

Sorption of Remazol Brilliant Blue R onto Polyurethane-Type Foam Prepared from Peanut Shell

M. Hilal Bilir,¹ Neslihan Şakalar,² Bilal Acemioğlu,¹ Evrim Baran,¹ M. Hakki Alma³

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

²Department of Chemistry, Faculty of Science and Arts, Kahramanmaraş Sutcu İmam University, Kahramanmaraş 46060, Turkey

³Department of Industrial Engineering of Forestry, Faculty of Forestry, Kahramanmaraş Sutcu İmam University, Kahramanmaraş 46060, Turkey

Correspondence to: B. Acemioğlu (E-mail: acemioğlu@kilis.edu.tr)

ABSTRACT: The powders of peanut shell is first liquefied with the mixture of polyethylene glycol-400 and monoethylene glycol (MEG) using sulfuric acid at 160°C for 2 h. Polyurethane (PU)-type rigid foam is prepared from the reaction between peanut shell liquefied with the MEG and diphenylmethane diisocyanate. Then the PU foam is used as a sorbent for the removal of the remazol brilliant blue R from aqueous solution. The sorption of the dye increases with increasing initial concentration, temperature, and ionic strength, while decreasing with increasing pH. From the isotherm and kinetic studies, it is seen that the sorption process is in the best agreement with the Langmuir isotherm and the pseudo second-order kinetic model. Desorption and FTIR studies show that a chemisorption process occurs between dye and foam, probably indicating electrostatic interactions. The thermodynamic parameters (i.e., standard free energy, standard enthalpy, and standard entropy) are determined, and the results obtained are discussed in detail.

© 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: polyurethane foam; peanut shell; sorption; remazol brilliant blue R; isotherm; kinetics; thermodynamics

Received 12 August 2011; accepted 25 February 2012; published online 00 Month 2012

DOI: 10.1002/app.37614

INTRODUCTION

It is known that the polyurethanes (PUs) are one of the most useful three-dimensional polymers due to their use in various forms of materials, for example, sheets, foams, elastomers, adhesives, paints, and so on. The properties of PUs can be tailored to meet the requirements of different applications. For instance, these include flexible foams for upholstery, semi-rigid integral skin foams for automotive parts, rigid foams for insulation, flexible coating foams for textile, leather, and elastic fibers, high-performance rigid coating foams for different substrates and requirements, thermoplastic elastomers. There are various PU foams with different composition and various properties. Moreover, it is mentioned that PU foams have been used to extract and separate organic and inorganic substances from liquid and gas phase.¹ The polyether and polyester type PUs have been used to removal these kinds of the pollution by extraction process in literature. For example, the polyether and polyester PUs have been utilized as adsorptive materials for the sorption of 59 organic dyes which are anionic, cationic, and neutral by Chow et al.² Werbowesky and Chow have studied the extraction

of 12 mono-azo dyes by using polyester and polyether type PU foams.¹ However, Fong and Chow have also studied the extraction of salicylic acid, 8-hydroxquinoline, 1-amino-2-naphthol-4-sulphonic acid and cinnamic acid.^{3–5} Tanaka et al. have used the polyether type PU for the sorption of methylene blue (MB) and crystal violet.² In these articles mentioned, all PU foams are commercial materials. In another study, wood based PU type foams have also been produced, and their physicochemical properties have been studied by Alma et al.⁶ In this study, the PU type foam is prepared from peanut shell which is an agricultural waste. Peanut shell is a natural polymer, which consists of cellulose, lignin, hemicellulose, and tannins. It has more groups than two hydroxyl groups per molecule, and it can be used as polyol for the preparation of PU foam. When the PU foam produced from the peanut shell is compared with some commercial sorbents, it is seen that the PU-foam is an economical adsorptive material for the removal of organic and inorganic pollutants from aquatic environments. Any work with regard to the sorption of dyes on the PU-foam produced with peanut shell has been not recorded in literature, so far. Therefore the present

© 2012 Wiley Periodicals, Inc.

Table I. Chemical Composition of Peanut Shell

Components	%
Lignin	32.80
Cellulose	45.30
Hemicellulose	8.10
Protein	4.90
Ash	2.30

work aims to study the effects of initial dye concentration, pH, temperature, and ionic strength on the sorption of remazol brilliant blue R (RBBR), an anionic dye, onto the PU-foam. Moreover, this article explains the isotherm, kinetics, and thermodynamic studies of the sorption process and desorption. Therefore, this article reflects an original work.

EXPERIMENTAL

Materials

The powders of the peanut shell of 80 meshes are used as a primary natural polyol for making the PU-type foam. The chemical composition and elemental analysis results of the peanut shell are given in Tables I and II, respectively.⁷ In addition, poly(ethylene glycol)-400 (PEG-400) and monoethylene glycol (MEG) as polyol, and 1,4-dioxan as solvent have reagent grade, and they are used without any further purification.

The ingredients used in the making of foam are as follows: Polyethylene glycol (PEG-400, commercial polyol), triethylenediamine (TEDA-D33LV, foaming catalyst), MEG (polyol), and polymeric diphenylmethane diisocyanate (PMDI-TED-31, cross-linking agent). All these ingredients have been donated by Ispol, Turkey.

Procedure of Preparation of PU Foam

The preparation of PU foam with the peanut shell occurs at two stages. The peanut shell is first turns from solid state to liquid form. Then, the liquefied mixture is used in the production of PU foam with the foaming catalyst, surfactant, and blowing

Table II. Elemental Analysis of Peanut Shell and PU-Foam

Components	PU-Foam	PS
C	61.20	41.53
H	5.848	5.55
N	6.975	2.12
S	0.274	0.245

agent (water). The preparation of PU foam can be clearly described as follows.⁶

Liquefaction of the Peanut Shell

A mixture of oven-dried powders of the PS, PEG-400, glycerin, and sulfuric acid are heated in a three-necked round bottom glass at 160°C for 120 min. The resulting mixture dissolve in a binary solvent (dioxane/water: 4/1), and then it is filtrated through a glass-fiber filter paper. The amount of unliquefied PS is determined as described below.

To determine the unliquefied amount of PS (i.e., the percent dioxan-insoluble part), the mixture obtained at the end of the liquefaction of the PS is diluted with 1,4-dioxan and filtered as described above. Then, percent dioxan-insoluble part was determined by the following equation:

$$\text{DIP (\%)} = \frac{w_{B0} - w_B}{w_{B0}} \times 100 \quad (1)$$

where w_{B0} and w_B are the oven-dry weight of starting peanut shell (g) and the oven-dry weight of unliquefied peanut shell determined after the liquefaction (g), respectively. Herein, the w_{B0} and the w_B are found to be 40 g and 11.20 g, respectively. The percent of liquefied and unliquefied PS is calculated as 72 and 28%, respectively. However, acid and hydroxyl values in medium during the liquefaction are determined as 30.60 and 315.0 mg KOH/g according to methods expressed in literature, respectively.

Preparation of PU Type Rigid Foam

After the pH of the concentrated liquefied peanut shell resulted is adjusted to 7, the concentrated liquefied peanut shell of 35 g,

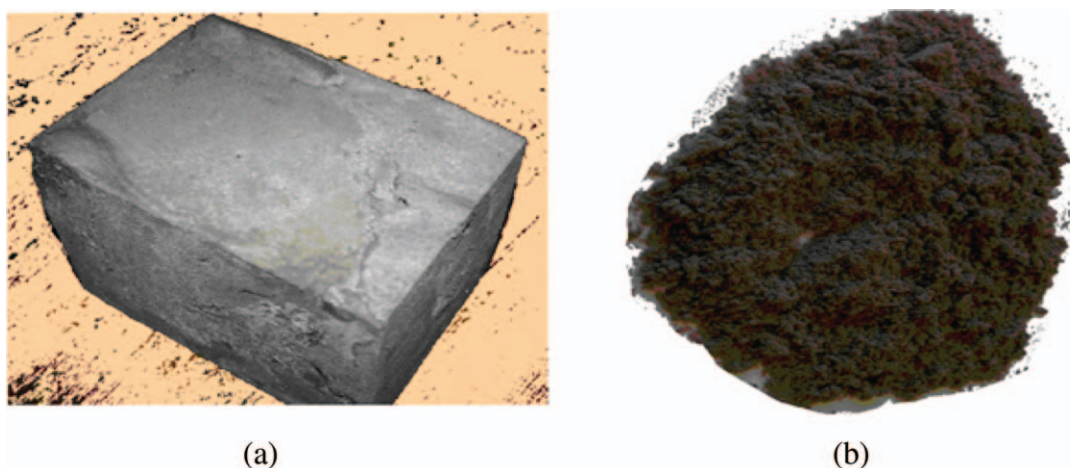
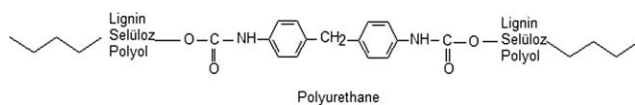


Figure 1. The photograph of PU type foam prepared from peanut shell (a) solid foam and (b) powder foam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



ED1 **Figure 2.** PU structure of foam obtained from the reaction of diphenylmethane diisocyanate (MDI) and natural/synthetic polyols.

