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Research Article

Adsorption of safranin-O dye by peanut shell-based polyurethane type foam

Bilal ACEMİOĞLU[1,*], Melike Hilal BİLİR[1], Mehmet Hakkı ALMA[2]

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[1]Department of Chemistry, Faculty of Science and Arts, Kilis 7 Aralık University, 79000, Turkey

[2]Rectorate of Iğdır University, Iğdır, 76000, Turkey

ABSTRACT

The adsorption of safranin-O dye was performed in batch and continuous column sysytems by polyurethane-type rigid foam produced from peanut shell. In batch system, effects of contact time, initial dye concentration, solution pH and temperature on the adsorption were investigated. In column system, solution flow rate and initial dye concentration effect were studied. Under conditions studied, the adsorption of safranin-O was 95-99% for batch system, and 93-99% for column system. Adsorption isotherm best followed the Langmuir model ($R^2 = 0.986$). Adsorption kinetics was in consistent with best the pseudo-second order model (R^2 values ≥ 0.998). Adsorption was of sponteneous nature and in favor of increasing temperature (i.e. endothermic nature). For example, when the temperature was increased from 20 to 60°C, standard Gibbs free energy change ($\varDelta G^\circ$) dereased regularitly from -5303 to -8170 J mol^{-1}. The values of standard enthalpy (ΔH°) and standard entropy (ΔS°) were estimated as 13.35 kJ mol^{-1} and 0.64 kJ mol^{-1} K^{-1}, respectively. Moreover, FTIR and SEM analyses were done, and the results were interpreted in detail.

Keywords: Peanut shell, polyurethane foam, safranin-O, adsorption.

Yerfıstığı kabuğu esaslı poliüretan tipi köpük ile safranin-O boyasının adsorpsiyonu

ÖZ

Safranin O boyasının adsorpsiyonu yerfıstığı kabuğundan üretilen poliüretan tipi sert köpük ile kesikli ve sürekli kolon sisteminde gerçekleştirilmiştir. Kesikli sistemde adsorpsiyon üzerine temas süresi, başlangıç boyar madde konsantrasyonu, çözelti pH'sı ve sıcaklığın etkileri araştırıldı. Kolon sisteminde çözelti akış hızı ve başlangıç boyar madde konsantrasyonunun etkisi incelendi. İncelenen şartlar altında Safranin O'nun adsorpsiyonu kesikli sistem için %95-99, ve kolon sistemi için %93-99 idi. Adsorpsiyon izotermi en iyi Langmuir modelini ($R^2 = 0.986$) takip etti. Adsorpsiyon kinetiği en iyi yalancı ikinci dereceden model ile (R^2 values ≥ 0.998) uyumluydu. Adsorpsiyon sponten tabiatlıydı ve artan sıcaklığın lehindeydi (yani endotermik tabiatlıydı). Örneğin, sıcaklık 20 den 60°C' ye arttırıldığında standart Gibss serbest enerji değişimi ($\varDelta G^\circ$), -5303 den -8170 J mol^{-1}'e düzenli olarak azaldı. Standart entalpi (ΔH°) ve standart entropi (ΔS°) değerleri sırasıyla 13.35 kJ mol^{-1} ve 0.64 kJ mol^{-1} K^{-1} olarak belirlendi. Ayrıca FTIR ve SEM analizleri yapıldı ve sonuçlar ayrıntılı olarak yorumlandı.

Anahtar Kelimeler: Yerfıstığı kabuğu, poliüretan köpük, safranin-O, adsorpsiyon.

1. INTRODUCTION

Recently, various low cost adsorbent materials have been used as an alternative to activated carbon to remove dyes from environment by using adsorption technique. These inexpensive materials can be listed as organic (poly(N-isopropylmethacrylamide-acrylic acid) microgels[1], polydopamine microspheres[2], inorganic (fly ash[3], perlite[4], clay[5,6], and biological materials (fungus[7,8], yeast[9], and alge[10]). Besides these, lignocellulosic

materials such as wood apple[11], tree barks[12,13], fruit peels[14], banana[15,16], orange peel[15,17], and peanut hull[18] are mostly used, also.

On the other hand, new adsorbents produced from lignocellulosic materials are also utilized as adsorbent the removal of dyes, metal ions, and organic contaminents. For example, phenolated wood resin[19] have been used for the adsorption of various metals. Polyurethane cross-linked pine cone biomas[20] has been utilized for 2- nitrophenol adsorption.

Lignin-based hydrogels[21] has been utilized for dye adsorption.

In the present work, as an alternative to activated carbon, the polyurethane type rigid foam produced from peanut shell was used as an adsorbent for the removal of safranin-O dye from aqueous solution. In our another work, the sorption of Remazol brilliant blue R using peanut shell-based polyurethane type foam is studied[22], but any workhas been not meet for the sorption of safranin-O dye by this foam in the literature. Thus, this paper is an orijinal work. The formation of the peanut shell-based polyurethane-type foam is explained in the following.

