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Adsorption Of Safranin From Wastewater Using Pinecone Powder

Ali Savran[1], Ali Rıza Kul[1], Veysel Benek[2]
[1]*Chemistry Department, Science Faculty,University Of Van YYU, Turkey*
[2]*Ministry Of National Education, Vakıfbank Secondary School, Turkey*

Abstract:
This study is aimed to investigate and to develop a low-cost adsorption method to remove the safranin dye from wastewater by using pine cone powders (PCP) as an adsorbent. In this method used for the removal of safranin, parameters such as adsorbate concentration, temperature, contact time at specific pH, particle size and adsorbent dose were investigated. Dye adsorption on PCP was evaluated by considering Langmuir, Freundlich, Temkin and DKR adsorption isotherm models. Various thermodynamic parameters were calculated to evaluate the adsorption processes. Adsorption kinetics were tested with pseudo-first order, pseudo- second order and intraparticle diffusion methods.

Keywords: *Adsorption, kinetic, isotherms, pinecone, Safranin*

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I. Introduction

Dyes have been widely used in many industrial areas such as textile, rubber, plastic, leather dyeing, cosmetics, paper, medicine, agriculture, food technology, hair coloring, ink production, photoelectrochemical cells [Tkaczyk et al, 2020; Al-Quodah et al, 2007]. Since most of the dyes are toxic, their mixing with water is extremely harmful to human health, the flora of the waters they are in and the living creatures living in the water [Al-Quodah et al, 2007]. Exposure to dyes for a long time can cause skin irritation, respiratory, neurological diseases, genetic changes, and effects that increase the risk of cancer [Ahmet and Dhedan, 2021, Amirza et al, 2017]. Therefore, it is extremely important to search for suitable methods to remove dyes from wastewater. There are many methods to remove dyes from wastewater, including coagulation [Shi et al, 2007], membrane separation [Zhao et al. 2021], adsorption [Yagub et al. 2014], oxidation processes [Nidheessh et al. 2018], solvent extraction [Pandit and Basu, 2004], electrochemical processes [Faouzi et al, 2007], photocatalytic degradation [Chiu et al, 2019], biodegradation [Telke et al, 2010]. Among these methods, adsorption technique; it stands out due to its simplicity, low cost, environmental friendliness and regeneration possibility of the adsorbent [El Maguana et al, 2018].

Safranin is one of the oldest well-known synthetic cationic dyes [Dutta et al., 2020]. This dye, whose molecular formula is $C_{20}H_{19}N_4Cl$, is also called basic red 2 and safranin O [Bhateria and Singh, 2019]. This dye, which dissolves well in water, is used in the food industry such as flavouring and colouring of candies and cookies, in the production of sugar and confectionery [Gupta et al, 2006]. This dye is also used in the textile industry to dye different materials such as paper, cotton, silk, wool, leather and cloth [Gupta et al, 2006]. Exposure to these effluents may be irritating to respiratory systems, skin, and digestive tract infections when ingested [Gubta et al, .2006].

Pine tree cones are produced in large quantities at forest industries as a litter. Utilization of these cones has been limited to domestic fuel in some rural areas, extraction of essential oils for therapeutic purposes when they are still unripe, and on seasonal decoration [Fernandez et al, 2010]. Pine cones are mainly composed of cellulose, hemicellulose, and lignin, which have functional groups such as carbonyl (ketone), carboxyl, sulfhydryl (thiol), sulfonate, thioether, amine, alcohols, and esters that can bind heavy metals. Moreover, the cones have excellent physicochemical properties, including water retention, swelling capacity, and mechanical strength, that make them particularly suitable for use as an adsorbent [Altundoğan et al, 2016]. Pine cone has been used as adsorbent in the removal of textile dye [Mahmoodi et al, 2011]. The natural pine cone adsorbent has also been used in the adsorption of cationic dyes such as methylene blue [Dawood and Sen, 2012, Yagub et al, 2011, Elmourbaki et al, 2016i Aldemir et al, 2019], and anionic dyes such as Congo red[Sen et al, 2011].

In the present work, Pine cone powder (PCP) was used as an agricultural natural adsorbent to remove safranin from aqueous solution. Effective parameters such as dye concentration, contact time and temperature were investigated on dye removal. Kinetic, isotherm and thermodynamic studies were conducted to evaluate the adsorption of PCP.