33% the foaming catalyst (TEDA-D33LV), 2.5% surfactant (PEG-400), 10% monoethylene glycol (MEG), and 1% blowing agent (water) are uniformly premixed in a paper cup. Then, a certain amount of polymeric diphenylmethane diisocyanate as crosslinking agent (PMDI, isocyanate index of 130) is added to the premixed components and stirred at a speed of 14,000 rpm by a homogenizer for about 20 s. Eventually, the foam is waited to form and rigid at room temperature for a day, and after then the dried foam is used for the sorption experiments. The photograph of the obtained foam is shown in Figure 1. PU structure of the foam is demonstrated in Figure 2.⁸ Elemental analysis of the foam is done on a LECO CHNS-932 analyzer, and the results were given in Table II. Moreover, some physical properties such as specific BET surface area, porosity, density, and color the obtained foam are determined, and they are presented in Table III. However, FTIR spectra for the functional groups of the foam were recorded, and the results are interpreted in FTIR analysis section.

Sorption Experiments

First, the PU-foam is grounded by using a sandpaper of 80 micron, the particle size of the foam is found to be 80 meshes by using a molecular sieve. It was prepared for sorption experiments. It is seen that the capacity of the foam is very less for the sorption of RBBR, and thus the foam is pretreated with HCl before batch sorption experiments. Pretreatment process is described in following.

Pretreatment of the PU-Foam for Sorption Experiments

The PU-foam was modified by doing pretreatment with 0.5N HCl before sorption process. Modification process is performed by reacting by the ratio of foam/HCl of 0.10 g/10 mL (w/v) at a temperature of 140°C for 6 h. At the end of the reaction of 6 h, the reaction mixture is filtered and the modified PU-foam is washed a few times with pure water to remove impurities on its surface. Washing process is continued until all residual chlorine ions on the foam were transferred into waste washing water. To make sure whether the residual Cl on the modified PU-foam is present, a continuous titration process with AgNO₃ is applied to waste washing water. This process is expressed as follows: In the result of washing the foam, after HCl pretreatment, Cl ions on the foam passes into waste washing water. The presence of

Table III. Some Physical Properties of Modified PU-Foam

BET surface area (m ² /g)	2.824
Pore volume (cm ³ /g)	0.00215
Density (g/cm ³)	0.0341
Particle size (mesh)	80
Color	Brownish

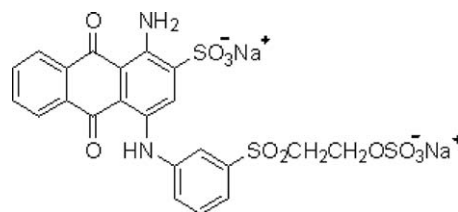


Figure 3. The structure of RBBR.

Cl ions within the waste washing water is controlled by titration with AgNO₃. The waste washing water has become turbid with AgNO₃, indicating the formation of AgCl in medium. Washing process of the foam is continued until the waste washing water has become clear. At the end, the foam is used by drying for sorption experiments.

Preparation of Dye Solutions

RBBR is provided from dystar, and it is used as received without further purification. The chemical structure of the dye is shown in Figure 3, and some physicochemical characteristic of the dye is also given in Table IV. The stock solutions of 500 mg/L of RBBR are prepared with distilled water, and then they are diluted to the desired concentrations. The pH values of the solutions are adjusted with 0.1N NaOH and HCl solutions using a pH meter (Elmetron pH Meter).

Batch Sorption Studies

Batch sorption experiments are performed using 0.10 g of the modified PU-foam with 50 mL of RBBR solution in 150-mL Erlenmeyer flasks as functions of initial dye concentration, pH, temperature, and ionic strength. The samples are shaken in a temperature-controlled shaking water bath at 130 rpm. After the desired contact time, the samples are taken from shaking bath and they are centrifuged at 5000 rpm for 5 min. The concentrations of RBBR remained in supernatant are determined using T80 UV-vis Spectrophotometer at a wavelength of 593 nm, which is maximum absorbance. The amounts of RBBR sorbed onto the modified PU-foam are calculated using the following equation⁷:

$$q_t = (C_0 - C_e)V/m \quad (2)$$

where q_t is the amount of dye sorbed per unit of sorbent at any time (mg/g), C_0 is the initial concentration of RBBR solution

Table IV. Some Physical Properties of Remazol Brilliant Blue R

Common name	Remazol brilliant blue
Other name	Reactive blue
Class	Acidic
Solubility in ethanol	Good
Solubility in water	Good
Color Index	61,200
λ_{\max} (nm)	593
Color	Blue
Molecular weight (g/mol)	626.54
Molecular formula	C ₂₂ H ₁₆ N ₂ Na ₂ O ₁₁ S ₃

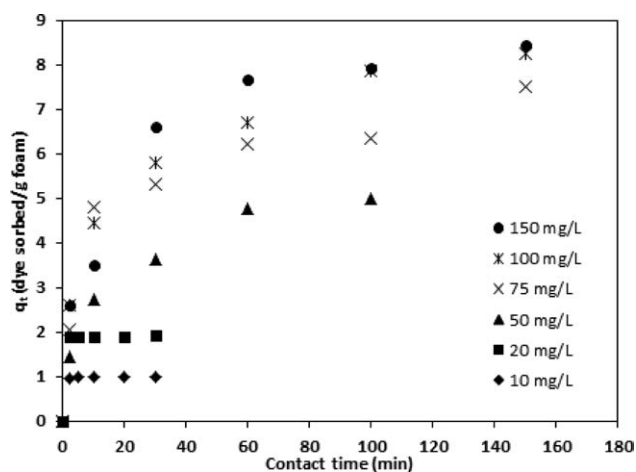


Figure 4. The effect of initial concentration to the sorption of dye on the foam ($\text{pH} = 3$; $T = 60^\circ\text{C}$).

(in mg/L), C_e is the concentration of RBBR remained in solution at equilibrium time (mg/L), m is the mass of sorbent (g), and V is the volume of dye solution used (L). The percent sorption of dye can be calculated as follows²:

$$\text{Sorption \%} = (C_o - C_e/C_o) \times 100 \quad (3)$$

where C_o and C_e (mg/L) are the liquid-phase concentrations of RBBR at the initial and equilibrium times, respectively.

Desorption Studies

First, the modified PU-foam used for the sorption of the initial dye concentration of 50 mg/L is separated from the dye solution after the sorption. Second, the dye-loaded modified PU-foam is washed gently with water to remove any unsorbed dye. Then the foam is shaken in a temperature controlled water bath with 10 mL of distilled waters at different pHs, 0.1N HCl solution, and CH_3COOH solution (50% v/v), one by one.⁹ Desorbed dye is determined as mentioned before.

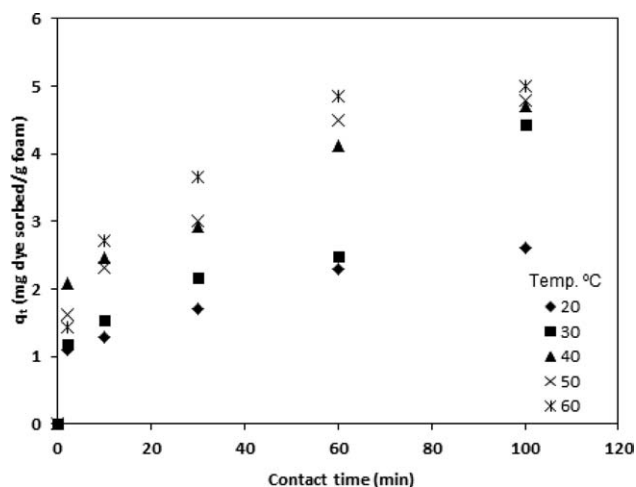


Figure 5. The effect of temperature to the sorption of dye on the foam ($C_o = 50 \text{ mg/L}$; $\text{pH} = 3$).

