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Adsorption of Cu^{2+} ions by polyurethane-type rigid foam produced from peanut shell

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ABSTRACT

Polyurethane-type rigid foam produced from peanut shell (peanut shell-based polyurethane foam (PSPUF)) was used as an adsorbent for the removal of Cu^{2+} ions from aqueous solution. The effects of contact time, solution pH, and temperature on the adsorption were investigated at a constant concentration of Cu^{2+} ions. The equilibrium time of the adsorption was determined as 60 min. The maximum adsorption for Cu^{2+} ions onto the PSPUF was revealed to be between 597.75 and 632.63 mg g^{-1} under all the experimental conditions such as contact time, solution pH, and temperature. The distribution coefficients for Cu^{2+} ions adsorbed onto the PSPUF were found to be between 781 and 984 L kg^{-1} for all the pH and temperatures. The distribution coefficients indicated that Cu^{2+} ions could be adsorbed by extraction from aqueous solution. Adsorption kinetics followed the pseudo-second-order and the intraparticle diffusion models. The negative values of Gibbs free energy change ($\Delta G°$) showed spontaneous nature of the adsorption. The value of 2.68 kJ mol^{-1} of the standard enthalpy change of the adsorption ($\Delta H°$) indicated a physical adsorption. The positive value of 17.32 J $mol^{-1}K^{-1}$ of the standard entropy change of the adsorption ($\Delta S°$) showed a randomness adsorption of Cu^{2+} ions onto the PSPUF surface. Moreover, Fourier transform infrared, scanning electron microscopic, and the intraparticle diffusion studies indicated a surface adsorption of Cu^{2+} ions onto the PSPUF.

Keywords: Peanut shell; Polyurethane-type rigid foam; Cu^{2+} ions; Adsorption; Distribution coefficient

1. Introduction

Metal pollution such as copper, iron, cadmium, zinc, lead, chromium from industrial effluents leads to human health and various environmental problems. Therefore, the removal of such contaminations from the effluents is highly necessary. For this purpose, many methods such as electrolysis, chemical coagulation and flocculation, reverse osmosis, adsorption, and biological treatments have been used for treating metal-containing effluents [1]. Since each of these methods includes some advantages and disadvantages [2], the adsorption method has been preferred and used commonly by the scientists. The adsorption is seen to be an effective method for the removal of metals or dyes in the effluents. Activated carbon is known to be most effective in the adsorption method. Due to the high price of activated carbon, however, the researchers commonly prefer low-cost adsorptive materials such as lignocellulosic wastes (wood sawdust [3,5], tree barks [6–9], fruit peels [10,11], orange peel [12], and pumpkin seed hull [13]), organic materials (peat [14–16], carbotrap, and chromosorb 106 polymer [17]), inorganics (clay [18–20], silicate [21], perlite [2,22], fly ash [1,23]), and biological materials (fungus [24,25], yeast [26], alge [27]). Apart from these materials, low-cost new adsorbent materials have also been prepared and used intensely in the adsorption studies recently. For example,

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core@shell SiO_2@CeO_2 nanoparticles [28], Fe_3O_4 magnetic nanoparticles and gum xanthan-based hydrogel nanocomposites [29], and phenolated wood resin [30] can be given as examples of new adsorbent substances in the adsorption of metals. Moreover, polyurethane foams (PUFs) [31–34] have also been used as sorbent or extractant materials for the removal of metals from solution.

The importance of this study, as an alternative to activated carbon, is to use the polyurethane-type rigid foam as a new adsorbent (peanut shell-based polyurethane foam (PSPUF)) that we have produced from peanut shell (PS) for the adsorption of Cu^{2+} ions from aqueous solution [35]. At the same time, the PSPUF is an economic adsorbent material for adsorption; it is easily obtained. For the adsorption of Cu^{2+} ions, therefore, it was preferred and used as a new adsorbent.

The effects of contact time, solution pH, and temperature on the adsorption in a constant concentration of Cu^{2+} ions are studied. Moreover, distribution coefficients and kinetic and thermodynamic studies on the adsorption are performed. This study is original because the adsorption of Cu^{2+} ions with the PSPUF has not been reported in the literature so far.

2. Experimental

2.1. Materials

The PS powders (in 80 mesh size) were utilized as a natural polyol to produce the PUF. The ingredients used in the making of the foam were provided from Ispol Company in Turkey. These ingredients are polyethylene glycol (PEG-400, commercial polyol), triethylenediamine (TEDA-D33LV, foaming catalyst), monoethylene glycol (MEG, polyol), and polymeric diphenylmethane diisocyanate (PMDI-TED-31, cross-linking agent).

2.2. Methods

PSPUF from PS has been prepared according to the method described in another work made by us [35]. For the production of the PSPUF, the PS particles were first liquefied as mentioned in the literature [35], and then the PSPUF was prepared using the liquefied PS as mentioned below.