The peanut shell-based polyurethane foam has been produced from a reaction between peanut shell and methylenediphenyl diisocyanate (MDI) via polyaddition polymerization by us (Scheme 1).
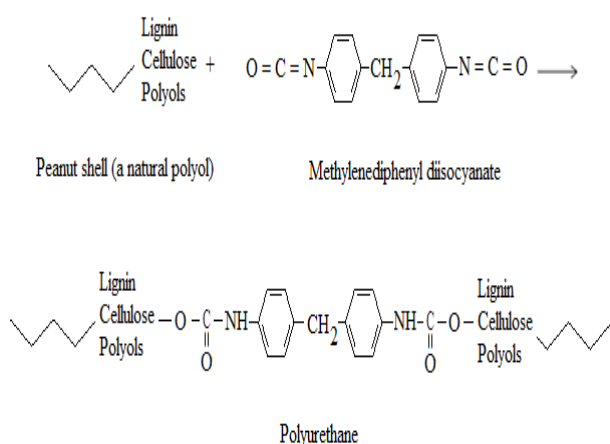
Scheme 1. The formation of polyurethane-type rigid foam from the chemical reaction between peanut shell and MDI.

Lignin and cellulose groups including OH⁻ groups in the structure of the peanut shell-based polyurethane-type rigid foam can adsorb the positively charged safranin-O dye.

In this study, therefore, effects of initial dye concentration, contact time, temperature, and pH on safranin-O dye adsorption were investigated. Moreover, adsorption isotherm, kinetics and thermodynamic studies were also done.

2. MATERIALS AND METHODS

2.1. Materials

Safranin-O dye was received from Carlo Erba. Some physical properties and chemical structure of safranin-O dye are given in Table 1.[23,24] Peanut shell was provided from Osmaniye province located in the east Mediterranean region of Turkey. The ingredients used in the making of foam was received from Ispol company in Turkey. These ingredients are polyethylene glycol (PEG-400, commercial polyol), monoethylene glycol (MEG, polyol), triethylenediamine (TEDA-D33LV, foaming catalyst), and polymeric diphenylmethane diisocyanate (PMDI-TED-31, crosslinking agent). On the other hand, for the elemental analysis, a LECO CHNS-932 analyzer device was used. For FT-IR spectra, a FTIR RX-1 Perkin Elmer brand ATR spectrophotometer was used. For SEM analyses, it was used a LEO 435 VP SEM brand device. For Specific surface area and porosity measurements, a nitrogen adsorption device was used.

2.3. Methods

Peanut shell powders with 100 micron size were utilized as a natural polyol to produce the polyurethane-type rigid foam. Peanut shell-based polyurethane type foam shell is prepared as described in our another work.[22] The resulting foam exhibited very little adsorption capacity. With aim to improve the adsorption capacity, the foam was pretreated with 0.1 N HCl for 5 min, then the mixture was filtered and washed well with pure water, and finally dried for 12 h at 103°C. Thus, the foam was become ready for use in adsorption experiments.

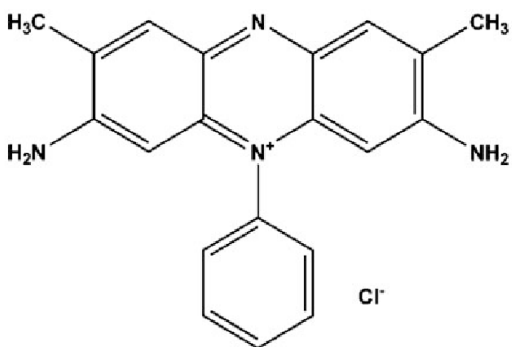The reason for pretreated with HCl of the foam can be interpreted in 2 different ways:

1) It is thought that HCl is effective in the modification, leading to the elimination of some impurities that may be present in the foam during foam formation,
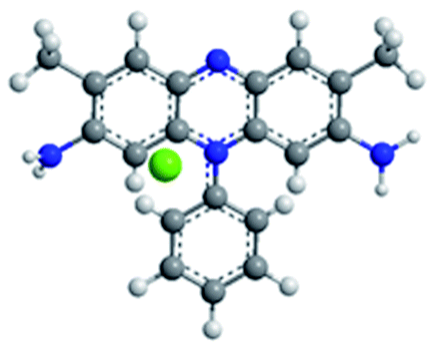
2) When the foam is washed with HCl, functional groups on the surface (i.e. end groups such as -OH groups) give rise, and these groups cause to the adsorption of positively charged safraninin dye.