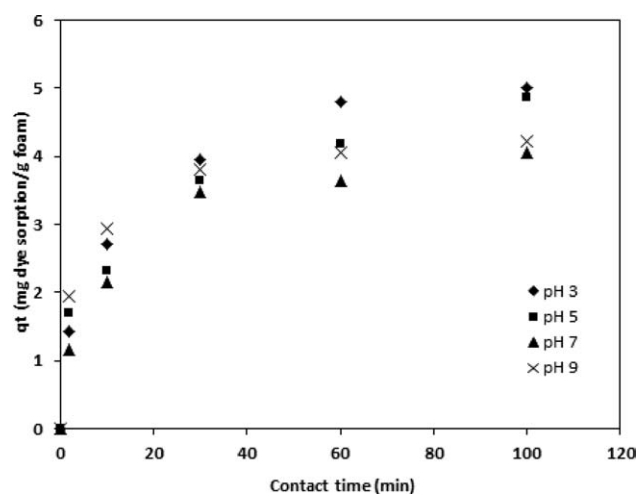


Figure 6. The effect of initial solution pH to the sorption of dye on the foam ($C_o = 50 \text{ mg/L}$; $T = 60^\circ\text{C}$).

FTIR Measurements. After sorption, each of the PU-foam, the modified PU-foam, and dye-loaded modified PU-foam samples is dried to the constant weight in an oven at 60°C for 12 h. Then, the infrared spectra of the samples were recorded in the wave number range of $4000\text{--}650 \text{ cm}^{-1}$ using an ATR spectrophotometer.

RESULTS AND DISCUSSION

Effect of Contact Time and Initial Dye Concentration on Sorption

The effect of initial dye concentration on the sorption is studied for six different concentrations of 10, 20, 50, 75, 100, and 150 mg/L at 60°C and $\text{pH} 3$ as a function of contact time, respectively. The obtained results are graphed in Figure 4. As shown in this figure, a gradual increase in the sorption occurs and it is attained to a maximum sorption with increasing contact time. It is seen that the maximum sorption occurs at a higher contact time for the higher dye concentrations, while it occurs at a lower contact time for the lower dye concentrations. For example, for the initial dye concentration of 10 mg/L, while the maximum amount of RBBR sorbed per gram of the modified

Table V. Final pH Values After Sorption for Each Initial pH and Various Initial Dye Concentrations

Initial pH	Final pH	Initial dye concentration (mg/L)
3	2.67	50
5	4.01	50
7	5.90	50
9	6.30	50
3	2.85	10
3	2.92	20
3	2.98	75
3	2.99	100
3	2.98	150

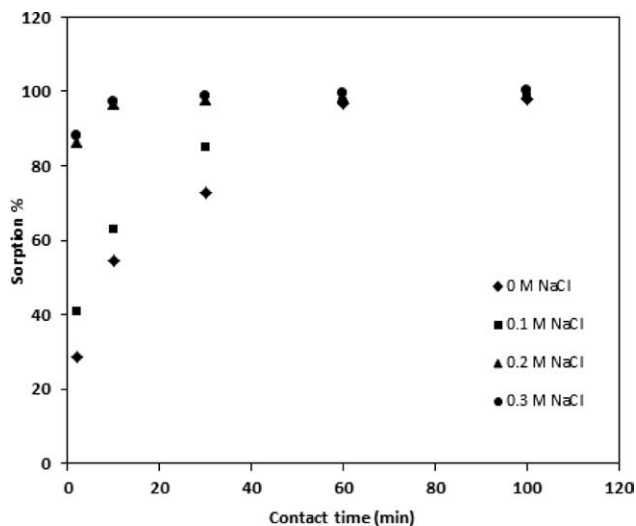


Figure 7. The effect of ionic strength NaCl to the sorption of dye on the foam ($C_0 = 50$ mg/L; $T = 60^\circ\text{C}$).

PU-foam is 1.00 mg/g (100%) at 5 min, it is found as 1.93 mg/g (96.83%) for the initial dye concentrations of 20 mg/L at 30 min. The maximum amount of RBBR sorbed per gram of the modified PU-foam is found to be 5.00 mg/g (100%) for the initial concentration of 50 mg/L at 100 min. For the initial dye concentrations of 75, 100, and 150 mg/L, the maximum sorptions are found to be 7.50 mg/g (100%), 8.24 mg/g (82.43%), and 8.42 mg/g (56.19%) at 150 min, respectively. For the initial dye concentration of 150 mg/L, after the 150 min, it is seen that the sorption goes up to 300 min, and the maximum sorption is found to be 9.34 mg/g (62.0%) at 300 min. Percent sorption decreases with increasing initial dye concentration. A similar result has also been recorded for the adsorption study of RBBR onto activated pine cone carbon by Geçgel and Kolancılar.¹⁰

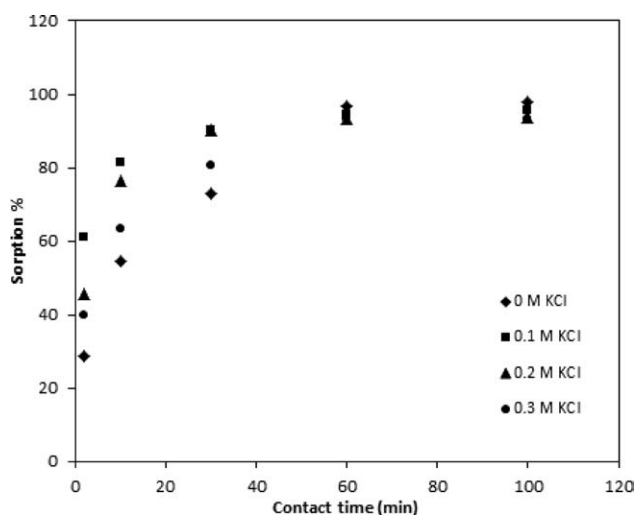


Figure 8. The effect of ionic strength KCl to the sorption of dye on the foam ($C_0 = 50$ mg/L; $T = 60^\circ\text{C}$).

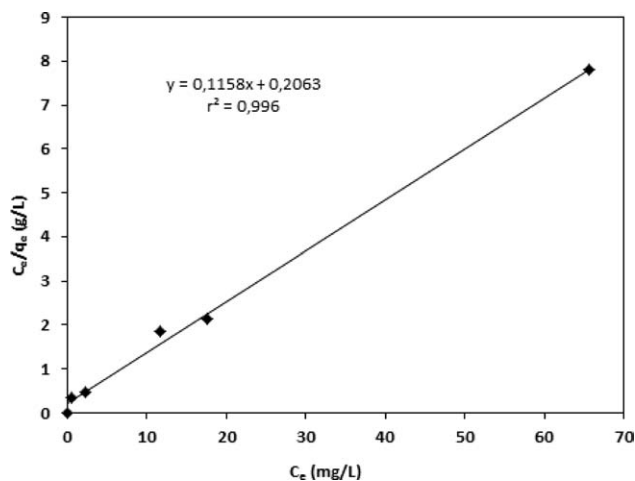


Figure 9. Langmuir isotherm of dye sorption ($\text{pH} = 3$; $T = 60^\circ\text{C}$).

