at three different temperatures. The parameters of these isotherm models were calculated by regression using the linear form of isotherm equations [1, 2].

The amount of AB25 adsorbed by per unit of adsorbent and the equilibrium concentrations for three temperatures are presented in Fig 4. The adsorption efficiency increased with increasing initial AB25 concentration.

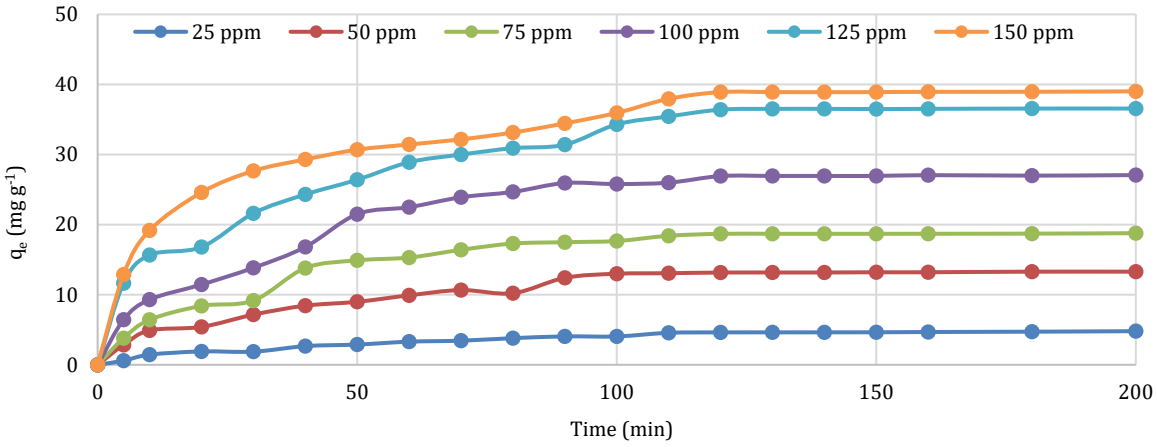

Fig 1. Effect of interaction time and initial concentration on AB25 removal at 298 K

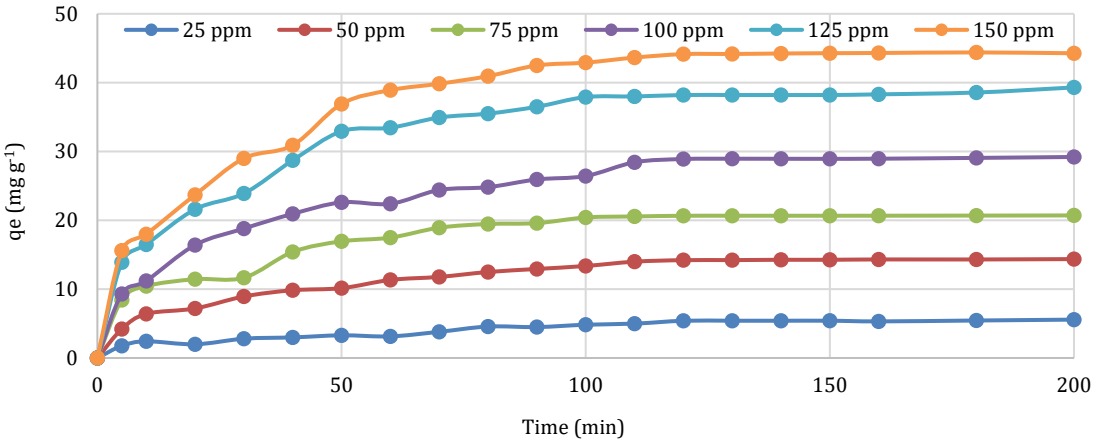

Fig 2. Effect of interaction time and initial concentration on AB25 removal at 308 K