On the other hand, the stock solution of 500 mg l⁻¹ of safranin-O dye was prepared with distilled pure water. Desired solutions were prepared from the stock solution. Adsorption experiments were done by shaking 0.125 g of peanut shell-based polyurethane type rigid foam with 25 ml-dye solution at 130 rpm. Shaking process was performed in a temperature-controlled water bath at various initial dye concnetrations (10, 20, 50, 75, 100 and 150 mg l⁻¹), pH values (3, 5, 7 and 9) and temperatures (20, 30, 40, 50, and 60°C) at early specified times, respectively. After shaking times, the mixtures were then centrifuged at 5000 rpm for 5 min. For aim of the determination of the concentrations of unadsorbed dye in the solutions, the supernatants were analyzed by an UV-Vis spectrophotometer (T80 UV-Vis spectrophotometer). The pH values of the dye solutions were regulated by dropping diluted HCl or NaOH solutions. The amounts of dye adsorbed per gram of the foam (q_t) and percent adsorption values were estimated using following Equitions, respectively.

Table 1. Some physical properties of safranin-O dye

Common name	Safranin-O
C.I. name	Basic red 2
IUPAC name	3,7-Diamino-2,8-dimethyl-5-phenylphenazinium chloride
C.I. number	50240
Ionization	Basic
Solubility in water (%)	5.45
Solubility in ethanol (%)	3.41
Max. wavelength (nm)	517
Color	Red
Molecular weight (g mol^{-1})	350.85
Molecular formula	$C_{20}H_{19}N_4Cl$
Chemical structure	3D model structure

$$q_t = \frac{(c_0 - c_t)}{m}$$

$$Adsorption \% = \frac{(c_0 - c_t)}{c_0} \, x \, 100$$

where C_o is initial dye concentration (mg l^{-1}). C_t points to the concentration of the unadsorbed dye in the solution at any time (mg l^{-1}). The q_t indicates the amount of the dye adsorbed per unit mass of the foam at any time (mg g^{-1}). m indicates adsorbent mass (g), and V is dye solution volume (l). At the equilibrium time, q_t and C_t can be expressed as q_e and C_e.

3.   RESULTS AND DISCUSSION

3.1. Characterization of the foam

Specific BET surface area, porosity, density, and color of the foam pretreated with HCl have been determined as 2.824 m^2 g^{-1}, 0.00215 cm^3 g^{-1}, and 0.0341 g cm^{-3}, and brownish, respectively. According to elemental analysis results, the foam pretreated with HCl includes 61.98% C, 5.832% H, 67.478% N, 0.231% S.

SEM image shows the surface morphology of the peanut shell-based polyurethane typ rigid foam (see Figure 1). As seen in Figure 1, the surface of the foam has a porous, rough and heterogeneous structure which may adsorb dye molecules.
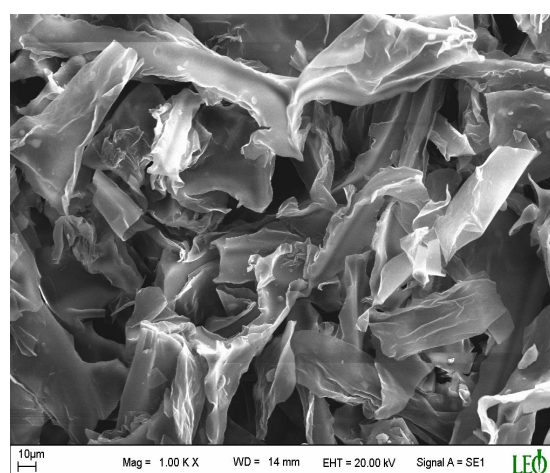
Figure 1. SEM image of the peanut shell-based polyurethane foam pretreated with HCl.