First, the pH of the liqufied PS was regulated to 7. Second, 35 g of the PS, 33% of the foaming catalyst (TEDA-D33LV), 2.5% surfactant (PEG-400), 10% MEG, and 1% blowing agent (i.e. water) were premixed homogeneously in a paper cup. Then, a certain amount of the PMDI-TED-31 as cross-linking agent was added to the premixed component and then stirred at a constant speed of 14,000 rpm by using a homogenizer for 20 s. Finally, the foam obtained was left to harden and shaped at room temperature for a day [35]. The shaped PSPUF was crumbled using sandpaper and then sieved throughout an 80-mesh molecular sieve. Thus, the obtained powdered PSPUF was stoked for the adsorption experiments.

The adsorption experiments were performed by adding 0.15 g of the PSPUF to 50 mL of Cu^{2+} solution. The mixtures obtained were shaked in a temperature-controlled shaking bath at various pH values (2.01, 3.40, and 5.50) and temperatures (15°C, 25°C, 35°C, and 50°C) using a constant initial concentration of 2×10^{-3} M $CuSO_4{\cdot}5H_2O$ solution (Cu: 127 mg L^{-1}) for various contact times (5, 10, 20, 30, 45, 60, and 90 min), respectively. After contact times, the samples of 5 mL were withdrawn from the mixture and centrifuged at 5,000 rpm for 5 min. After centrifugation, the clear solution which does not include particles was analyzed using an atomic absorption spectrometer (Perkin-Elmer 3110, US). The pH values of the solutions were regulated with 0.1 N HCl or NaOH solution before the adsorption. The amounts of Cu^{2+} ions adsorbed per gram of the PSPUF (q_t) and the percent adsorption of Cu^{2+} ions were determined by means of Eqs. (1) and (2), respectively.

$$q_t = \frac{\left(C_0 - C_t\right)}{m} \times V \tag{1}$$

$$\text{Adsorption \%} = \frac{\left(C_0 - C_t\right)}{C_0} \times 100 \tag{2}$$

where C_0 indicates the initial concentration of Cu^{2+} ions (mg L^{-1}). C_t shows the concentration of the metal remained in the solution at any time (mg L^{-1}). q_t points to the amount of Cu^{2+} ions adsorbed per unit mass of the PSPUF at any time (mg g^{-1}). V indicates the volume of the metal solution used (L), and m is adsorbent mass (g). At the equilibrium time, q_t and C_t can be expressed as q_e and C_e.

For the characterization of the adsorbent, first, the PSPUF samples were dried to a constant weight in an oven at 60°C for 12 h. Then Fourier transform infrared (FTIR) spectra were recorded in the wave number range of 4,000–650 cm^{-1} using an attenuated total reflectance spectrometer (FTIR RX-1, Perkin-Elmer). Scanning electron microscopic (SEM) analyses were also performed using a LEO 435 VP SEM device. Brunauer, Emmett and Teller (BET) surface area and porosity measurements were performed by a Gemini VII 2390 Surface Area Analyzer. Density measurement of the adsorbent was done by means of graded measure.

3. Results and discussion

3.1. Mechanism of the formation of the PSPUF

Some information is given on the formation of PUF from PS.

The mechanism of the formation of PUF may be explained as follows. The PSPUF occurs from a reaction between PS and methylenediphenyl diisocyanate via polyaddition polymerization (Fig. 1).

3.2. Characterization of the PSPUF

3.2.1. FTIR studies

The PSPUF includes lignin, cellulose, hemicellulose, and tannin in its structure. Analysis of FTIR spectrum of the PSPUF is important to determine the functional groups which are responsible for Cu^{2+} ion adsorption. Therefore, FTIR spectra of the PSPUF were obtained before and after the adsorption (Fig. 2). In FTIR spectrum, the broad band at 3,292.18 cm^{-1} points to –OH groups of cellulose and the vibration of –NH and $–NH_2$ groups [36]. After the adsorption of Cu^{2+} ions, this band is slightly shifted to 3,290.25 cm^{-1}

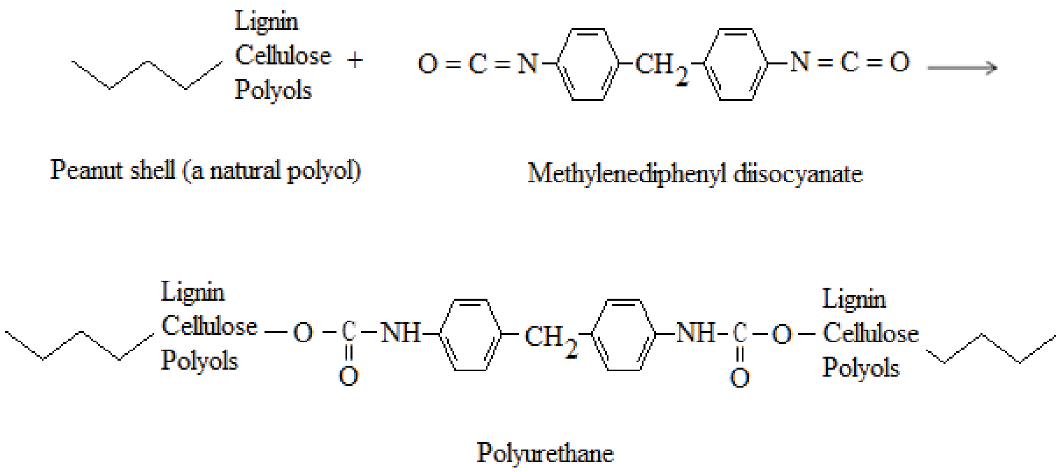

Fig. 1. Mechanism of the formation of PSPUF from the chemical reaction between PS and methylenediphenyl diisocyanate.