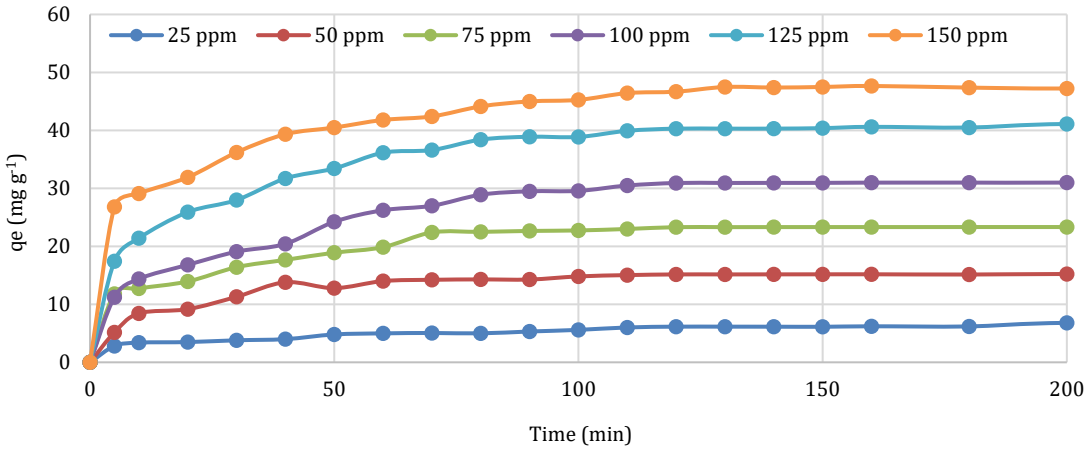

Fig 3. Effect of interaction time and initial concentration on AB25 removal at 323 K

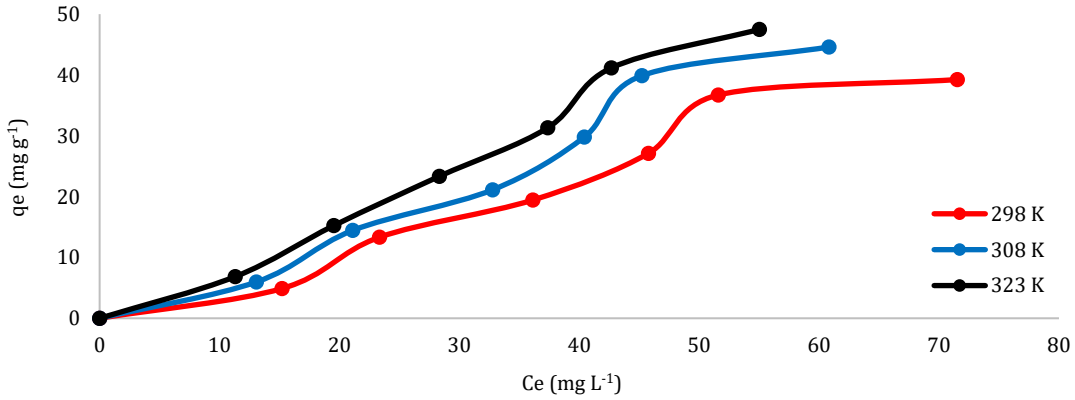

Fig 4. Adsorption isotherms for AB25 on the PSP for different temperatures

Langmuir isotherm has some assumptions for adsorption on a homogenous surface and no interaction between the adsorbates in the plane of the surface. The Langmuir isotherm equation is given with Eq. (2);

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

where q_{max} denotes the maximum capacity of adsorption (mg g^{-1}), C_e represents the equilibrium concentration of the solution (mg L^{-1}), K_L is a Langmuir constant associated with the affinity of the binding sites and energy of adsorption (L g^{-1}). The q_m and K_L values are determined from the slope and intercept of C_e/q_e versus C_e graph. The coefficients of determination R^2 of the Langmuir equation demonstrate that the adsorption onto PSP tracks and isotherm results of AB25 adsorption on PSP for 298, 308 and 323 K gives at Fig 5.

Freundlich isotherm which is an empirical model is based on adsorption on a heterogeneous surface and this isotherm equation is given with Eq. (3);

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \quad (3)$$

where K_F is a Freundlich constant linked to adsorption capacity (L g^{-1}), $1/n$ is an empirical parameter connected to adsorption intensity. The K_F and n values were determined from the intercept and slope of the plot between lnq_e against lnC_e, respectively. The Freundlich isotherm results of AB25 adsorption on PSP for 298, 308 and 323 K are given at Fig 6.