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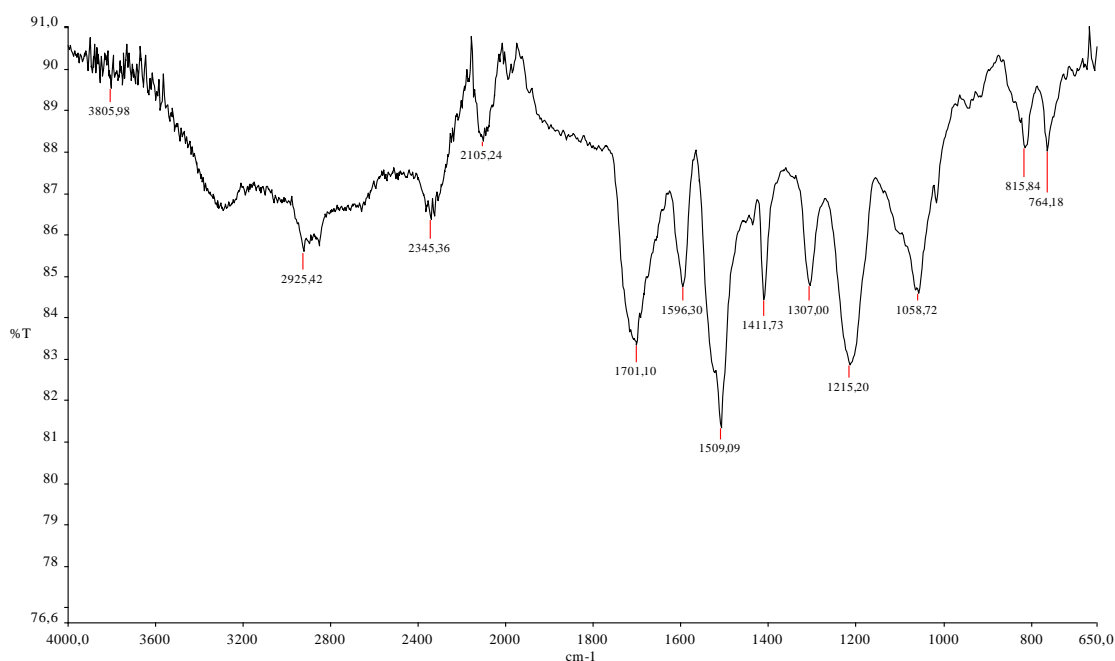
Figure 2. FT-IR spectrum of the peanut shell-based polyurethane foam pretreated with HCl.

FT-IR spectrum of the peanut shell-based polyurethane foam pretreated with HCl for Safranin-O adsorption is shown in Figure 2.

This spectrum can be interpreted as follows. In FT-IR spectrum, the broad band at 3293.58 cm^{-1} indicates the vibration of -NH and -NH$_2$ groups and -OH groups of cellulose.[25] The band at 2925.42 points to -CH stretching of carboxyl groups.[26] Very robust bands at 1701.10 and 1509.09 cm^{-1} denote the amide I and amide II bonds.[23] The robust peaks at 1411.73 and 1596.30 cm^{-1} indicate phenyl fragment in the structure of the foam.[25] The strong band at 1307.00 cm^{-1} points to the stretching of C-(CH$_3$)$_2$.[26] Peaks at around 1200–1000 cm^{-1} indicate C-O single bond in carboxylic acids, alcohols, phenols, and esters. Herein, the strong peak at 1058.72 and the weak band at 1018.02 cm^{-1} might be assigned to C-O and C-O-C stretching bonds in the structure of the foam.[26] A robust band observed at 1215.20 cm^{-1} indicates the C=O stretching band of carboxylic groups.[27] The bands at 815.84 and 764.18 cm^{-1} denotes the vibrations of aromatic skeleton in the structure of the polyurethane foam.[26] All these findings indicate that the dye molecules may be adsorbed by functional groups in the structure of the foam. When comparized according to bands in raw foam without pretreated with HCl[22], the intensity decrease and spectral shifts in bands obtained here are occurred with the effect of HCl.

3.2. Initial dye concentration effect

Figure 3 shows effect of initial dye concentration on safranin-O adsorption by the foam. As can be seen that

the adsorption is strongly influenced by the initial concentration of the dye.
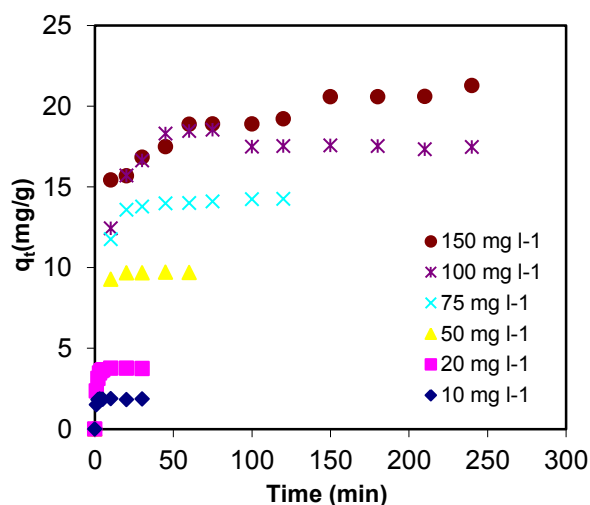

Figure 3. Effect of initial dye concentration on the adsorption of safranin-O by the foam (T: 60°C, pH: 9, w/v: 0,125 g/25 ml, 130 rpm).