II. Materials And Methods

Dye characterization

Safranin was chosen for this study because of its known strong adsorptive compound onto materials. Safranin (chemical formula: $C_{20}H_{19}ClN_4$; molecular weight =355.85 g/mol; maximum wavelength = 520 nm) supplied by Merck was used as adsorbate and was not purified prior to use. A stock solution of safranin of 1000 mg/L was prepared, which was diluted to the required initial concentrations. Other chemicals were obtained from Merck.

Pine Cone Powder (PCP)

Adsorption processes were carried out using PCP obtained from *pinus slyvertis* growing from the campus area of Van Yüzüncü Yıl University in Van, Turkey. Pine cones were washed with distilled water to remove contamination and dried at 65 ^{o}C for 48 hours to remove water. After the pine cones were ground in the mill and pulverized in a mortar, they were passed through a 230 mesh sieve. The prepared PCP adsorbent was preserved in plastic containers to be used in the experiments. In order to characterize the raw adsorbent, the specific surface area was determined, the FTIR spectrum was taken for functional groups, XRD analysis was performed, XRF for elemental composition and SEM data for surface morphology were obtained [Aldemir et al, 2023].

Adsorption Procedure

The stock solution of safranin (1000 mg/L) was prepared and suitably diluted to the required initial concentrations (25–125 mg/L). The experiment were carried out in 1500 mL beaker containing 1000 mL of synthetic dye solution. The effect of the contact time on the amount dye adsorbed was investigated at different initial concentration of dye (25, 50, 75, 100 and 125 mg/L) at different temperatures (298 K, 308 K and 318 K). 2.5 g PCP were mixed with 1000 mL dye solutions at different concentrations, at pH 7 and desired temperatures at 150 rpm for specific time intervals. At the end of the adsorption process, the solution was centrifuged for 10 min at 3000 rpm. After centrifugation, the dye concentration in the supernatant solution was analyzed using a UV spectrophotometer (T80+ UV/Vis) by monitoring the absorbance changes at a wavelength of maximum absorbance (520 nm).

The amount of equilibrium adsorption q_e (mg/g) was calculated using the formula:

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

The dye removal percantage can be calculated as follows:

(2)

here q_e is the amount adsorbed per gram of adsorbent, C_e is the equilibrium concentration of dye (mg/L), C_0 is initial concentration W is mass of adsorbent (g) and V is volume of solutions.

III. Results And Discussion

Effect of contact time and safranin dye concentration

In the study on the adsorption of safranin on the PCP adsorbent, the values at which the adsorption process came to equilibrium were determined. Adsorption experiments related to the determination of the contact time in the adsorption of safranin on the adsorbent used in this study were carried out at an initial concentration of 25-125 mg/L at 45°C for 320 minutes. Determination of contact time in adsorption processes is required for the determination of data used in adsorption isotherms. This time information is extremely useful in determining the adsorption type and maximum adsorption capacity [Miyah et al, 2015] . The results in Figure 1 show that the adsorbed amount of safranin increased rapidly in the first 160 min, and the amount of adsorbed material remained constant in the following minutes, indicating that the equilibrium state was formed. From these results, it is determined that the equilibrium in adsorption on the solid surface is achieved in 160 min. It is observed from the graph that the initial concentration does not have a significant effect on the equilibrium time. As the initial concentration increases, the amount of adsorbed material also increases. This can be explained by the increase in the number of molecules interacting with the adsorbent surface with increasing concentration.