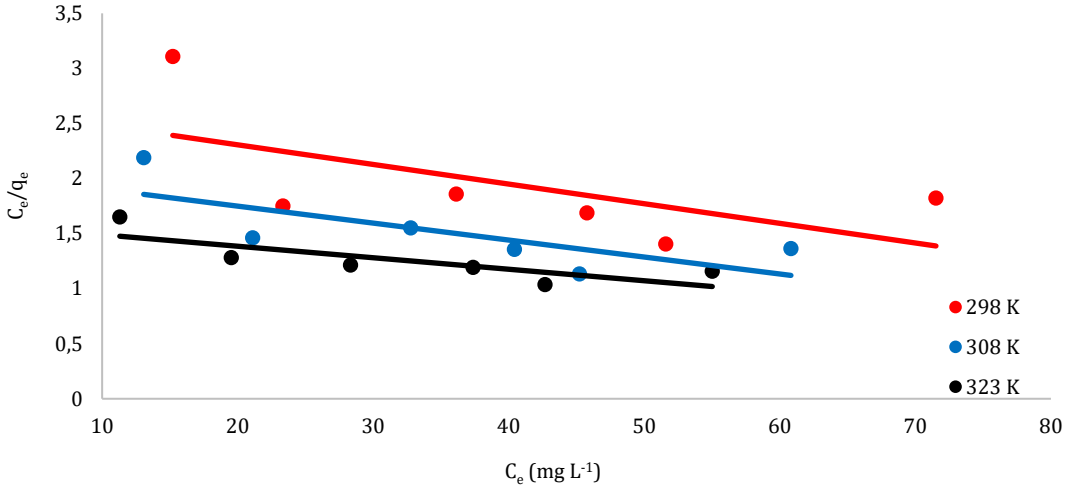

Fig 5. Langmuir isotherms of AB25 adsorption on PSP for different temperatures

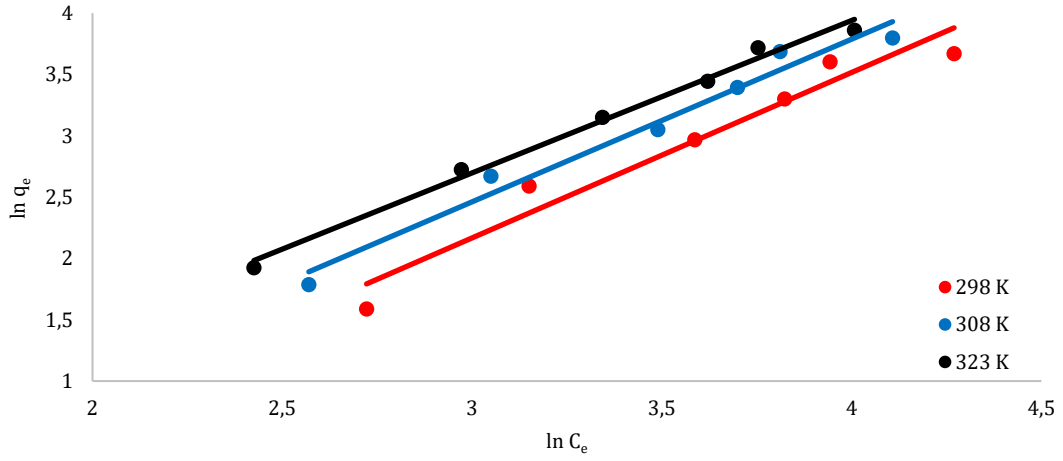

Fig 6. Freundlich isotherms of AB25 adsorption on PSP for different temperatures

Temkin isotherm refers to the interaction of solute molecule from aqueous phase with heterogeneous solid surface. This isotherm is based on the concept that the heat of adsorption decreases on the covering of solid surface. Temkin equation used to calculate the isotherm parameters is given with Eq. (4);

$$q_e = \frac{RT}{b_T} lnK_T + \frac{RT}{b_T} lnC_e \quad (4)$$

where K_T and b_T are related to the binding energy and heat of adsorption, respectively and can be obtained from the slope and intercept of q_e versus lnC_e plot. Temkin isotherm results of AB25 adsorption on PSP for 298, 308 and 323 K are given in Fig 7.