Effect of Solution Temperature on Sorption

The effect of temperature on the sorption of RBBR on the modified PU-foam was studied at five different temperatures of 20, 30, 40, 50, and 60°C for the initial dye concentration of 50 mg/L at pH 3. The obtained results are illustrated in Figure 5. As shown in Figure 5, the results indicate that the amount of RBBR sorbed onto the modified PU-foam increases with increasing solution temperature from 20 to 60°C . The maximum sorption is attained within 100 min for the initial dye concentration of 50 mg/L. For example, for the initial dye concentration of 50 mg/L at a contact time of 100 min, when initial solution temperature increases from 20 to 60°C , the maximum amount of RBBR sorbed per unit gram of the modified PU-foam increases from 2.59 mg/g (51.99%) to 5.00 mg/g (100%). It is seen that the temperature has an important effect on sorption. The fact that the sorption increases with an increase in temperature indicates that a higher temperature is in favor of sorption, and thus the sorption process is of endothermic nature. Similar results have also been determined for the sorption

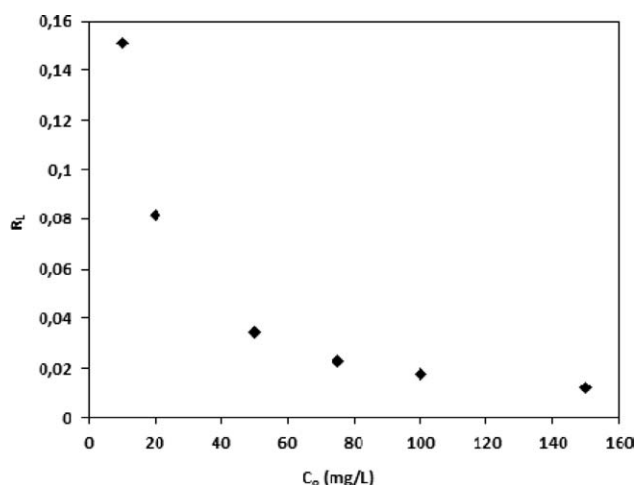


Figure 10. Dimensionless separation factor of dye sorption ($\text{pH} = 3$; $T = 60^\circ\text{C}$).

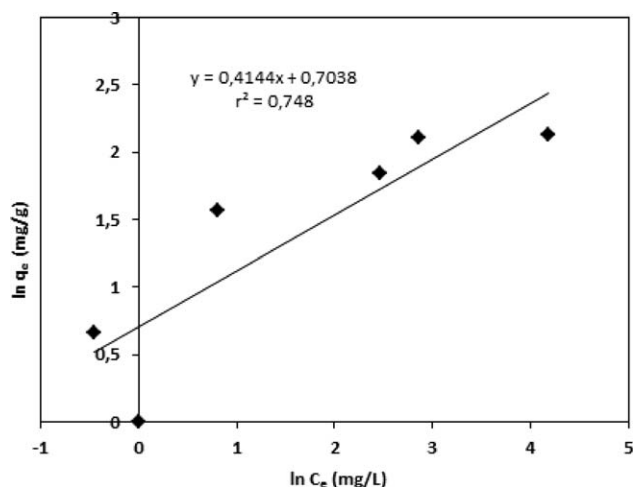


Figure 11. Freundlich isotherm of dye sorption (pH = 3; $T = 60^{\circ}\text{C}$).

of RBBR on pine cone activated carbon¹⁰ and peanut shell charcoal.¹¹

Effect of Initial pH on Sorption

The values of the initial pH of dye solution on the sorption are selected as 3, 5, 7, and 9 for the initial dye concentrations of 50 mg/L at 60°C and a contact time of 100 min. The results are graphed in Figure 6. As shown in this figure, the maximum amounts of RBBR sorbed per gram of the modified PU-foam decrease from 5 mg/g (100%) to 4.21 mg/g (84.37%) while initial solution pH increases from 3 to 9. Namely, acidic pH has a

high effect on the sorption. This phenomenon may be interpreted as follows.

If it notices to the PU structure of the rigid foam shown in Figure 2, it can be seen that the functional OH^- groups from cellulose and lignin on the surface of the PU-foam is present. As the initial pH of the dye solution decreases, the H^+ ions is released into solution medium, and thus negatively charged OH^- groups on the PU-foam has become more positive with excess H^+ ions. However, the surface of the foam may be more positively charged with HCl modification, also. This situation may be caused to a high sorption via the electrostatic interaction of anionic dye with more positively functional groups on the foam surface in acidic medium.

Moreover, to better clarify the sorption mechanism, the pH final values after sorption process are also measured for all initial dye concentrations and each initial dye pHs. The final pH values obtained are given in Table V. It can be seen from this table that the final pH values decrease after both the initial dye concentrations of 10, 20, 50, 75, 100, and 150 mg/L and initial pH values between 3 and 9. The reason for this drop in the initial pH values is not exactly known but may be attributed to the removal of the protons of some hydroxyl groups on the surface of the foam. Herein, it may be concluded that the first electrostatic effect mentioned above is dominant in the sorption process. However, the lowest sorption is observed at neutral pH (i.e., at pH 7). The low sorption may be attributed that the amounts of H^+ and OH^- ions is equal to each other in neutral pH medium. Because, the equal amounts of hydrogen and hydroxyl

Table VI. Comparison of Experimental Adsorption Capacities of RBBR to Some Sorbents

Capacity (mg/g) (in %)	Experimental conditions	Biosorbent/ Adsorbent	References
5.0 (100)	$C_o = 50 \text{ mg/L}$, $T = 60^{\circ}\text{C}$, pH = 3, $V = 10 \text{ mL}$, and $m = 0.10 \text{ g}$	PU-Foam	This study
9.34 (62)	$C_o = 150 \text{ mg/L}$, $T = 60^{\circ}\text{C}$, pH = 3, $V = 10 \text{ mL}$, and $m = 0.10 \text{ g}$	PU-Foam	This study
49.35 (98.70)	$C_o = 50 \text{ mg/L}$, $T = 25^{\circ}\text{C}$, pH = 7.0, $V = 100 \text{ mL}$, and $m = 0.10 \text{ g}$	Activated pine cone	10
9.41 (94.10)	$C_o = 50 \text{ mg/L}$, $T = 40^{\circ}\text{C}$, pH = 3, $V = 50 \text{ mL}$, and $m = 0.25 \text{ g}$	Peanut shell	11
9.35 (93.50)	$C_o = 50 \text{ mg/L}$, $T = 60^{\circ}\text{C}$, pH = 3, $V = 50 \text{ mL}$, and $m = 0.25 \text{ g}$	Peanut shell charcoal	11
12.59 (25.18)	$C_o = 100 \text{ mg/L}$, $T = 30^{\circ}\text{C}$, pH = natural pH, $V = 100 \text{ mL}$, and $m = 0.20 \text{ g}$	Corn corb activated carbon	17
45.70 (83.73)	$C_o = 150 \text{ mg/L}$, $T = 30^{\circ}\text{C}$, pH = 2, $V = 100 \text{ mL}$, and $m = 0.0534 \text{ g}$	Immobilized active <i>Scenedesmus quadricauda</i>	18
47.90 (90.28)	$C_o = 150 \text{ mg/L}$, $T = 30^{\circ}\text{C}$, pH = 2, $V = 100 \text{ mL}$, and $m = 0.0513 \text{ g}$	Immobilized heat inactive <i>S. quadricauda</i>	18
53.46 (53.46)	$C_o = 100 \text{ mg/L}$, $T = 25^{\circ}\text{C}$, pH = 2, $V = 100 \text{ mL}$, and $m = 0.10 \text{ g}$	<i>Phanerochaete chrysosporium</i>	19
65.18 (65.18)	$C_o = 100 \text{ mg/L}$, $T = 25^{\circ}\text{C}$, pH = 2, $V = 100 \text{ mL}$, and $m = 0.10 \text{ g}$	Loofa sponge immobilized <i>P. Chrysosporium</i>	19

C_o , initial dye concentration; T , temperature, V , solution volume; and m , adsorbent/biosorbent amount.

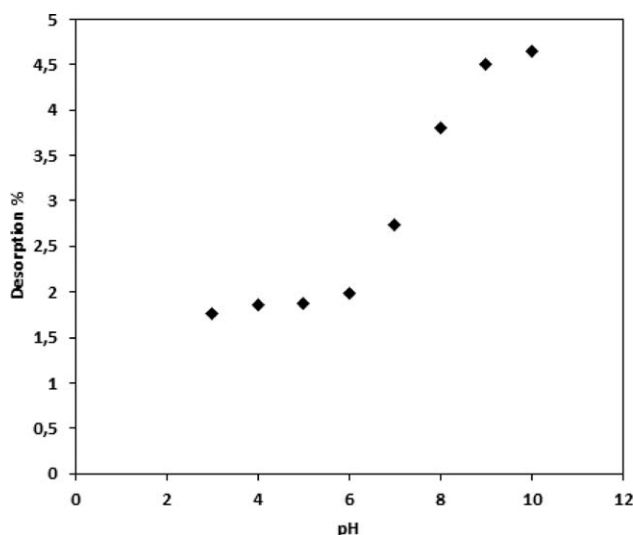


Figure 12. The effect of pH on the desorption of RBBR ($C_0 = 50$ mg/L; pH = 3; $T = 60^\circ\text{C}$).

ions in solution medium may lead to less ionization of dye molecule, and therefore the low sorption may be resulted.