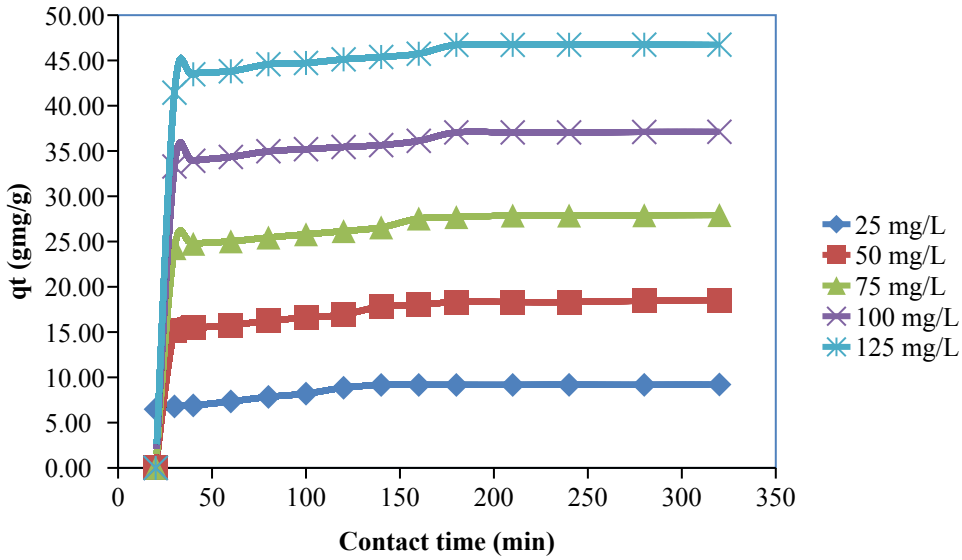

Figure 1 Effect of contact time and safranin dye concentration. PCP dose 2.5 g/L, pH =7 T=45 °C, agitation speed 150 rpm.

Effect of temperature

The variation of the adsorption process with temperature is extremely important as it will contribute to our idea of whether this event is exothermic or endothermic. In this study, the effect of temperature on safarin adsorption on PCP was measured between 25-45 °C and the results are given in figure 2. In the study, it is determined that the adsorption process is endothermic, since the amount of substance adsorbed with temperature increases. The increase in adsorption with temperature can be explained by the increase in the number of binding sites of dye molecules on the adsorbent surface [Singh et al, 2011]. Since the viscosity of the solution decreases with the increase in temperature, it can also be explained by the increase in the diffusion rate of the adsorbate molecules that diffuse into the internal pores of the adsorbent and in the outer limit layers [Güzel et al, 2015]. In addition, it can be explained that the increase in the mobility of the adsorbate molecules with the increase in temperature facilitates the formation of a monolayer surface [Almeida et al, 2009].

Adsorption kinetics

Kinetic models are used to understand the control mechanism in adsorption processes. Pseudo-first order, pseudo-second order and intraparticle diffusion models were used to test the suitability of the experimental data of dye adsorption on PCP. Pseudo-second order plot of safarin adsorption on PCP is given in figure 3 in various concentrations at 45 °C. Data on pseudo-first order, pseudo-second order models are given in table 1 and data on intraparticle diffusion model are given in table 2.

The pseudo-first order model assumes that the adsorbate molecule can be adsorbed to active sites on the outer surface of the adsorbent. According to this model, the rate of occupation of adsorption sites is proportional to the number of unoccupied sites. The linearized integral form of the pseudo-first-order model is generally expressed as (Lagergren, 1898):

(3)

where q_t and q_e are the adsorption capacity at time t and at equilibrium, respectively (mg/ g), K_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) and t is the contact time (min). The slope and intercept of a linear plot of log ($q_e - q_t$) vs. t will give the value of K_1 and q_e, respectively.

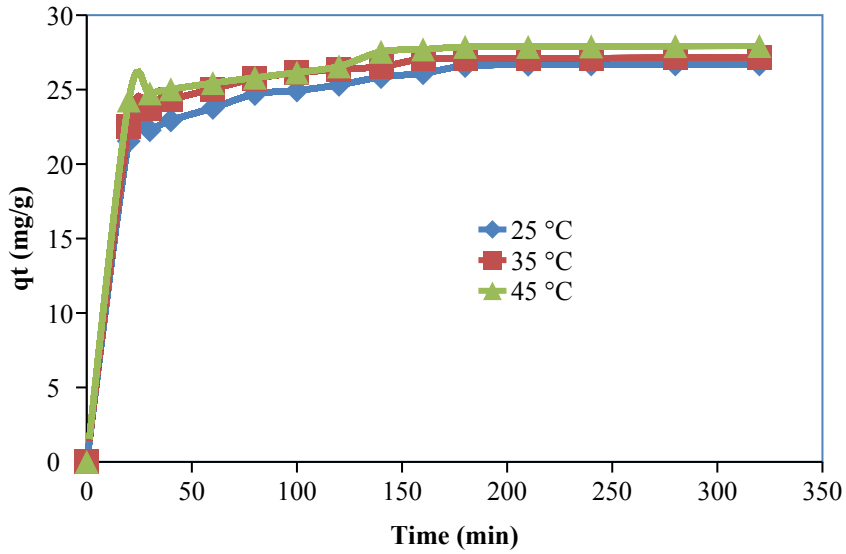

Figure 2 Effect of temperature on dye removal of safranin. Initial dye concentration 75 mg/L, PCP dose 2.5 g/L, pH =7, agitation speed 150 rpm.