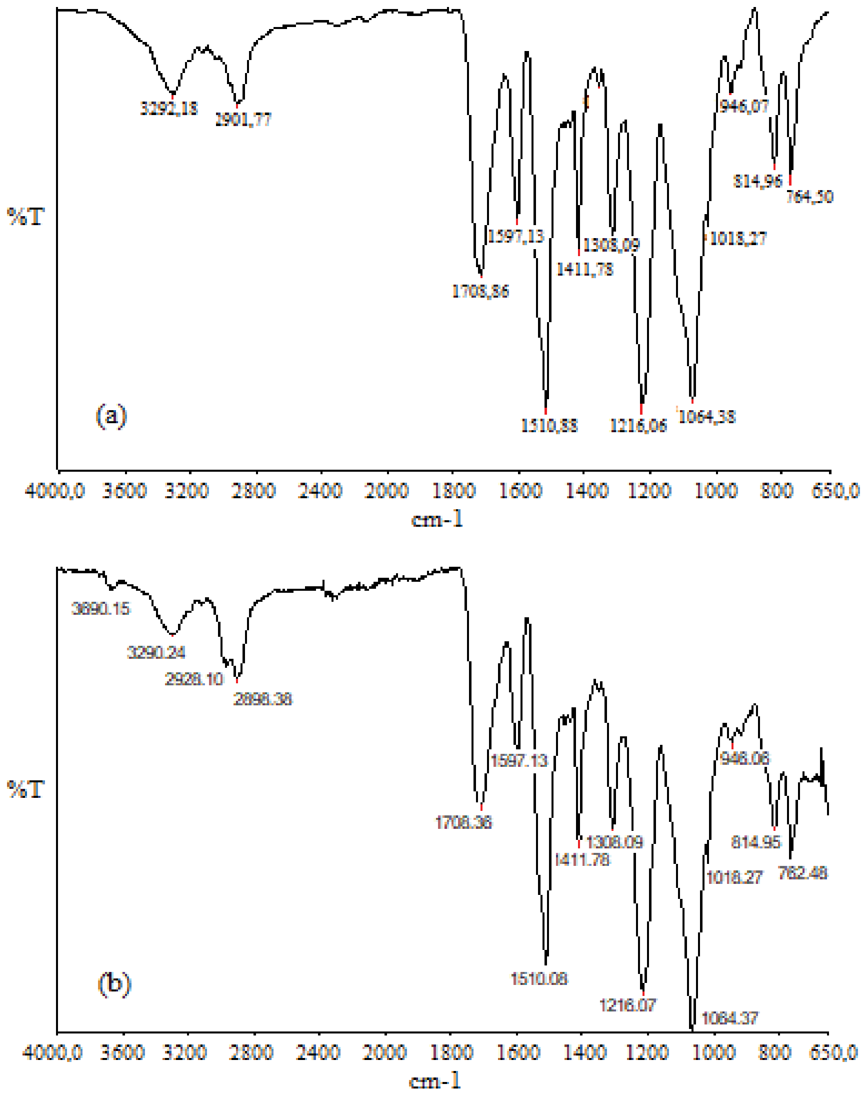

Fig. 2. FTIR spectrum of PSPUF. (a) Before adsorption and (b) after adsorption.

and its intensity decreased. The strong band at 2,901.77 cm^{-1} can be attributed to CH stretching of carboxyl groups. After the adsorption, the intensity of this band slightly increased. The very strong peaks at 1,708.36 and 1,510.08 cm^{-1} can be assigned to the amide I and amide II bonds [36]. After the adsorption, the intensities of these bands did not change. Peaks at 1,411.78 and 1,597.13 cm^{-1} indicate phenyl fragment in the structures of the foam [36]. After the adsorption, any change at the intensities of these bands did not occur. The band at 1,308.09 cm^{-1} indicates the stretching of C–$(CH_3)_2$ [37]. Any change at the intensity of this band did not occur. Peaks between 1,200 and 1,000 cm^{-1} point to C–O single bond in the structures of alcohols, phenols, carboxylic acids, and esters. Very strong peak at 1,064.38 and very light band at 1,018.27 cm^{-1} might be attributed to C–O and C–O–C stretching in foam [37]. After the adsorption, the intensity of peak at 1,064.38 cm^{-1} slightly increased and any change in band at 1,018.27 cm^{-1} did not occur. Strong band obtained at 1,216.06 cm^{-1} indicates C=O stretching of the carboxylic groups [38]. After the adsorption, the intensity of this band slightly increased. The bands at 946.07, 814.96, and 764.30 cm^{-1} show the vibrations of aromatic skeleton in the PSPUF [37]. After the adsorption, the intensities of these three peaks at bands decreased, and they slightly shifted. Moreover, two new bands with slight intensity at 3,690.15 and 2,918 cm^{-1} occurred. The band at 3,690.15 cm^{-1} probably indicates free O–H stretching in the structure of the foam, and the very weak band at 2,928.10 cm^{-1} probably indicates –CH aliphatic lineage between adsorbent and adsorbate copper ions [39]. These spectral shifts and the decreases or increases in the intensities of the peaks probably occurred as a result of interaction between Cu^{2+} ions and the functional groups on the surface of the PSPUF. With these interactions, a physical adsorption occurred. This situation is confirmed by SEM image and $\Delta H°$ value.