The calculated parameters of the Langmuir, Freundlich and Temkin isotherms for the adsorption of AB25 on PSP are presented in Table 1. Regarding the coefficients determined, the Freundlich model is more fitting than the Langmuir and Temkin models. It should be noted that the K_F and n values increased as the temperature increased and the adsorption is approving at higher temperatures. The R^2 values of these three isotherm models were high, while the R^2 values of the Temkin model were higher than the other model values for PSP. The monolayer adsorption capacity (q_m) of PSP was determined to be 56.18, 64.94, 95.24 mg g^{-1} for 298, 308 and 323 K, respectively. The maximum adsorption capacity (q_m) was calculated with the Langmuir isotherm model for different adsorbents towards AB25 given in Table 2, and different adsorbents such as agricultural, industrial wastes towards AB25 were given in [3, 4].

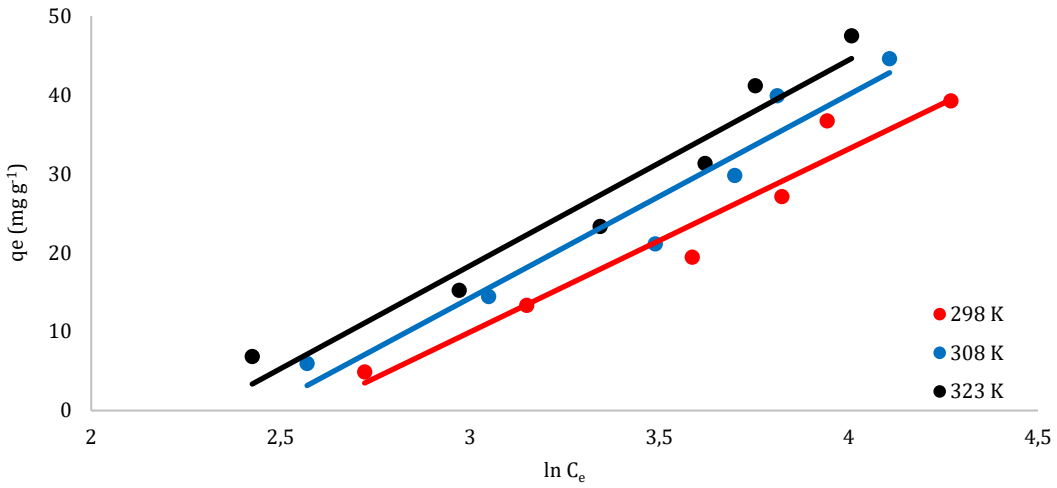

Fig 7. Temkin isotherms of AB25 adsorption on PSP for different temperatures

Table 1. Isotherm model parameters of AB25 adsorption on PSP at different temperatures

Temp	Langmuir			Freundlich			Temkin		
(K)	KL (L g^{-1})	q_m (mg g^{-1})	R^2	KF (L g^{-1})	n	R^2	KT (L g^{-1})	bT (J mol^{-1})	R^2
298	0,0668	56,179	0,371	0,1526	0,7413	0,947	0,0764	106,787	0,908
308	0,0748	64,935	0,537	0,2193	0,7541	0,973	0,0865	99,333	0,934
323	0,0658	95,238	0,631	0,3565	0,8046	0,991	0,1006	103.000	0,948

Table 2. Maximum adsorption capacity of AB25 on various adsorbents

Adsorbent	q_m (mg g^{-1})	References
Rubber leaf powder	28.09	[2]
Natural sepiolite	56.53	[3]
Shorea dasyphylla sawdust	24.39	[4]
Ficus racemosa dead leaves	83.33	[6]
Egg shell modified activated carbon	109.80	[14]
Soya bean waste	38.30	[29]
Azolla pinnata	50.50	[29]
Hazelnut shell	60.21	[31]
Sawdust walnut	36.98	[31]
Sawdust cherry	31.98	[31]
Sawdust oak	27.85	[31]
Sawdust pitch pine	26.19	[31]
Peach seed powder	95.24	This work