While maximum adsorption occurs at lower times for lower concentrations, it occurs at longer periods for higher concentrations. For example, the time of the maximum adsorption is determined, as 10 min for low concentrations such as 10 and 20 mg l^{-1}, as 45 min for 50 mg l^{-1}, as 120 min for 75 and 100 mg l^{-1}, and as 240 min for 150 mg l^{-1}, respectively. These different times denote the different equilibrium time for each concentration. Different equilibrium times for different

concentrations probably indicate an equilibrium shift. The maximum adsorption and percentages are determined as 1.87 mg g^{-1} (93.83%), 3.76 mg g^{-1} (94.18%), 9.71 mg g^{-1} (97.14%), 14.25 mg g^{-1} (95.03%), 17.53 mg g^{-1} (87.67%) and 21.28 mg g^{-1} (70.94%) for the initial dye concentrations of 10, 20, 50, 75, 100 and 150 mg l^{-1}, respectively. If it is paid attention to these values, it can be seen that as the amount of adsorbed dye increases with increasing concentration, the adsorption percent decreases. This situation denotes the saturation of the surface of the adsorbent as the adsorbent surface is covered with more dye molecules with effect of increasing dye concentration. Thus the decrease of active sites on the adsorbent leads the decrease of percent adsorption. A similar trend has been obtained for malachite green adsorption by orange peel.[17]

3.3. pH effect

Solution pH in an adsorption proccess affects the ioniztion of a dye molecule and the charge of an adsorbent surface. Herein, pH values of dye solutions are seleceted as 3, 5, 7 and 9. The results obtained are graphed in Figure 4.
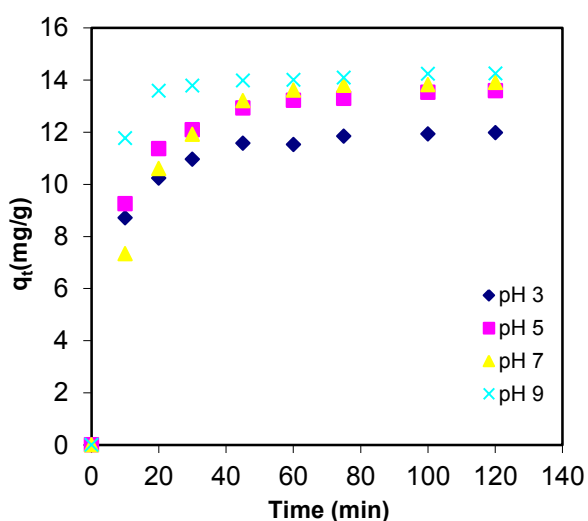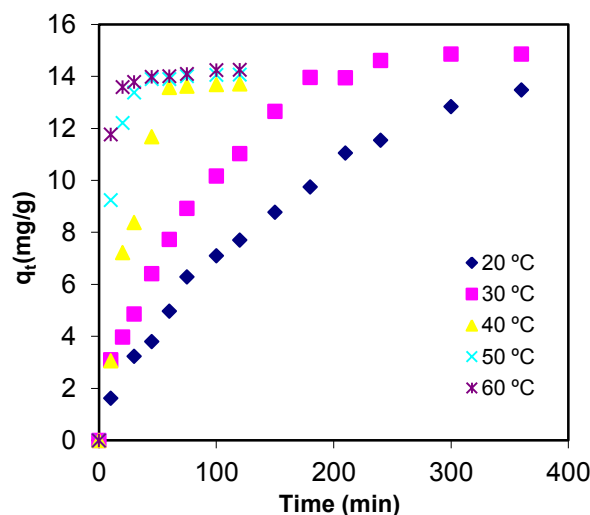

Figure 4. Effect of pH on the adsorption of safranin-O by the foam (T: 60°C, C$_o$:75 mg l^{-1}, w/v: 0,125 g/25 ml, 130 rpm).

As seen in Figure 4, it is seen that the adsorption increases with a rise in pH from 3 to 9. The adsorption equilibrium is reached at 120 min for all pHs. The reason for the increase in adsorption with increasing pH indicates that the adsorbent surface becomes more negative due to the excess hydroxyl ions released at higher pH, and therefore electrostatically attracted between the foam and positively charged safranin-O molecules. This situation comes to a rise in adsorption. While the maximum adsorption is 14.25 mg g^{-1} (95.03%) at pH 9, it determined as 11.94 mg g^{-1} (79.82%) at pH 3. A similar reult has been obtained for safranin adsorption

onto coal fly ash.[28]

3.4. Temperature effect

Figure 5 demonstrates the effect of temperature on safranin-O adsorption by the foam. As seen from Figure 5, the adsorption is strongly influenced by tempetaure. Whille maximum adsorption occurs at higher times for lower temperatures, it occurs at longer periods for higher temperatures.


Figure 5. Effect of temperature on the adsorption of safranin-O by the foam (C$_o$: 75 mg l^{-1}, pH: 9, w/v: 0,125 g/25 ml, 130 rpm).