3.2.2. SEM studies

SEM images were recorded to analyze the surface morphology of the PSPUF (Mag: 250 KX, 100 μm) (see Fig. 3). As seen in Fig. 3(a), the surface of the PSPUF has a porous, rough, and heterogeneous structure which may adsorb Cu^{2+} ions. After the adsorption, it is seen from Fig. 3(b) that the surface of the PSPUF is in the appearance of clouds, covering with Cu^{2+} ions.

3.2.3. Specific surface area, porosity, and density measurements

Specific BET surface area, porosity, and density of the PSPUF are determined as 2.824 m^2 g^{-1}, 0.00215 cm^3 g$^{-1,}$ and 0.0341 g cm^{-3}, respectively. Color of the PSPUF is brownish.

3.3. The effect of contact time on the adsorption and the determination of equilibrium time

The effect of contact time on the adsorption of Cu^{2+} by the PSPUF was studied at the contact times of 5, 10, 20, 30, 45, 60, and 90 min for various pH values and temperatures at a constant concentration of Cu^{2+} ions, respectively (see Figs. 4 and 5). A rapid adsorption of Cu^{2+} ions occurred

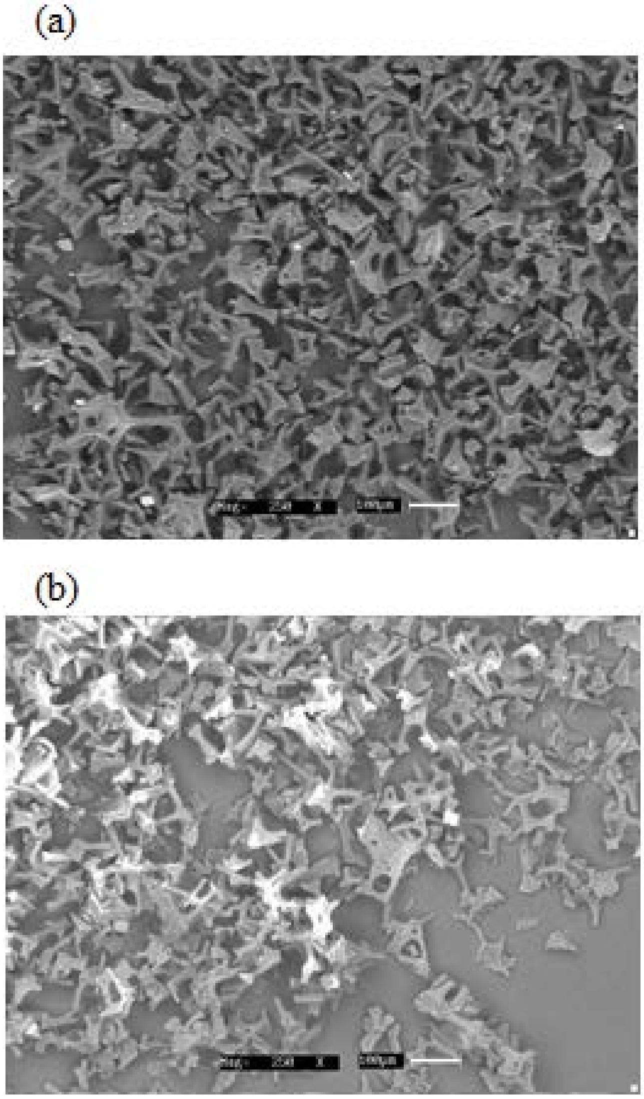

Fig. 3. SEM images of PSPUF. (a) Before adsorption and (b) after adsorption.

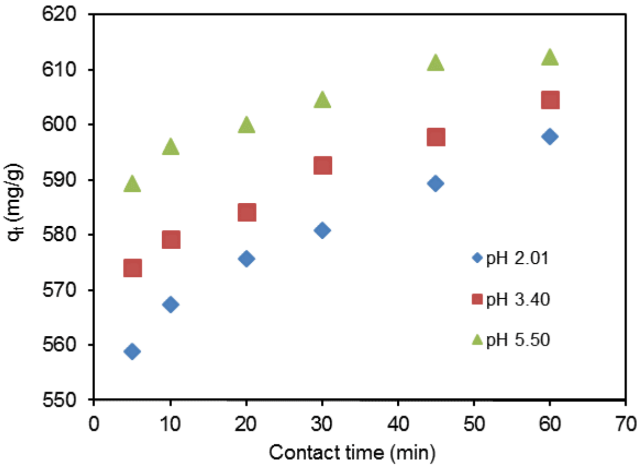

Fig. 4. Effect of pH on the adsorption of Cu^{2+} ions by PSPUF.