3.3. Temperature and adsorption thermodynamics

The effect of the temperature on AB25 adsorption was investigated through the experiments performed with three different temperatures and the results showed that dye adsorption capacity increased with an increase in temperature. This decrease was a result of the escaping of the adsorbed AB25 ions on getting higher temperature or energy, which indicated the physical nature of the adsorption. Thermodynamic investigation is necessary in determining the importance of adsorption process. Thermodynamic parameters such as free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) are significant in detecting heat alteration in the adsorption process for the dye and PSP [9]. These parameters are calculated by the equations given below;

$$K_C = \frac{C_{Ads}}{C_e} \quad (5)$$

$$\Delta G^{\circ} = -RTlnK_C \quad (6)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (7)$$

$$lnK_C = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (8)$$

where, K_c is the equilibrium constant, C_{Ads} is the dye amount adsorbed on the PSP per litter of the solution at equilibrium, the adsorbent of adsorbent per unit litter of the solution. Furthermore, C_e represents the equilibrium concentration of the dye in the solution. R and T represent the universal gas constant (8.314 J mol^{-1} K) and temperature, respectively. The parameters of $\Delta H°$ and $\Delta S°$ are analyzed from the slope and intercept of the natural plot logarithm of K_c versus $1/T$. From the graphical representation according to Equation (8), namely lnK_c vs. $1/T$, a straight line is obtained in Fig 8. The thermodynamic parameters were presented in Table 3.

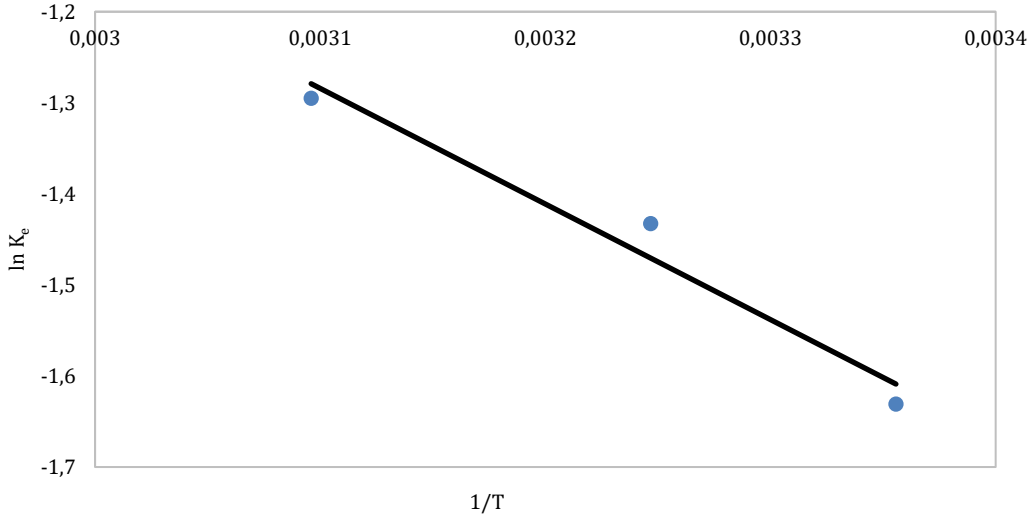

Fig 8. Plots ln K_c versus 1/T for AB25 adsorption on PSP

The thermodynamic parameters of AB25 adsorption onto PSP are calculated with Equations 5-8. The free energy values of AB25 onto PSP were obtained as -1.358, -1.579 and -2.019 kJ mol^{-1} for the temperatures of 298, 308 and 323K, respectively. The enthalpy and entropy values of AB25 adsorption onto PSP were found as 5.211 kJ mol^{-1} and 22.047 kJ mol^{-1} K^{-1} respectively. The negative ΔG° values show that the adsorption was physisorption and ΔG° suggest the feasibility and the spontaneous nature of the adsorption. The absolute values of $\Delta G°$ decreased with the increase in temperature which shows that this separation process was constructive at low temperatures. The positive $\Delta H°$ value shows that the adsorption process was endothermic and the positive $\Delta S°$ value developed the enhanced randomness at the solid–solute interface and the affinity of the PSP for AB25.