Effect of Ionic Strength on Sorption

The effects of ionic strength to the sorption of RBBR onto the modified PU-foam are studied in the presence of NaCl and KCl ions at 60°C and pH 3, respectively. The concentrations of NaCl and KCl are selected as 0.1, 0.2, and 0.3M (mol/L). The results obtained are graphed in Figures 7 and 8. From these figures, it is seen that the sorption remarkably increases in the presence of NaCl and KCl within 30 min. After this time, the sorption slows down and then it levels off. The addition of NaCl and KCl into the solution causes an increase in the degree of dissociation of the dye molecules by facilitating the protonation.¹² Therefore this effect leads to the increase of the amount of dye adsorbed on a sorbent's surface. A similar effect has also been recorded for the sorption of remazol brilliant FCF in soil.¹³ However, it is seen that it is more at higher NaCl concentrations while the sorption is less at higher KCl concentrations.

Isotherm Studies on Sorption

The sorption equilibrium data are fitted for the Langmuir¹⁴ and Freundlich¹⁵ isotherms using commonly in the literature. The Langmuir sorption isotherm indicates monolayer sorption, and the Freundlich isotherm points a multilayer sorption on heterogeneous surfaces.

These isotherm equations can be expressed as follows:

$$\text{Langmuir equation : } C_e/q_e = 1/Q_o \cdot b + C_e/Q_o \quad (4)$$

$$\text{Freundlich equation : } \ln q_e = \ln k + 1/n \ln C_e \quad (5)$$

where q_e is the amount of dye sorbed at equilibrium time (mg/g) and C_e is the equilibrium concentration of the dye remained in solution (mg/L). k and n are the Freundlich isotherm constants, which indicate the capacity and intensity of the sorption, respectively. Q_o and b are the Langmuir constants, which indicate the capacity and energy of sorption, respectively.

The plot of C_e/q_e versus C_e is shown in Figure 9. The plot is in the best harmony with the Langmuir isotherm with a correlation coefficient of 0.996. The values of Q_o and b are calculated from the slope and intercept of the plot of C_e/q_e against C_e . The estimated values of Q_o and b are 8.63 mg/g and 0.56 L/mg, respectively. The fact that the sorption process obeys the Langmuir isotherm with a high correlation value of 0.996 indicates a monolayer sorption on the surface of the modified PU-foam.

However, the essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L , that is given by the following equation¹⁶:

$$R_L = 1/(1 + b C_0) \quad (6)$$

where C_0 is the initial sorbate concentration (mg/L) and b is the Langmuir constant (L/mg). The value of R_L indicates the shape of the isotherm for a sorption process:

$$R_L > 1 : \text{unfavorable}$$

$$0 < R_L < 1 : \text{favorable}$$

$$R_L = 0 : \text{irreversible}$$

$$R_L = 1 : \text{linear}$$

Herein, the values of R_L are found to be between 0 and 1, indicating a favorable sorption (see Figure 10). If it is noticed to Figure 10, it is seen that the R_L values decrease with increasing initial dye concentration. The fact that the R_L value decreases from 1 to zero indicates a more favorable sorption.

However, it is seen that the sorption is in a low harmony with the Freundlich isotherm due to a lower correlation coefficient of 0.748 (see Figure 11). The values of k and n are calculated from the slope and intercept of the plot of $\ln q_e$ versus $\ln C_e$. The values of k and n are found to be 2.02 mg/g and 2.41 g/L, respectively.

The Comparison of Experimental Sorption Capacity of the Modified PU-Foam to Some Sorbents

The maximum amounts of dye adsorbed by various adsorbents in equilibrium time vary as a function of various experimental conditions such as initial concentration, temperature, pH, adsorbent dose, solution volume, etc. Especially, the amount of adsorbent dose has a very important effect on the estimation of the maximum amounts of dye adsorbed per unit of adsorbent. In this study, it is seen that the most sorption occurs at pH 3 and 60°C for all initial concentrations of RBBR. For example, the experimental sorption capacities determined for the initial dye concentrations of 50 and 150 mg/L at pH 3 and 60°C are compared with that of other adsorbents, and the comparisons are given in Table VI. As shown in the table, when the mass of the modified PU-foam used for the sorption of RBBR is 0.10 g (ratio adsorbent dose/solution volume = 10.0 g/L), the sorption capacities of the foam are found as 5.0 mg/g and 9.34 mg/L for the initial concentrations of 50 and 150 mg/L, respectively. The values of percent sorption are also 100 and 62% for the initial concentrations of 50 and 150 mg/L, respectively. If it is noticed to Table VI, in a work done by Geçgel and Kolancılar, it is seen that the adsorption capacity of activated

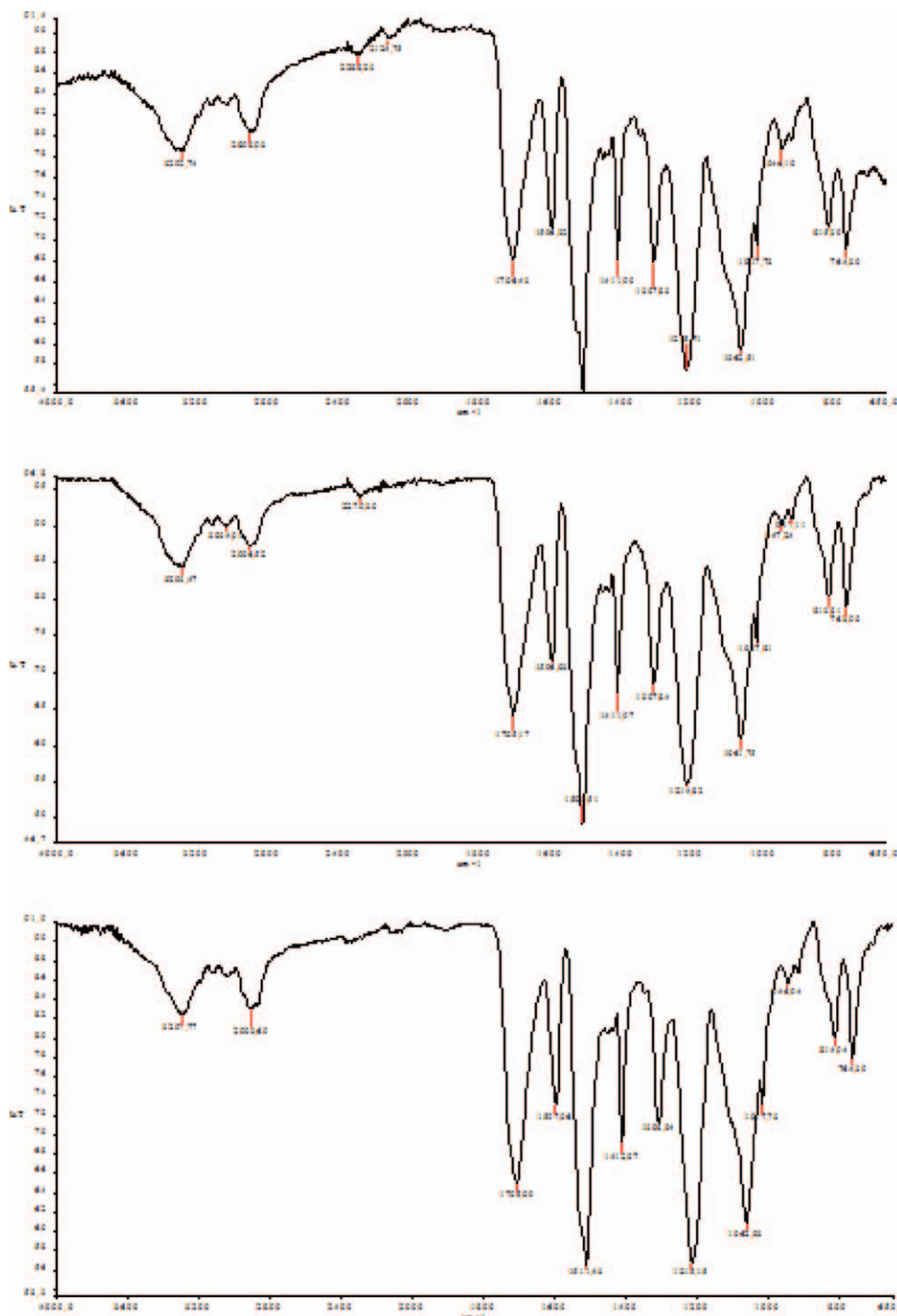


Figure 13. FTIR spectra of (a) PU foam, (b) modified PU-foam, and (c) dye sorbed modified PU-foam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