For example, the adsorption proceeds slowly by starting from first minutes at 20 and 30°C and reaches a maximum with gradual increases at 360 min. It progresses quickly and reaches a maximum value in 120 min time at the temperature of 40, 50 and 60°C. Namely, it is observed that the maximum adsorption occurs at 360 min at temperatures of 20 and 30°C, it occurs at 120 min at temperatures of 40, 50 and 60°C. Why of this can ascribable the swelling of the adsorbent particles at high temperatures and the faster act of the dye molecules. The maximum adsorption and percentages are found as 13.47 mg g^{-1} (89.81%) ve 14.85 mg g^{-1} (99.04%), 13.70 mg g^{-1} (91.39%) 14.06 mg g^{-1} (93.79%), and 14.25 mg g^{-1} (95.03%) for the temperatures of 20, 30, 40, 50 and 60°C, respectively.

3.5. Column adsorption study

Column with a diameter of 1 cm and a length of 20 cm was used for continuous adsorption system. The foam particles (dry weight 1 g) were packed between two layers of glass wool in column. 50 ml of dye solutions with desired concentrations (10, 20, 50, 75, 100 ve 150 mg l^{-1} solutions) were fed through the top of the column. Column height is 10 cm. The flow rate of feed solutions

was regulated as 0.35 ml min^{-1} (21 ml h^{-1}). The system was operated at 25°C and pH 9. The dye samples passed through column were collected from the bottom of column at specific times. The concentrations of dye unadsorbed within samples in the outlet of the column were estimated as described as before. The amounts of dye calculated from the analysis of the samples taken at the outlet of the column at all residence times are shown in Figure 6.
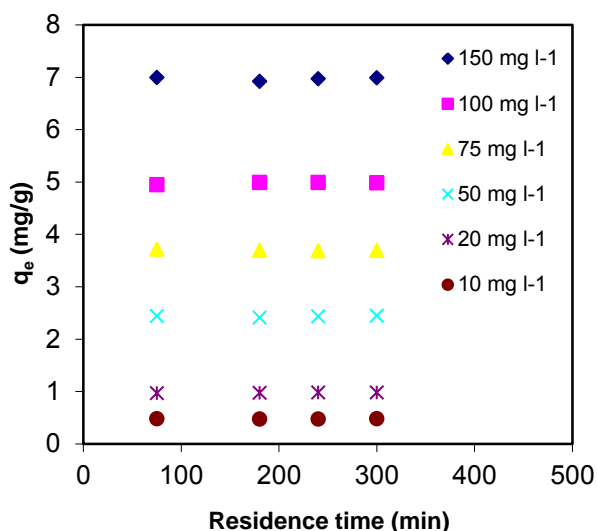

Figure 6. Effect of initial concentration on the column adsorption of safranin-O by the foam (pH: 9, T: 25°C, flow rate: 21 ml h^{-1}).

As seen from this figure, it is seen that the amounts of dye uptaken per unit gram of the foam in the column (i.e. column capacity) rise with an increase in initial dye concentration. For instance, while the initial dye concentration increases from 10 to 150 mg l^{-1}, maximum column capacity is determined to increase from 0.475 to 6.987 mg g^{-1}. On the other hand, while the percentage of column adsorption among the initial dye concentrations of 10 and 100 mg l^{-1} was determined to be between 94.90% and 99.79% between 60 and 300 min residence times. The percentage of column adsorption was estimated to be between 92% and 93% between 60 and 300 min residence times for the initial dye concentration of 150 mg l^{-1}. It is seen that the outlet samples of 99% are colourless and cleared off the red colour of safranin-O. This situation points to be a strong interaction between the functional groups of safranin-O dye and foam packed in column. Column exhaustion time was determined as 5 h.

3.6. Isotherm study

Isotehrm studies of the adsorption of safranin-O by the foam were investigated according to commonly given the Langmuir and Freundlich models.[29] The Langmuir isotherm is shown in Figure 7.
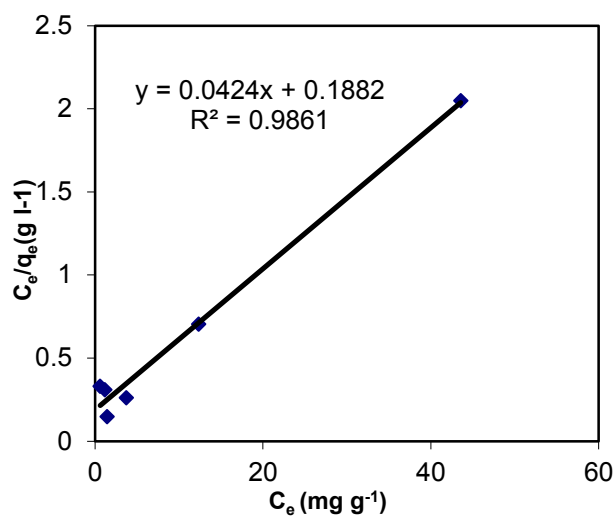
Figure 7. The Langmuir isotherm of safranin-O adsorption by the foam (C$_o$:10-150 mg l^{-1}, pH: 9, T: 60°C, w/v: 0,125 g/25 ml, 130 rpm).