Table 3. Thermodynamic parameters of AB25 adsorption on PSP

Temp (K)	K_c	ΔG° (J mol^{-1})	ΔH° (J mol^{-1})	ΔS° (J mol^{-1} K^{-1})	R^2
298	1.731	-1358.561			
308	1.853	-1579.031	5211.464	22.047	0.962
323	2.097	-2019.973			

3.4. Adsorption Kinetic Studies

Kinetic models were performed to check the experimental results of the adsorbates adsorption onto the adsorbents. The dyes adsorption kinetics is significant in choosing the most suitable test circumstances for the adsorption process with the batch technique. The useful kinetic parameters for the estimation of adsorption rate, provide vital knowledge for designing and modeling the adsorption processes [10]. In the present study, the AB25 kinetics was calculated using three kinetic models, namely PFO, PSO and IPD. The well-suited model was chosen depending on the linear regression coefficient of the correlation coefficients of R^2 values. These models were examined in accordance with the experimental data at varied temperatures and initial AB25 concentrations.

The PFO kinetic model is used to separate the kinetics equation depending on the concentration of solution and solid adsorption capacity. This kinetic model can be the first to be used for the characterization of the liquid-solid adsorption systems depending on solid capacity. This model is utilized for the analysis of sorption in liquid-solid systems which states that the number of unoccupied adsorptive sites determines the adsorption rate [4]. The PFO kinetic model is given with Equation (9);

$$\ln(q_e - q_t) = lnq_e - k_1 t \quad (9)$$

where the q_t and q_m (mg g^{-1}) values are adsorption capacities at time t and equilibrium, respectively. k_1 (min^{-1}) is the rate constant of the PFO adsorption. To achieve the constants of the model, the straight line plots of $ln(q_e-q_t)$ against t are drawn. The constants are detected from the slope and intercept of the plot.

Table 4. PFO, PSO and IPD kinetic model parameters of AB25 adsorption on PSP

	T (K)		25 (mg L^{-1})	50 (mg L^{-1})	75 (mg L^{-1})	100 (mg L^{-1})	125 (mg L^{-1})	150 (mg L^{-1})
	298	$q_{e\ exp}$(mg g^{-1})	4,894	13,331	19,438	27,117	36,707	39,241
	308	$q_{e\ exp}$(mg g^{-1})	5,967	14,447	21,117	29,792	39,891	44,591
	323	$q_{e\ exp}$(mg g^{-1})	6,848	15,237	23,337	31,317	41,164	47,493
PFO kinetic model	298	k_1(min^{-1})	0.0216	0.0311	0.0292	0.0345	0.0325	0.0285
		$q_{e\ cal}$ (mg g^{-1})	4.818	15.365	13.274	29.931	40.658	33.188
		R^2	0.9711	0.9552	0.9168	0.9578	0.9257	0.9151
	308	k_1(min^{-1})	0.0139	0.0278	0.0221	0.0209	0.0189	0.0295
		$q_{e\ cal}$ (mg g^{-1})	4.858	13.339	12.395	21.639	22.603	33.623
		R^2	0.9401	0.9651	0.9037	0.9437	0.9273	0.9515
	323	k_1(min^{-1})	0.0161	0.0355	0.0496	0.0265	0.0262	0.0274
		$q_{e\ cal}$ (mg g^{-1})	5.355	11.698	29.847	22.991	27.924	30.277
		R^2	0.8219	0.9351	0.9521	0.9383	0.9494	0.9637
PSO kinetic model	298	k_2(min^{-1})	0.0052	0.0029	0.0023	0.0017	0.0014	0.0017
		$q_{e\ cal}$ (mg g^{-1})	5.612	14.925	21.0970.	30.030	40.000	41.667
		R^2	0.9876	0.9946	9901	0.9985	0.9907	0.9944
	308	k_2(min^{-1})	0.0043	0.00371	0.00352	0.001931.7	0.0019	0.0016
		$q_{e\ cal}$ (mg g^{-1})	6.557	5.625	2.2720.9	46	41.667	47.619
		R^2	0.9838	0.9929	945	0.9943	0.9966	0.9956
	323	k2(min-1)	0.0068	0.0075	0.00452	0.0022	0.0023	0.0024
		qe cal (mg/g)	7.097	15.8980.	4.509	33.4450.99	42.918	49.751
		R^2	0.9846	9982	0.9967	43	0.9979	0.9984
IPD kinetic model	298	k_{id}(mg g^{-1} $min^{-0.5}$)	0.3453	0.9021	1.2673	1.8136	2.3055	2.2388
		C (mg g^{-1})	0.3705	2.1221	3.4799	5.0379	8.0755	11.526
		R^2	0.9304	0.8919	0.8602	0.8576	0.8882	0.8416
	308	k_{id}(mg $g^{-1}min^{-0.5}$)	0.3723	0.8938	1.2125	1.7907	2.2896	2.6772
		C (mg g^{-1})	0.7421	3.3477	6.2109	7.1607	11.409	12.276
		R^2	0.9356	0.8811	0.8252	0.8754	0.8162	0.8283
	323	k_{id}(mg g^{-1} $min^{-0.5}$)	0.3723	0.8292	1.2494	1.8681	2.2252	2.3386
		C (mg g^{-1})	1.6882	5.4353	8.4852	8.4515	14.113	19.667
		R^2	0.9034	0.7475	0.7795	0.8481	0.7985	0.7476