pine cone has been found as 49.35 mg/g when the mass of activated pine cone used for the sorption of RBBR is 0.10 g (ratio adsorbent dose/solution volume = 1.0 g/L), and the percent sorption has been found as 98.70% for activated pine cone.¹⁰ In another work, when the mass of corn corb activated carbon used for the sorption of RBBR is 0.20 g (ratio adsorbent dose/solution volume = 2.0 g/L), the adsorption capacity of corn corb activated carbon has been found as 12.59 mg/g, and the

percent sorption has been estimated as 25.18%.¹⁷ The capacity values determined for the other adsorbents used in the adsorption of RBBR by Ergene et al.¹⁸ and Iqbal and Saeed¹⁹ can be seen in Table VI.

Desorption of Dye from the Modified PU-Foam

To investigate the desorption possibility of the RBBR from the modified PU-foam, batch desorption experiments were

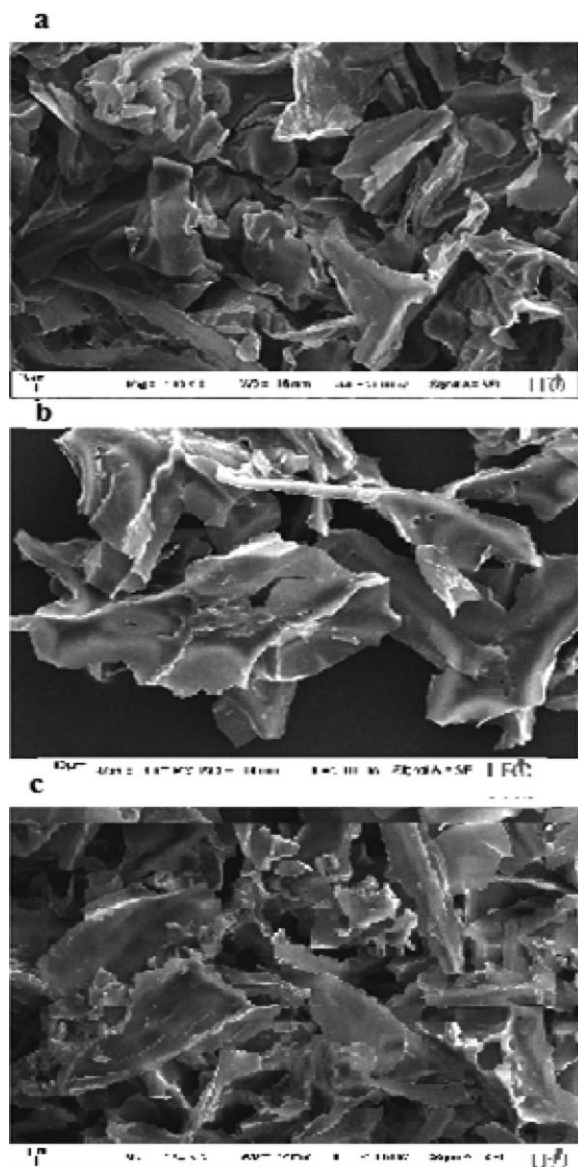


Figure 14. SEM Images of (a) PU foam, (b) modified PU-foam, and (c) dye sorbed modified PU-foam.

performed between pH 3 and 10 as in the sorption process. Herein, the dye-loaded modified PU-foam was shaken with 10 mL of various alkaline waters for 60 min, separately. The amounts of RBBR passing into the liquid phase from the surface of the foam are determined by UV-vis spectrometer as before. The obtained results are graphed in Figure 12. If it notice to this figure, a very low desorption is seen with various alkaline waters. For example, desorption percent between pH 3 and 10 are changed between 1.70 and 4.60%. A very low desorption of RBBR indicates that a chemical activation or chemisorption may be taken place between the active sites of the foam and the functional groups of RBBR. However, desorption process has also been performed using 0.1N HCl and H₂SO₄ acids and 50% CH₃COOH, and at the end any desorption from the surface of the modified PU-foam is no

observed. Therefore, it can be said that the sorption of RBBR onto the modified PU-foam carries out significantly via a chemisorption mechanism. This situation is also confirmed by FTIR results below. Similar results have also been reported for the removal of Rhodamine B from aqueous solution by biogas waste slurry²⁰ and the adsorption of Congo red onto fly ash.⁹

FTIR Study of Dye Sorption on Foam

Before and after sorption, FTIR spectra of the foam are shown in Figure 13(a–c), respectively. The broad band at 3292.74 cm⁻¹ indicates the existences of OH groups of cellulose and the vibration of NH and NH₂ groups.²¹ After treated with HCl of the foam, this band is slightly shifted to 3293.47 cm⁻¹. After the sorption of the dye, this band is shifted to 3297.77 cm⁻¹.²² The strong absorption bands at 2898.93 can be assigned to CH stretching of carboxyl groups.²³ After treated with HCl of the foam, the peak are slightly shifted to 2906.52 cm⁻¹. The peak at 2906.52 cm⁻¹, after the sorption of the dye, is slightly shifted to 2903.69 cm⁻¹ and its intensity is slightly increased. The very strong peaks at 1706.43 and 1596.32 cm⁻¹ can be attributed to the amide I and amide II bonds.²¹ After the treatment with HCl of the foam and the sorption of the dye, any change at the intensities of these both bonds did not occur. The peak at 1411.90 cm⁻¹ indicates to phenyl fragment in the structures of the foam.²¹ After the treatment with HCl of the foam and the sorption of the dye, any change at the intensity of the bond did not occur, also. The band at 1307.83 cm⁻¹ shows to the stretch of C-(CH₃)₂.²³ Absorption peaks at around 1200–1000 cm⁻¹ indicate to the existence of C–O single bond in carboxylic acids, alcohols, phenols, and esters. Herein, very strong absorption peaks at 1062.51 and 1017.78 cm⁻¹ may be assigned to C–O and C–O–C stretching bonds in the structure of the foam.²³ After treated with HCl, the intensity of this band at 1062.51 cm⁻¹ is slightly decreased and very slightly shifted to 1061.75 cm⁻¹. This bond is not affected with dye sorption. The band at 1017.78 cm⁻¹ is also not changed by dye sorption. A strong band at 1215.71 cm⁻¹ points to the C=O stretching band of carboxylic groups.²⁴ After adsorption, the intensity of this band is slightly increased.

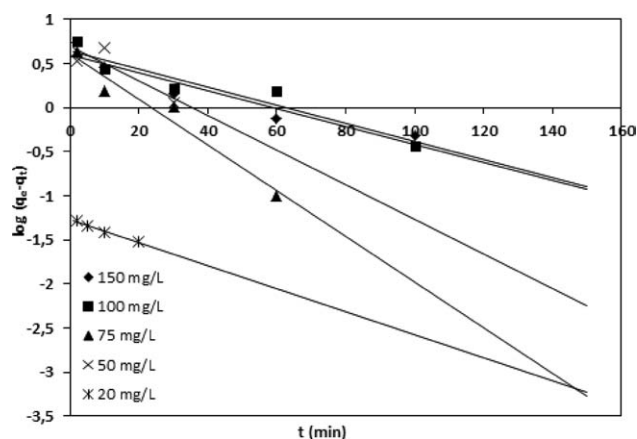


Figure 15. Pseudo-first order kinetics of dye sorption in various initial concentrations (pH = 3; T = 60°C).