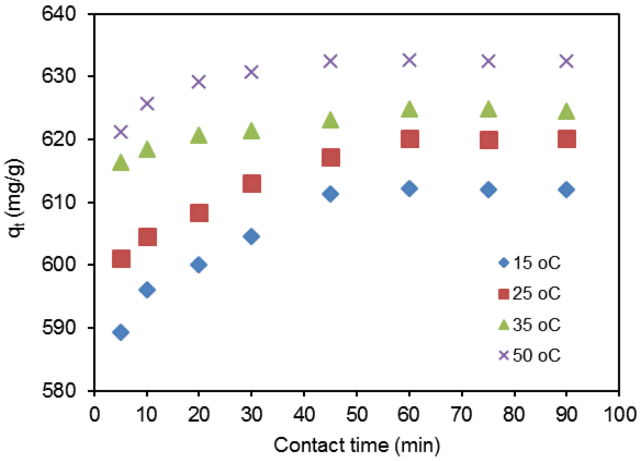

Fig. 5. Effect of temperature on the adsorption of Cu^{2+} ions by PSPUF.

within first 5 min under all the experimental conditions. After this time, a small rise in the adsorption continued to 60 min. At later times, the adsorption did not continue. Therefore, a period of 60 min was admitted as an equilibrium time for the maximum adsorption of Cu^{2+} ions.

3.4. pH effect on the adsorption

pH of solution medium for the removal of metals has an important effect because the pH value of an aqueous metal solution affects both the surface of an adsorbent and the charge density of a metal. Copper has various hydrolyzed species such as $Cu(OH)^+$, $Cu_2(OH)_2^0$, and $Cu_2(OH)_2^{2+}$ in higher solution mediums than pH 5.5 [40,41]. Therefore, in this study, the pH values of Cu(II) solutions were regulated as 2.01, 3.40, and 5.50, respectively. The results obtained for the adsorption of Cu^{2+} ions by the PSPUF are illustrated in Fig. 4. As seen in Fig. 4, the amount of Cu^{2+} ions adsorbed onto the PSPUF is quite high within the first 5 min. For example, the amounts of Cu^{2+} ions adsorbed onto the PSPUF are determined to be 558.80 mg g^{-1} (66%), 574.04 mg g^{-1} (67.80%), and 589.28 mg g^{-1} (69.60) at the pH values of 2.01, 3.40, and 5.50 within 5 min, respectively. At the equilibrium time of 60 min, the maximum amounts of Cu^{2+} ions adsorbed are 597.75 mg g^{-1} (70.60%), 604.53 mg g^{-1} (71.40%), and 612.22 mg g^{-1} (72.31%) at pH values of 2.01, 3.40, and 5.50, respectively. These values showed that the adsorption capacity of the PSPUF in removing Cu^{2+} ions was very high, and the PSPUF had a high affinity to Cu^{2+} ions.

3.5. Temperature effect on the adsorption

Fig. 5 shows temperature effect for the adsorption of Cu^{2+} ions by the PSPUF. From Fig. 5, a very high adsorption of Cu^{2+} ions can be seen for all temperatures within first 5 min. For instance, the amounts of Cu^{2+} ions adsorbed are found to be 589.28 mg g^{-1} (69.60%), 601.13 mg g^{-1} (71.00%), 616.34 mg g^{-1} (72.79%), and 621.20 mg g^{-1} (73.37%) at 15°C, 25°C, 35°C, and 50°C within 5 min, respectively. At the equilibrium time of 60 min, the maximum amounts of Cu^{2+} ions adsorbed are determined as 612.22 mg g^{-1} (72.31%), 620.13 mg g^{-1} (73.24%), 624.80 mg g^{-1} (73.96%), and 632.63 (74.72%) at the temperatures of 15°C, 25°C, 35°C, and 50°C, respectively. From these results, it is clear that the temperature is in favor of the adsorption of Cu^{2+} ions onto the PSPUF. A similar trend has also been obtained for Cu^{2+} ion adsorption onto pine sawdust [4].

3.6. Determination of distribution coefficient of Cu^{2+} ions

Distribution coefficient in an adsorption or extraction process can be determined from Eq. (3) [41,42].

$$D = \frac{R}{(100 - R)} \times \frac{V}{m} \tag{3}$$

where D is distribution coefficient (L kg^{-1}). V indicates solution volume (L), and m shows the adsorbent mass in kg (i.e. the mass of the PSPUF). R is percent removal (i.e. percent adsorption) of Cu^{2+} ions. Distribution coefficient (D) is the concentration of Cu^{2+} ions adsorbed onto foam/the concentration remained in solution. The value of D does not change at equilibrium time [42]. Distribution coefficient can also be expressed as distribution ratio [42]. At the same time, the distribution coefficient indicates the degree of Cu^{2+} ion removal via extraction or adsorption. The larger distribution coefficient is the larger Cu^{2+} ion removal. Distribution coefficients on the removal of some dyes from aqueous solution by extraction with polyether and polyester-type foams have been found between 500 and 12,000 L kg^{-1} at various pH values [43]. In a normal solvent extraction, the values of D are between 20 and 1,000. If the D value is more than 1,000, a kind of ion-exchange process might occur [42]. Herein, the D values are determined as 781, 832, and 889 L kg^{-1} for the pH values of 2.01, 3.40, and 5.50 and as 889, 900, 962, and 984 L kg^{-1} for the temperatures of 15°C, 25°C, 35°C, and 50°C, respectively (see Table 1). These results indicate that an ion-exchange process does not occur and, however, is probably adsorbed by the extraction of Cu^{2+} ions from aqueous solution.