The pseudo-second order model assumes that the adsorption rate of dye uptake is proportional with the square of difference between amount of dye absorbed with time and amount of dye absorbed at equilibrium [Heibati et al, 2015]. The pseudo-second order kinetic model can be expressed in a linear form as [McKay and Ho, 1999]:

(4)

where, K_2 (g/mg min) is the rate constant of pseudo-second order adsorption. The slope and intercept of a linear plot of t/q_t vs. t will give the value of K_2 and q_e, respectively.

Intraparticle diffusion model, which is one of the methods used to examine the kinetics of the data obtained in the adsorption process, is represented by the following equation (Weber and Morris, 1963):

(5)

where, K_{id} is the intraparticle rate constant (mg/g min1/2). C is a constant (mg/g) that gives an idea of the thickness of the boundary layers. Constants are found from the slope and intercept of the $t^{1/2}$-q_t plot.

From the data in Table 1, it is observed that there is a difference between the amount of adsorbed substance in the equilibrium calculated by the calculation in the pseudo-first order kinetic model and the amounts determined by the experiment. The amount of adsorbed substance in equilibrium calculated from the pseudo-second order model is close to the amounts found by experiment. The correlation coefficient values (R^2) determined by this model are also very close to one. Therefore, it can be inferred that second-order model do show good compliance with the experimental data.

Table 1 Comparison between the pseudo-first order and pseudo-second order models for various parameters at different initial safranin concentrations

Dye concentration (mg/L)	$(q_e)_{exp}$	Pseudo-first order			Pseudo-second order		
		$(q_e)_{cal}$	K_1	R^2	$(q_e)_{cal}$	K_2	R^2
25	9.21	4.93	0.020	0.899	9.52	0.0077	0.996
50	18.51	6.19	0.018	0.955	18.87	0.0084	0.999
75	27.93	11.20	0.025	0.936	28.49	0.0061	0.999
100	37.18	6.75	0.018	0.830	37.73	0.0059	0.999
125	46.74	16.65	0.039	0.809	47.39	0.058	0.999

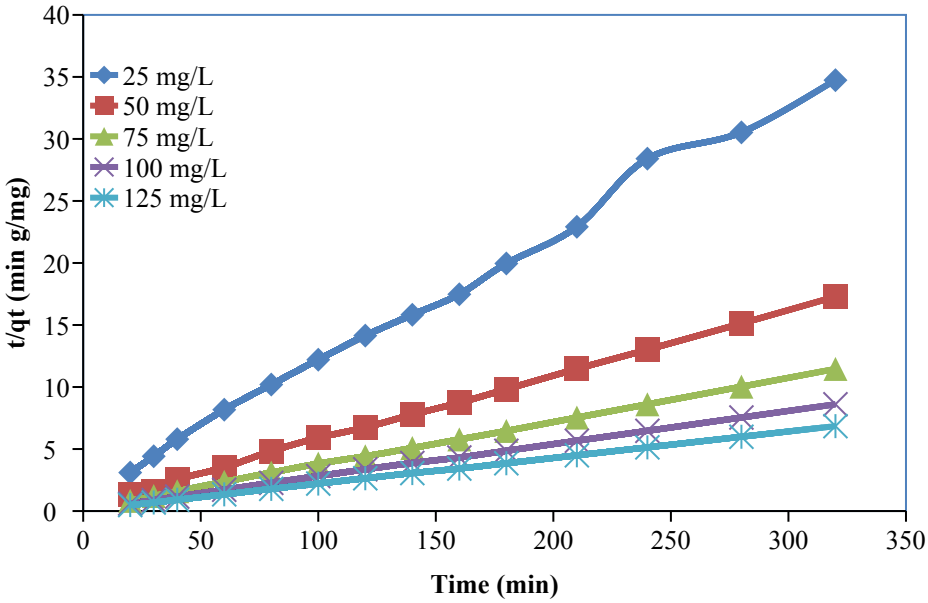

Figure 3 Pseudo-second order model of adsorption kinetics

Table 2 Data intraparticle diffusion models for various parameters at different initial safranin concentrations

Dye concentration (mg/L)	$(q_e)_{exp}$	Intraparticle diffusion					
		K_{id1}	C_1	R^2	K_{id2}	C_2	R^2
25	9.21	0.325	4.93	0.994	0.009	9.03	0.773
50	18.51	0.389	13.29	0.975	0.044	17.74	0.868
75	27.93	0.389	22.50	0.955	0.034	27.35	0.671
100	37.18	0.350	31.99	0.968	0.025	36.71	0.888
125	46.74	0.478	40.35	0.855	0.004	46.67	0.713