The PSO kinetic model explained with the chemical bond formation between the adsorptive site and solute molecule is the rate-limiting step based on adsorption capacity given with Equation (10);

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where k_2 is the rate of adsorption (g mg^{-1} min^{-1}), q_m denotes the amount of adsorbate which is adsorbed onto the adsorbent at equilibrium (mg g^{-1}) and q_t represents the amount of dye adsorbed at any time (mg g^{-1}). The plot of t/q_t vs. t has a linear link. The values of k_2 and equilibrium adsorption capacity q_e were identified from the intercept and slope of the plot of t/q_t versus t in accordance with Equation (10);

The adsorption process was slower when intra-particle diffusion (IPD) chosen as the rate controlling step. According to this model the chemical or physical bond between the solute and solid at the interspatial sites of solid control the overall speed of the adsorption. The IPD model equation was proposed by Weber and Morris and was conducted by testing the possibility of IPD as the rate-limiting step using model, which can be represented by Equation (11);

$$q_t = k_{ipd} t^{0,5} + C \quad (11)$$

where k_{ipd} (mg g^{-1} min$^{-1/2}$) is the IPD rate constant and C gives information regarding on the boundary thickness. A plot of q_t against $t^{0.5}$ at different AB25 concentrations gave two phases of linear plots [3].

The PFO, PSO and IPD kinetic model parameters of AB25 adsorption on PSP are given in Table 4. The experimental results indicated that R^2 coefficients were higher than 0.99. The experimental and analyzed q_e values were very close to each other which shows that this process fits the PSO kinetic model. The PSO model is generally preferred for the kinetic adsorption data for most dye adsorption systems.

The experimental and calculated q_e values of 323 K were higher than the 298K and 308K values. According to these tables, it is clear that the q_e values increased with the increasing concentration of AB25. When the kinetic constants were compared, it was seen that the constant values were closer to both temperatures and concentrations for the PSO model [11]. This result showed that AB25 adsorption kinetics on PSP results from PSO and suggested that the rate-limiting step can be the dye chemisorption.

4. CONCLUSIONS

The AB25 adsorption on PSP was examined at different experimental conditions. When the initial AB25 concentration increased from 25 to 150 mg L^{-1}, the adsorption capacity onto PSP increased from 4.80 to 39.01 mg g^{-1}, 5.57 to 44.27 mg g^{-1}and 6.80 to 49.22 mg g^{-1} for 298, 308 and 323 K, respectively. The equilibrium adsorption time was determined as 120 min for dye removal. The isotherm studies demonstrated that the Freundlich model can be considered as a more favorable option for AB25 adsorption on PSP compared to the Langmuir and Temkin models. The monolayer adsorption capacity (q_m) of PSP was determined to be 56.18, 64.94, 95.24 mg g^{-1} for 298, 308 and 323 K, respectively. According to the kinetic studies the adsorption of the AB25 process followed the PSO and suggested that the rate-limiting step could be the dye chemisorption. R^2 coefficients were higher than 0.99 and the evaluated qe values were very close to each other. The kinetic constants for three models were closer to both temperatures and concentrations and q_e values increased with the increasing concentration of AB25. The thermodynamic parameters demonstrated that AB25 adsorption onto PSP was endothermic. The negative $\Delta G°$ values indicated that the adsorption was physisorption and $\Delta G°$ suggested the feasibility and spontaneous nature of the adsorption. All of these results indicated that PSP could be used as a potential adsorbent in removing acidic dyes in wastewaters.

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