3.7. The comparison of the PSPUF with other PUFs and some sorbents in Cu^{2+} ion adsorption

Experimental parameters such as initial concentration of solution pH, temperature, solution volume, and the adsorbent quantity affect the amounts of adsorbate adsorbed by an

Table 1
Distribution coefficients at various pHs and temperatures

T (°C)	D (L kg^{-1})
15	889
25	900
35	962
50	984
pH	
2.01	781
3.40	832
5.50	889

adsorbent. Especially, the quantity of the adsorbent is quite effective on the determination of adsorbate amount removed by an adsorbent. Herein, the experimental capacities of the PSPUF in removing Cu^{2+} ions were compared with those of other adsorbents (see Table 2). For instance, when the mass of the PSPUF for the removal of Cu^{2+} ions is 0.15 g (m/v ratio, i.e. adsorbent dosage/solution volume ratio = 3.0 g L^{-1}), the experimental adsorption capacities of the PSPUF are determined to be increased from 612.22 mg g^{-1} (72.31%) to 632.63 mg g^{-1} (74.72%) with an increase in the temperature from 15°C to 50°C at pH 5.50, respectively. As seen from Table 2, in a work done by Zhou et al., when the quantities of PUF and microorganism-immobilized PUF for the removal of Cu^{2+} ions are 0.19 g (m/v ratio = 3.80 g L^{-1}), the adsorption capacities of these PUFs have been found approximately to be 2.36 mg g^{-1} (45%) and 4.32 mg g^{-1} (82%), respectively [44]. In another work performed by Soriano and Cassella, when the mass of modified PUF with Eriochrome Black T for the removal of Cu(II) ions is 0.2 g (m/v ratio = 1.0 g L^{-1}), its adsorption capacity has been determined to be 0.63 mg g^{-1} (63%) [45]. In another study made by Moftakhar et al., when the mass of modified PUF with Schiff base for Cu^{2+} ion removal is 6.0 g (m/v ratio = 60 g L^{-1}), its adsorption capacity has been calculated to be 0.083 mg g^{-1} (100%) [46]. The capacities of different adsorbents used for the removal of Cu^{2+} ions in the studies conducted by some other researchers are submitted in Table 2. As a result, the adsorption capacity of the PSPUF to remove Cu^{2+} ions was very high than those of other adsorbents, indicating a very high affinity of the PSPUF to Cu^{2+} ions.

3.8. Kinetic studies

Adsorption kinetics of Cu^{2+} ions adsorbed by the PSPUF was studied in terms of the pseudo-first and second-order kinetics and the intraparticle diffusion models. The linearized equations of these kinetic models can be expressed as follows, respectively [3,14,15,47].

$$\log\left(q_e - q_t\right) = \log q_1 - \frac{k_1}{2.303}t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_2}t \tag{5}$$

$$q_t = k_i \times t^{1/2} + C \tag{6}$$

Table 2
Comparison of PSPUF with other PUFs and some sorbents in removing copper(II)

Adsorbent/biosorbent/extractant	Experimental conditions	Capacity (mg g^{-1})	Adsorption (%)	References
PSPUF	C_0 = 127 mg L^{-1} Cu^{2+}, T = 15°C, pH = 5.5, V = 50 mL, m = 0.15 g	612.22	72.31	This study
PSPUF	C_0 = 127 mg L^{-1} Cu^{2+}, T = 50°C, pH = 5.5, V = 50 mL, m = 0.15 g	632.63	74.72	This study
Calabrian pine bark wastes	C_0 = 19 mg L^{-1} Cu^{2+}, T = 30°C, pH = 5.5, V = 50 mL, m = 1.0 g	0.68	71.26	[7]
Organosolv lignin	C_0 = 19.06 mg L^{-1} Cu^{2+}, T = 20°C, pH = 5.5, V = 35 mL, m = 0.25 g	1.10	40.74	[39]
Crushed brick	C_0 = 200 mg L^{-1} Cu^{2+}, T = 25°C, pH = 6, V = 100 mL, m = 0.5 g	272	68	[40]
Cedar sawdust	C_0 = 200 mg L^{-1} Cu^{2+}, T = 25°C, pH = 6, V = 100 mL, m = 0.5 g	388	97	[40]
Pine sawdust	C_0 = 25.42 mg L^{-1} Cu^{2+}, T = 30°C, pH = 5.5, V = 50 mL, m = 0.40 g	2.46	77.52	[41]
Polyurethane foam	C_0 = 20 mg L^{-1} Cu^{2+}, T = 25°C, pH = 6, V = 50 mL, m = 0.19 g	2.36	45	[44]
Microorganism-immobilized polyurethane foam	C_0 = 20 mg L^{-1} Cu^{2+}, T = 25°C, pH = 6, V = 50 mL, m = 0.19 g	4.32	82	[44]
PUF modified with Eriochrome Black T	C_0 = 1.0 mg L^{-1} Cu^{2+}, T = Room temperature, pH = 1.50, V = 200 mL, m = 0.2 g	0.63	63	[45]
PUF modified with Schiff base (Column)	C_0 = 5.0 mg L^{-1} Cu^{2+}, T = Room temperature, pH = 4–6, V = 100 mL, m = 6.0 g	0.083	100	[46]
Peanut hull	C_0 = 30 mg L^{-1} Cu^{2+}, T = 30°C, pH = 5.5, V = 100 mL, m = 0.2 g	12.85	85.60	[51]
Dried activated sludge	C_0 = 100 mg L^{-1} Cu^{2+}, T = 25°C, pH = 5.0, V = 100 mL, m = 0.2 g	35.03	70.05	[52]