The adsorption is observed to obey best the Langmuir isotherm model (with R^2 = 0.986). The compatibility with the Langmuir isotherm indicates a monolayer adsorption on the foam surface. A similar trend has been repoted for safranin O adsorption onto carbonized spent coffee ground.[30] The Correlation coefficient value (R^2 value) obtained from Freundlich isotherm model is found as 0.744. Due to this low R^2 value, the Freundlich plot is not given here. The k value indicating the Freundlich adsorption capacity and n value indicating adsorption intensity are found as 4.38 and 1.97, respectively. It is determined that Langmuir adsorption capacity (Qo value) is 23.58 mg g^{-1}, and the adsorption energy (b value) is 0.225 mg^{-1}. In safranin-O adsorption, the Langmuir adsorption capacity of the foam are comparized with other some sorbents (see Table 2).

3.7. Kinetic study

Adsorption kinetics of dye adsorbed by the foam was studied in terms of the pseudo-first and-second order kinetics, and intra-particle diffusion models. The linearized equations of these kinetic models are given in Table 3.[31-34] At the same time, Table 3 shows all of kinetic parameters obtained. As seen from this table, the R^2 values obtained for the pseudo-second order kinetics are the highest than the pseudo-first order and intra-particle diffusion models. The R^2 values for the pseudo-second order kinetics are found between 0.998 and 0.999. On the other hand, the theoretical q_2 values are close to the values of the experimental q_e. (see Table 3). Therefore, both the high correlation coefficients and the compliancy of the theoretical and experimental adsorption capacities indicate that the adsorption follows the pseudo-second order kinetic model.

Table 2. Comparison of the Langmuir adsorption capacity (Q_o) of the foam to some other adsorbents for the adsorption of safranin-O

Adsorbent/Biosorbent	Q_o (mg g^{-1})	References
Peanut shell-based polyurethane foam	23.58	This study
Coal fly ash	1.76	(28)
Coffee spent grounds	3.76	(30)
Magnetic clay	18.48	(38)
Kaolinite clay	16.23	(39)
Pineapple peels	26.08	(40)
Rice husk	35.65	(41)
Activated red mud	894	(42)
NaOH treated bambusa tulda	32.26	(43)
Untreated Sugarcane Bagasse	1.80	(44)
H$_2$SO$_4$ Sugarcane Bagasse	1.39	(44)
NaOH Sugarcane Bagasse	2.64	(44)

Similar results have been found for safranin-O adsorption onto carbonized spent coffee ground[28] and safranin-O adsorption onto Miswak.[35]

Plots for the pseudo-second order kinetic model are illustrated in Figure 8. Because the R^2 values for the pseudo-first order and intra-particle diffusion kinetic models are low, it is not possible to mention for fit to these models. Therfore, these plots kinetics are not shown.

3.8. Thermodynamics study

Thermodynamics of safranin-O adsorption by the foam was by means of thermodynamic equations given elsewhere.[36,37] From the thermodynamic parameters, standard The equilibrium constant of the adsorption (K_c), Gibbs free energy change (ΔG^o), standard enthalpy (ΔH^o) and standard entropy (ΔS^o) values were determined. All of thermodynamic parameters obtained are given in Table 4.

As seen from Table 4, the values of ΔG^o were determined as negative at all temperatures. These values indicate the spontaneous nature of dye adsorption. The fact that the values of ΔG^o decrease with increasing temperature denotes the increase of spontaneous tendency of the adsorption. The values of ΔH^o and ΔS^o are estimated as 13.35 kJ mol^{-1} and 0.64 kJ mol^{-1} K^{-1} from Van't Hoff equation respectively. The low value of ΔH^o

indicates a physical adsorption. The positive value of ΔS^o points to a randomness adsorption of dye molecules onto the foam surface. Similar results for ΔG^o, ΔH^o and ΔS^o have also been repored for the adsorption of magnetic mesoporous clay.[38]
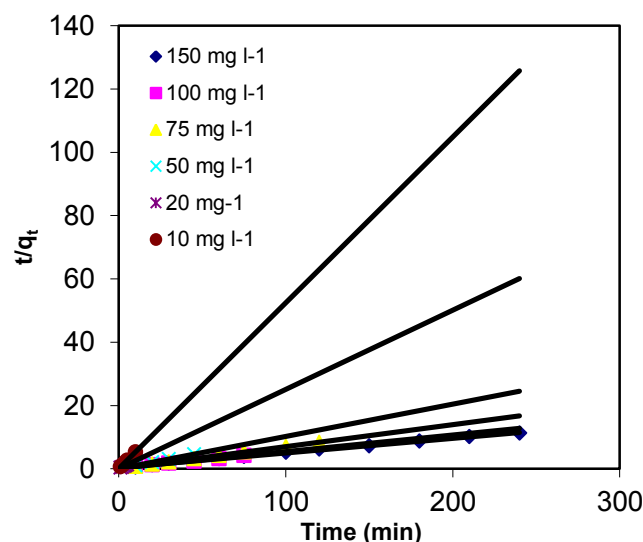
Figure 8. The pesudo-second order plots of safranin-O adsorption by the foam (C$_o$:10-150 mg l^{-1}, pH: 9, T: 60°C, w/v: 0,125 g/25 ml, 130 rpm).