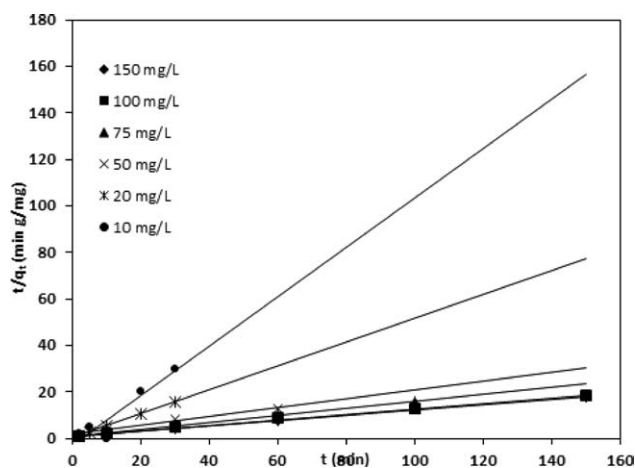


Figure 16. Pseudo-second order kinetics of dye sorption in various initial concentrations (pH = 3; $T = 60^{\circ}\text{C}$).

The bands at 815.30 and 764.30 cm^{-1} indicate to the vibrations of aromatic skeleton in the structure of the PU-foam.²¹ All these findings show that the dye molecules is sorbed with a chemical activation or chemisorption process onto the foam, probably indicating electrostatic interactions.

SEM Studies

The SEM images of the foams are demonstrated in Figure 14(a–c). Figure 14(a–c) show SEM images of the raw foam, the modified PU-foam treated with HCl and the dye loaded modified PU-foam, respectively. It is evident from Figure 14(a) that the pores within the particles of the PU-foam are highly heterogeneous. After treated of the foam with HCl, the some caves have taken place on the surface of the foam to adsorb the dye molecule [Figure 14(b)]. After the sorption, the surface of the PU-foam is remarkably coated with the molecules of RBBR, indicating a surface sorption due to a heterogeneous surface [Figure 14(c)].

Kinetic Studies on Sorption

Several models have been proposed to express the sorption mechanism of solute molecules onto a sorbent: (a) pseudo-first order kinetic model, (b) pseudo-second order kinetic model, and (c) intraparticle diffusion model.

A pseudo-first order kinetic model of Lagergren²⁵ is given as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

a pseudo-second order kinetic model of Ho and McKay is as follows^{26,27}:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

and an intraparticle diffusion model of Weber and Morris^{28,29} is shown as

$$q_t = k_i \cdot t^{1/2} \quad (9)$$

where k_1 is rate constant for pseudo-first order model, k_2 is rate constant for pseudo-second order model, and k_i is intraparticle diffusion rate constant. q_e and q_t are the amount sorbed of solute per unit adsorbent at equilibrium and any time, respectively. In eq. (8), the initial sorption rate is $h = k_2 q_e^2$.

The sorption of RBBR on the PU-foam in this study was investigated in terms of the above-mentioned kinetics models for understanding the sorption kinetics.

First, the plots of $\log(q_e - q_t)$ against t for the pseudo first-order model given in eq. (7) are drawn for all initial concentrations at 60°C and pH 3. The plots obtained for the pseudo-first order kinetic model are showed in Figure 15. The results of the linear regression analysis of these plots are given in the following.

$$\text{For } 20 \text{ mg/L; } y = -0.013x - 1.269 \quad r_2 = 0.970$$

$$\text{For } 50 \text{ mg/L; } y = -0.019x + 0.693 \quad r_2 = 0.753$$

$$\text{For } 75 \text{ mg/L; } y = -0.026x + 0.619 \quad r_2 = 0.954$$

$$\text{For } 100 \text{ mg/L; } y = -0.010x + 0.651 \quad r_2 = 0.912$$

$$\text{For } 150 \text{ mg/L; } y = -0.10x + 0.5950 \quad r_2 = 0.904$$

From the linear regression analysis obtained, it is determined that the values of correlation coefficients, r^2 , obtained are 0.970, 0.753, 0.954, 0.912, and 0.904 for the initial concentrations of

Table VII. Kinetic Parameters of the Sorption of RBBR on PU-Foam (pH = 3; $T = 60^{\circ}\text{C}$)

C_o (mg/L)	Pseudo-first order kinetics			Pseudo-second order kinetics			Intraparticle diffusion		
	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	k_2 (g/mg/min)	R^2	k_i (mg/g/min ²)	R^2	q_e^a (mg/g)
10	-	-	-	1.003	20.708	1	0.008	0.434	1
20	0.053	0.029	0.97	1.937	3.598	0.999	0.011	0.887	1.936
50	4.931	0.043	0.753	5.263	0.022	0.980	0.511	0.986	4.775
75	4.159	0.059	0.954	6.666	0.030	0.998	0.449	0.788	6.329
100	4.477	0.023	0.912	8.547	0.014	0.994	0.455	0.842	8.243
150	3.935	0.023	0.904	8.695	0.187	0.998	0.455	0.825	8.429

^aExperimental sorption capacity.

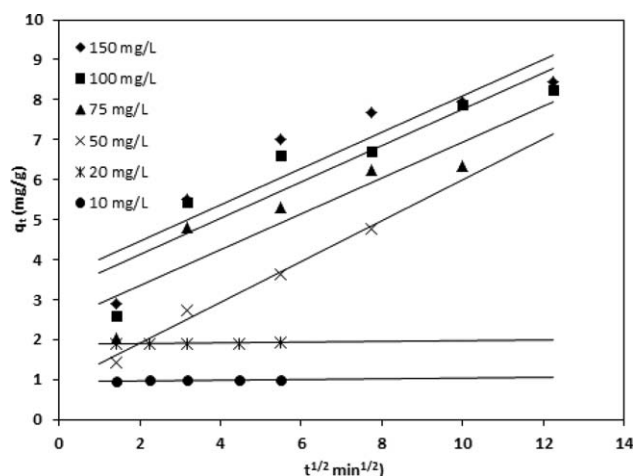


Figure 17. Intraparticle diffusion of dye sorption in various initial concentrations (pH = 3; T = 60°C).

20, 50, 75, 100, and 150 mg/L, respectively. The plot is not occurred for the initial concentration of 10 mg/L due to a sorption of 100% within 5 min.

Second, the linear plots of t/q_t versus t for the pseudo-second order model in eq. (8) are obtained for all initial concentrations at 60°C and pH 3. These plots are shown in Figure 16. The results of the linear regression analysis of these plots are given in the following.

For 10 mg/L; $y = 0.997x + 0.048$ $r_2 = 1$
 For 20 mg/L; $y = 0.516x + 0.074$ $r_2 = 0.999$
 For 50 mg/L; $y = 0.19x + 1.6230$ $r_2 = 0.980$
 For 75 mg/L; $y = 0.150x + 0.740$ $r_2 = 0.998$
 For 100 mg/L; $y = 0.117x + 0.930$ $r_2 = 0.994$
 For 150 mg/L; $y = 0.115x + 0.704$ $r_2 = 0.998$

From linear regression analysis obtained, the values of r^2 are found to be 1.0, 0.999, 0.980, 0.998, 0.994, and 0.998 for the initial concentrations of 10, 20, 50, 75, 100, and 150 mg/L, respectively. The correlation coefficients from the pseudo first and second order models have very high values. Kinetic parameters of the sorption are also given Table VII.

As can be seen from the Table VII, because the values of q_e obtained from pseudo-first order kinetic model is not in agreement with experimental data $q_e(exp)$, even though the correlation coefficients have high values, the sorption does not obey this model. But the values of q_e determined from the pseudo-second order kinetic model are in harmony with experimental data, $q_e(exp)$, and therefore the sorption obeys the pseudo-second order kinetics. Similar results have also been reported for the adsorption of Congo red onto fly ash⁹ and the adsorption of MB onto perlite.³⁰ This situation may be attributed to a chemical activation between RBBR molecules with the functional groups of the PU-foam.

Finally, due to mass transfer effects, the plots of q_t versus $t^{1/2}$ for intraparticle diffusion model given in eq. (9) are obtained

for all initial dye concentrations at 60°C and pH 3. These plots are demonstrated in Figure 17. The results of linear regression analysis of these plots are given in the following.