If the plot goes through the origin in the intraparticle diffusion model, it is said that the adsorption process only fits this model. In this model, if the data is given in the form of multi-linear graphs, the adsorption process can be studied in two or more steps. As seen in Table 2, in our experiments, the adsorption process was evaluated by dividing into two different phases. The first phase is the region where these sites are used intensively, where there are many places to adsorb on the surface of the adsorbent. The second phase is the region where the adsorption from the surface cite to the inner pores enters very slowly by diffusion. In the adsorption of safarin on PCP, it shows that there is initially surface diffusion and then pore diffusion. However, intercept of line does not pass through the origin is due to the difference in mass transfer rate at the beginning and end of adsorption [Pandey et al, 1986]. These deviations indicate that pore diffusion is not a sole rate control step [Poots et al, 1978].

Adsorption isotherms

Adsorption equilibrium information is important for a good understanding of the adsorption process. The adsorption equilibrium mechanism can be examined from the isotherms obtained from the adsorption equilibrium data. Adsorption capacity data, which is important in evaluating the performance of the adsorbent, is also obtained from the adsorption isotherms.The data obtained from adsorption equilibrium studies were analyzed according to Langmuir, Freundlich, Temkin and DKR isotherm equations. These isotherm equations are commonly used to describe adsorption at specified temperatures for water and wastewater treatment applications.

The Langmuir model, which is generally applied to solid-gas adsorption, is based on the chemical interaction between the adsorbent and the adsorbed molecule [Langmuir, 1916]. According to this model, the adsorption of molecules is in a single layer. The linear Langmuir models are presented as following:

(6)

where *qe* (mg/g) and *Ce* (mg/L) are the amounts of adsorbed dye per unit weight of adsorbent and unadsorbed dye concentration in solution at equilibrium, respectively. q_m(mg/g) and K_L(L/mg) are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

A dimensionless parameter used in the Langmuir isotherm, R_L, is called the separation factor and is represented by the following expression [Webber and Chakkravorti, 1974]:

$$R_L = \frac{1}{1 + K_L C_o} \quad \textbf{(7)}$$

The values of $R_L > 1$, $R_L = 1$, $R_L < 1$ and $R_L = 0$ reflect that the adsorption is unfavorable, linear, favorable, and irreversible, respectively.

Freundlich isotherm accepts that adsorption occurs on heterogeneous surfaces by multilayer adsorption mechanism [Freundlich, 1916]. The linear expression of this equation, which expresses the change between the adsorbed amount and the equilibrium concentration, is as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \textbf{(8)}$$

where K_F ($L^{1/n} \cdot mg^{1-1/n} \cdot g^{-1}$) is Freundlich constant and n is a constant related to adsorption intensity.

The Temkin isotherm accepts that adsorption is a multilayered process [Temkin and Pyzhev, 1940]. This isotherm, which does not give appropriate results at very high and low adsorbate concentrations, indicates that the differential adsorption heat changes inversely with coverage. The Temkin isotherm is represented linearly by the following expression:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad \textbf{(9)}$$

where b Tempkin constant related to the heat of adsorption (J/mol), and A_T empirical Tempkin constant related to the maximum binding energy at equilibrium (L/mg).

The DKR isotherm is important in calculating the apparent adsorption energy. Thanks to this isotherm, adsorption is predicted to be either physisorption or chemisorption. The DKR isotherm is used to explain the adsorption mechanism by considering heterogeneous surfaces and Gausian energy distributions. The model can be represented as[Dubinin and Radushkevich, 1947]:

$$\ln q_e = \ln q_m - K_{DKR} \varepsilon^2 \quad \textbf{(10)}$$

where q_m is adsorption capacity at equilibrium (mg/g), K_{DKR} is a constant related to sorption energy(mol/kJ)^2, ε is Polanyi potential (J/mol). The Polanyi potential is calculated from the following equation:

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \quad \textbf{(11)}$$

E(kJ/mol) mean free energy of adsorption per molecule of the adsorbate is calculated from the following equation:

$$E = \frac{1}{\sqrt{2K_{DKR}}} \quad \textbf{(12)}$$

E is frequently applied to determine whether the adsorption is dominated by physical process ($E < 8$ kJ mol^{-1}) or chemical process ($8 < E < 16$ kJ mol^{-1}) (Chabani et al., 2006).