4. CONCLUSIONS

Peanut shell-based polyurethane type rigid foam produced was used as a new adsorbent material for the removal of safranin-O dye from aqueous solution. The adsorption of dye onto the foam increased with rises in initial dye concentration, pH and temperature. The maximum percent adsorption was determined to be between 95% and 99% for batch system and 93% and 99% for column system under studied conditions. Adsorption isotherm was in consistent with best the Langmuir model. The Langmuir adsorption capacity was determined as 23.58 mg g^{-1}. Adsorption kinetics followed the pseudo-second order model. The negative ΔG^o values indicated the spontaneous tendency of dye adsorption onto the foam. The spontaneous tendency increased with increasing temperature. The values of ΔG^o were determined as -5.303, -6.513, -6.146, -7.291, and -8.170 kJ mol^{-1} for 20, 30, 40, 50, and 60°C, respectively. The adsorption of dye was physical with a low ΔH^o value of 13.35 kJ mol^{-1}.Adsorption entropy was estimated as 0.64 kJ mol^{-1} K^{-1}. Peanut shell-based polyurethane type rigid foam could be preferably used as a new adsorbent, as an alternative to activated carbon, in dye removal due to its low cost.

Table 3. Kinetic parameters for safranin-O adsorption by the foam at initial dye concentrations.

	Pseudo-Second order				Pseudo-Second order			Intra-particle Difussion		
	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_2^2} + \dfrac{1}{q_2}\, t$				$\log(q_e - q_t) = \log q_1 - \dfrac{k_1}{2.303}\, t$			$q_t = k_i\, x\, t^{1/2}$		
$C_e{}^a$	$q_2{}^b$	$k_2{}^c$	h^d	$r_2{}^{2e}$	$q_1{}^f$	$k_1{}^g$	$r_1{}^{2h}$	$k_i{}^i$	$r_i{}^{2j}$	$q_e{}^k$
10	1.91	3.419	12.47	0.999	0.309	0.614	0.652	0.129	0.480	1.87
20	4.01	0.466	7.49	0.998	2.46	0.670	0.984	0.588	0.689	3.76
50	9.90	0.217	21.26	0.999	0.857	0.112	0.701	0.111	0.706	9.71
75	14.49	0.039	8.18	0.999	2.529	0.043	0.908	0.236	0.616	14.25
100	20.40	0.008	3.32	0.999	9.484	0.087	0.977	1.072	0.863	18.55
150	21.73	0.004	1.88	0.998	6.309	0.011	0.927	0.472	0.941	21.28

[a]Initial dye concentration (mg l^{-1}),
[b]Equilibrium adsorption capacity obtained from the pseudo-second order equation (mg g^{-1}),
[c]The rate constant of the pseudo-second order reaction (g mg^{-1} min^{-1}),
[d]The initial adsorption rate drom the pseudo-second (mg g^{-1} min^{-1}),
[e]Correlation coefficient from the pseudo-second-order kinetics order kinetics (mg g^{-1} min^{-1}),
[f]Equilibrium adsorption capacity of the pseudo-first order reaction (mg g^{-1}),
[g]The rate constant of the pseudo-first order reaction (min^{-1}), [h]Correlation coefficient from the pseudo-first order kinetics
[i]Intra-particle diffusion rate (mg g^{-1} min$^{-1/2}$),
[j]Correlation coefficient from intra-particle diffusion equation,
[k]Equilibrium adsorption capacity obtained as experimental (mg g^{-1}).

Table 4. Thermodynamic parameters of the adsorption of safranin-O by the foam

Temperature (in K)	K_c	$\Delta G°$ (J mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1}K^{-1})
20	8,820	-5303		
30	13,274	-6513		
40	10,617	-6146	13.35	0.64
50	15,111	-7291		
60	19,139	-8170		

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Conflict of interest

We declare that there is no a conflict of interest with any person, institute, and company, etc.

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ORCİD

0000-0002-0728-2747 (B. Acemioğlu)

0000-0001-9987-1882 (M. H. Bilir)

0000-0001-6323-7230 (M. H. Alma)