where t indicates contact time (min). q_t and q_e show the amounts of Cu^{2+} ions adsorbed by adsorbent PSPUF at any time and the equilibrium time (mg g^{-1}), respectively. q_1 and q_2 are theoretical adsorption capacities determined from the pseudo-first and second-order kinetic models, respectively. k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the rate constants for the pseudo-first and second-order kinetic models, respectively. The term h (mg g^{-1} min^{-1}) is equal to $k_2q_2^2$, indicating the initial adsorption rate. k_i (mg g min$^{-1/2}$) is the rate constant for the intraparticle diffusion. C is a boundary layer thickness between adsorbent and adsorbate.

The values of the k_1 and q_1 from the slopes and the intercepts of the linear plot of $\log(q_e - q_t)$ vs t, the values of the q_2 and k_2 from the slopes and the intercepts of the linear plot of t/q_t against t, and the values of the k_i and C from the slopes and the intercepts of the linear plots of q_t versus $t^{1/2}$ were determined, respectively. The obtained kinetic parameters can be seen in Table 3. Correlation coefficients for the pseudo-first order, the pseudo-second order, and the intraparticle diffusion are shown as r_1^2, r_2^2, and r_i^2, respectively (see Table 3).

As seen in Table 3, the values of r_1^2 were determined to be between 0.823 and 0.996 for all the pH values and the temperatures. The experimental values of the q_e are not compatible with the theoretical values of the q_1. Therefore, the adsorption kinetics of Cu^{2+} ions onto the PSPUF was not consistent with the pseudo-first-order model, and therefore, the obtained plots are not shown.

The plots drawn for the pseudo-second order at the temperatures of 15°C, 25°C, 35°C, and 50°C and the pH values of 2.01, 3.40, and 5.50 are given in Figs. 6(a) and (b), respectively. As can be seen from Fig. 6(a), the effect of the temperature on the pseudo-second-order kinetics is very less, and the plots are obtained as overlapping. Therefore, the values of the theoretical q_e are found as 625 mg g^{-1} for all the temperatures. From the regression analyses of the plots in Fig. 6(a), the r_2^2 values are determined as 1 for all the temperatures. The values of the k_2 were determined to be 0.0043, 0.0051, 0.0012, and 0.0012 g mg^{-1} min^{-1} for the temperatures of 15°C, 25°C, 35°C, and 50°C, respectively. From the regression analyses of the plots in Fig. 6(b), the values of the r^2 are found to be 0.999, 0.999, and 1 for the pH values of 2.01, 3.40, and 5.50, respectively. The values of the k_2 are calculated as 0.0026, 0.0028, and 0.0051 g mg^{-1} min^{-1} for the pH values of 2.01, 3.40, and 5.50, respectively. The theoretical values of the q_2 are estimated as 588, 625, and 625 mg g^{-1} for the pH values of 2.01, 3.40, and 5.50, respectively. Theoretical q_2 values are close to the values of the experimental q_e (see Table 3). Both the high correlation

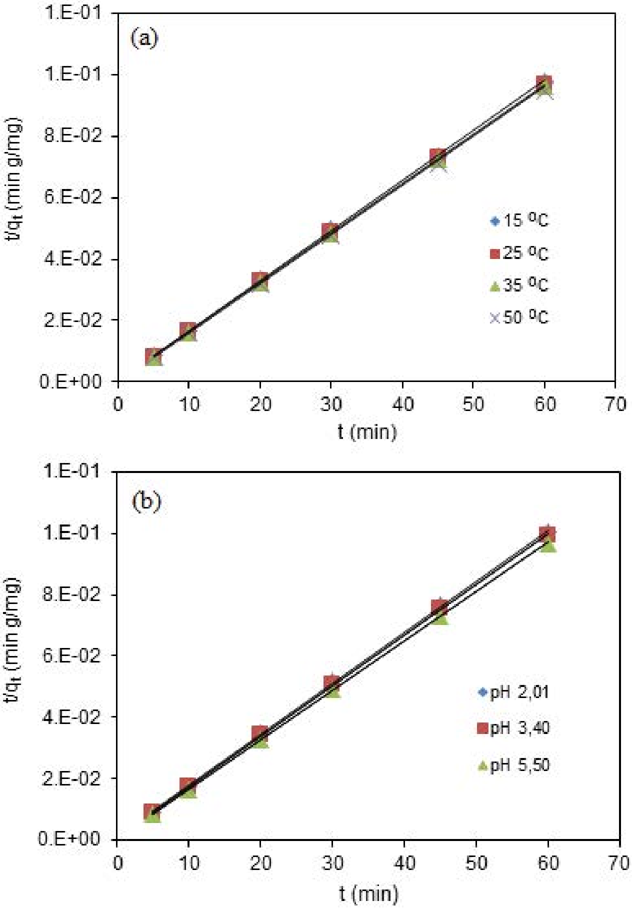

Fig. 6. Pseudo-second-order kinetic plots of the adsorption of Cu^{2+} ions by PSPUF: (a) for different temperatures and (b) for different pH values.