Table 3 Isotherm constans for safranin adsorption at different temperatures onto PCP

Temperature (°C)	Langmuir isotherm model			Freundlich isotherm model		
	q_m	K_L	R^2	n	K_F	R^2
25	35.48	0.049	0.8591	0.6183	0.7772	0.9792
35	100.00	0.030	0.9399	0.8340	2.6800	0.9933
45	175.43	0.026	0.8708	0.8875	4.2537	0.9986

Table 4 Dimensionless seperation factor R_L onto PCP for dye adsorption onto PCP

Initial dye concentrations	Temperature (K)

(mg/L)	298	308	318
25	0.4494	0.5714	0.6098
50	0.2898	0.4000	0.4385
75	0.2139	0.3077	0.3425
100	0.1695	0.2500	0.2808
125	0.1404	0.2105	0.2380

Table 5 Isotherm constans for dye adsorption from solution at different temperatures onto PCP

Temperature (°C)	Temkin isotherm model			DKR isotherm model		
	b_T	A_T	R^2	K_{DKR}	E	R^2
25	73.0739	0.2715	0.9077	$1.29x10^{-8}$	6.23	0.9798
35	101.3260	0.4960	0.9292	$8.00x10^{-8}$	7.91	0.9896
45	104.4010	0.6472	0.9389	$7.07x10^{-8}$	8.41	0.9978

Tables 3, 4 and 5 show the calculated values for the Langmuir, Freundlich, Temkin and DKR isotherm model parameters. R_L values related to the adsorption of safranin on PCP indicate that the adsorption is favorable under the current experimental conditions. When the correlation coefficient values (R^2) are compared, it seems that the data fit the Freundlich and DKR isotherms better. The fact that the adsorption obeys the Freundlich equation indicates that there is adsorption on heterogenous surfaces. The adsorption free energy value (E) data obtained from the DKR isotherm indicate that the physical adsorption process is dominant.

Thermodynamics of Adsorption

Thermodynamic reaction of adsorption process can be determined via thermodynamic parameters, such as the changes in the standard free energy (ΔG^o), the enthalpy (ΔH^o) and entropy (ΔS^o) using the following relations for the adsorption process:

$$K_e = \frac{C_{Ads}}{C_e} \quad \textbf{(13)}$$

and $$\Delta G^o = \Delta H^o - T\Delta S^o \quad \textbf{(14)}$$

$$\ln K_e = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad \textbf{(15)}$$

Where K_e is the equilibrium constant, which is the ratio of the equilibrium concentration of adsorbate to the equilibrium concentration of the adsorbate in solution. R is the constant of perfect gas (R=8.314 J/mol K), T is the absolute temperature of solution (K). Values of ΔG^o (kJ/mol) at different temperatures were calculated from equation 14. The values of ΔH^o (kJ/mol) and ΔS^o (J/mol K) were calculated from the slope and the interception of graphs ln Ke versus 1/T.

Table 6 The thermodynamic parameters for the adsorption of safranin onto PCP adsorbent

C_o (mg/L)		25	50	75	100	125
ΔG^o (kJ/mol)	298 K	-3.90	-4.42	-5.17	-5.11	-5.59
	308 K	-5.47	-5.54	-5.78	-5.96	-6.22
	318 K	-6.50	-6.67	-6.88	-6.82	-7.04
ΔH^o (kJ/mol)	-	34.35	18.08	19.82	19.09	15.74
ΔS^o (J/mol K)	-	128.64	73.88	83.64	84.25	71.45

ΔH^o positive values show that the adsorption is endothermic process. ΔS^o positive values show the increasing randomness at solid/solution interface during adsorption process [Mahmoodi et al., 2011]. Negative values of free energy (ΔG^o) at each temperature indicate the feasible and spontaneity. The fact that the adsorption process is endothermic indicates that adsorption increases with increasing temperature. Since the free energy data given in Table 6 are in the range of 0-20 kJ/mol, it can be said that a physical reaction is dominant in the adsorption process.

IV. Conclusions

In the current study, illuminating information about the adsorption of the safranin dye from the aqueous solution on the PCP adsorbent under suitable conditions is shown. In this adsorption process, it was determined that the amount of adsorbed dye increased with increasing temperature and concentration at constant pH and constant amount of adsorbent. Kinetic studies of dye adsorption on PCP were performed at different concentrations and it was determined that the results fit better with the pseudo-second order model. The data

obtained in studies on adsorption isotherms were found to fit the Freundlich and DKR model better. Thermodynamic studies show that the adsorption process is spontaneous, physical adsorption and endothermic in nature. As a result, PCP can be used as an alternative adsorbent in the adsorption of the safranin dye from the solution.

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