For 20 mg/L; $y = 0.011x + 1.864$ $r_2 = 0.887$
 For 50 mg/L; $y = 0.511x + 0.867$ $r_2 = 0.986$
 For 75 mg/L; $y = 0.449x + 2.445$ $r_2 = 0.788$
 For 100 mg/L; $y = 0.455x + 3.250$ $r_2 = 0.842$
 For 150 mg/L; $y = 0.455x + 3.534$ $r_2 = 0.825$

From the linear regression analysis obtained, except the initial concentration of 10 mg/L, the values of r^2 are found to be 0.887, 0.986, 0.788, 0.842, and 0.825 for the initial concentrations of 20, 50, 75, 100, and 150 mg/L, respectively. Because the values of the correlation coefficients between 0.825 and 0.986 are not very high, it may be said that the sorption process is partially in consistent with the intraparticle diffusion kinetics.

Thermodynamic Studies on Sorption

For the better understanding of the effect of temperature on the sorption, it is important to study the thermodynamic parameters such as standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°). Herein, the values of ΔG° , ΔH° , and ΔS° related to the sorption of RBBR onto the modified PU-foam were determined using the following equations: The Gibbs free energy of the sorption by using equilibrium constant (K_c) can be determined from the following equation^{31,32}:

$$\Delta G^\circ = -RT \ln K_c \quad (10)$$

The values of K_c at various temperatures is estimated from the following equation:³³

$$K_c = \frac{C_{Ae}}{C_{Se}} \quad (11)$$

where C_{Ae} is the equilibrium concentration (mg/L) of dye sorbed on the sorbent. C_{Se} is the concentration of dye unsorbed in solution at the equilibrium time. The values of ΔH° and ΔS° of the sorption can be calculated by using Van't Hoff equation given in the following^{31,32}:

$$\ln K_c = \frac{-\Delta K_{ads}^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (12)$$

Table VIII. Thermodynamic Parameters of Sorption of RBBR onto Polyurethane Type Foam at Various Temperatures (pH = 3; $C_o = 50$ mg/L)

Temperature (°C)	ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (J/mol K)
20	-187		
30	-5168	109,869	381
40	-16,167		
50	-8521		
60	-17,200		

where R is the gas constant, K_c is sorption equilibrium constant. The plot of $\ln K_c$ versus $1/T$ (in Kelvin) should be linear. The slope of Van't Hoff plot is equal to $-\Delta H_{\text{ads}}^{\circ}/R$, and its intercept is equal to $\Delta S^{\circ}/R$. Thermodynamic parameters estimated from Van't Hoff plot for the sorption of RBBR onto the PU-foam are given Table VIII. As shown in this table, the negative values of ΔG° obtained for all temperatures indicate the spontaneous nature of the sorption process. ΔH° is found to be 109.86 kJ/mol, indicating an endothermic sorption. Namely, the sorption is in favor of increasing temperature. ΔS° is found as 381 J/mol K. The positive value of ΔS° indicates that a structural change may be occurred between the PU-foam and RBBR molecules. Similar values of negative ΔG° , positive ΔH° and ΔS° have also been reported for the removals of MB, methyl violet, and toluidine blue O by almond shell (*Prunusdulcis*), an agricultural byproduct.³⁴

CONCLUSIONS

PU-type rigid foam was first fabricated by using the powders of peanut shell, and then it was used as a sorbent for the removal of RBBR, an anionic dye. Effects of initial dye concentration, pH, temperature, and ionic strength on the sorption were investigated. It was seen that the sorption of the dye increased with increasing initial dye concentration, temperature, and ionic strength while it was decreasing with increasing pH. Desorption and FTIR studies showed that a chemisorption process could be occurred between dye and the modified PU-foam, probably indicating electrostatic interactions. Sorption process was in the best agreement with the Langmuir isotherm and the pseudo-second order kinetic model. From the thermodynamic studies, the standard Gibbs free energy, ΔG° was negative for all temperatures. The values of standard enthalpy ΔH° and standard entropy ΔS° were determined as positive. From these results, it could be said that the PU-type rigid foam prepared with peanut shell would be used an alternative sorbent for the removal of dye pollution from wastewaters.

ACKNOWLEDGMENTS

This study was supported by The Scientific and Technical Research Council of Turkey (TUBITAK), project number: 107Y043.

REFERENCES

- Werbowski, R.; Chow, A. *Talanta* **1996**, *43*, 263.
- Chow, A.; Branagh, W.; Chance, J. *Talanta* **1990**, *37*, 407.
- Fong, P.; Chow, A. *Sep. Sci. Technol.* **1992**, *27*, 1291.
- Fong, P.; Chow, A. *Talanta* **1992**, *39*, 497.
- Fong, P.; Chow, A. *Anal. Chim. Acta* **1992**, *260*, 123.
- Alma, M. H.; Baştürk, M. A.; Diğrak, M. *Mater. Sci. Lett.* **2003**, *22*, 1225.
- Sakalar, N.; Bilir, M. H.; Acemioğlu, B.; Alma, M. H. *Asian J. Chem.* **2010**, *22*, 5649.
- Philips, L. N.; Parker, D. B. V. *Polyurethanes Chemistry, Technology and Properties*, Illife Books Ltd, London, **1965**.
- Acemioğlu, B. J. *Colloid Interface Sci.* **2004**, *274*, 371.
- Geçgel, Ü.; Kolancılar, H. *Nat. Product Res. First* **2011**, *1*.
- Şakalar, N. Investigation of use as adsorbent of peanut shell and the charcoal of peanut shell for the removal of Safanine and remazolbrillant blue R by adsorption technique. MSc Thesis, Kahramanmaraş Sutcu Imam University, K. Maraş, **2009** (in Turkish).
- Dogan, M.; Abak, H.; Alkan, M. *J. Hazard. Mater.* **2009**, *164*, 172.
- German-Heins, J.; Flury, M. *Geoderma* **2000**, *46*, 129.
- Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1361.
- Freundlich, H. *Phys. Chem.* **1906**, *57*, 384.
- Khattry, S. D.; Singh, M. K. *Indian J. Chem. Technol.* **1999**, *3*, 114.
- Ahmad, M. Z. C.; Yun, E. T. C.; Abustan, I.; Sulaiman, S.K. *Int. J. Eng. Technol.* **2011**, *11*, 283.
- Ergene, A.; Ada, K.; Tan, S.; Katircioğlu, H. *Desalination* **2009**, *249*, 1308.
- Igbal, M.; Saeed, A. *Process Biochem.* **2007**, *42*, 1160.
- Namasivayam, C.; Yumuna, R. T. *Water Air Soil Pollut.* **1992**, *65*, 101.
- Dmitrienko, S. G.; Sviridova, O. A.; Pyatkova, L. N.; Senyavin, V. M. *Anal. Bioanal. Chem.* **2002**, *374*, 361.
- Kapoor, A.; Viraraghavan, T. *Bioresour. Technol.* **1997**, *61*, 221.
- Haamed, B. H.; Mahmoud, D. K.; Ahmad, A. L. *J. Hazard. Mater.* **2008**, *158*, 499.
- Bayramoğlu, G.; Arica, M. Y. *J. Hazard. Mater.* **2007**, *143*, 135.
- Lagergren, S. *Kung Sven Vetén Hand* **1898**, *24*, 1.
- Ho, Y. S.; McKay, G. *J. Environ. Sci. Health Part B* **1998**, *76*, 183.
- Ho, Y. S.; McKay, G. *Chem. Eng. J.* **1998**, *70*, 115.
- Weber, W. J.; Morris, J. C. *J. Sanit Eng. Div. Proc. ASCE* **1963**, *89*, 31.
- Balci, S. *Clay Miner.* **1999**, *34*, 647.
- Acemioğlu, B. *Chem. Eng. J.* **2005**, *106*, 73.
- Hema, M.; Arivoli, S. *Int. J. Phys. Sci.* **2007**, *2*, 10.
- Acemioğlu, B. *Bioresour. Technol.* **2004**, *93*, 99.
- Acemioğlu, B.; Alma, M.H. *J. Colloid Interface Sci.* **2001**, *243*, 81.
- Duran, C.; Ozdes, D.; Gundogdu, A.; Senturk, H. B. *J. Chem. Eng. Data* **2011**, *56*, 2136.