Table 3
Kinetic parameters of the adsorption of Cu^{2+} ions onto PSPUF

	Pseudo-first-order kinetics			Pseudo-second-order kinetics				Intraparticle diffusion			
T (°C)	q_1 (mg g^{-1})	k_1 (min^{-1})	r^2	q_2 (mg g^{-1})	h (mg g^{-1} min^{-1})	k_2 (g mg^{-1} min^{-1})	r^2	k_i (mg g^{-1} min$^{-1/2}$)	C	r_i^2	q_e^*
15	41.34	0.074	0.897	625	1,680	0.0043	1	4.201	581	0.974	612.22
25	26.06	0.045	0.979	625	1,992	0.0051	1	3.508	593	0.996	620.13
35	9.61	0.037	0.986	625	469	0.0012	1	1.450	613	0.983	624.80
50	21.92	0.099	0.955	625	469	0.0012	1	2.010	618	0.892	632.63
pH											
2.01	46.16	0.036	0.989	588	909	0.0026	0.999	6.677	545	0.995	597.75
3.40	38.32	0.037	0.986	625	1,093	0.0028	0.999	5.518	557	0.992	604.53
5.50	25.85	0.045	0.979	625	2,000	0.0051	1	3.508	592	0.996	612.22

*Experimental adsorption capacity (mg g^{-1}).

coefficients and the consistency of the theoretical and experimental adsorption capacities indicate that the adsorption obeys the pseudo-second-order kinetic model. A similar trend has also been reported for the adsorption of Cu^{2+} ions onto alginate and alginate-immobilized bentonite [48].

The plots obtained for the intraparticle diffusion model at the temperatures of 15°C, 25°C, 35°C, and 50°C and the pH values of 2.01, 3.40, and 5.50 are given in Figs. 7(a) and (b), respectively. From the regression analyses of the plots in Fig. 7(a), the values of the r_i^2 are found to be 0.974, 0.996, 0.983, and 0.892 mg g^{-1} $min^{-1/2}$ for the temperatures of 15°C, 25°C, 35°C, and 50°C, respectively. The values of the k_i for the intraparticle diffusion model are estimated to be 4.201, 3.508, 1.450, and 2.010 mg $g^{-1}min^{-1/2}$ for the temperatures of 15°C, 25°C, 35°C, and 50°C, respectively. In the case of pH, from the regression analyses of the plots in Fig. 6(b), the values of the r_i^2 are determined to be 0.995, 0.992, and 0.996 for the pH values of 2.01, 3.40, and 5.50, respectively. These high correlation coefficients indicate that the adsorption obeys the intraparticle diffusion model with a surface adsorption. The values of the k_i are found to be 6.667, 5.518, and 3.508 mg g^{-1} $min^{-1/2}$ for the pH values of 2.01, 3.40, and 5.50, respectively. Moreover, the values of the C are determined to be 581, 593, 613, and 618 for the temperatures of 15°C, 25°C, 35°C, and 50°C, and they were found as 545, 561, and 592 for the pH values of 2.01, 3.04, and 5.50, respectively. From these values, it is seen that the C values rise with an increase in pH and the temperature. This situation indicated that the boundary layer thickness on the surface of the PSPUF slightly increased with increasing pH and temperature. Consequently, the kinetic results indicate that the adsorption of Cu^{2+} ions on the PSPUF obeys the pseudo-second-order kinetic and the intraparticle diffusion models.

3.9. Thermodynamic studies

In order to understand the effect of the temperature on the adsorption of Cu^{2+} ions, it is important to perform thermodynamic studies. For this purpose, the thermodynamic parameters of the adsorption are calculated from the equations below [7].

$$K_c = \frac{C_{\text{ads}}}{C_e} \tag{7}$$

$$\Delta G^\circ = -RT \ln K_c \tag{8}$$

$$\ln K_c = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{9}$$

where K_c indicates the equilibrium constant. ΔG° is standard Gibbs free energy change (J mol^{-1}). ΔH° is standard enthalpy change (J mol^{-1}), and ΔS° is standard entropy change (J $mol^{-1}K^{-1}$). C_{ads} and C_e indicate the amounts of Cu^{2+} ions adsorbed onto the PSPUF and remained in the solution in the equilibrium time, respectively. R is ideal gas constant (8.314 J $mol^{-1}K^{-1}$). T is absolute temperature (in Kelvin). The values of ΔH° and ΔS° were determined from the Van't Hoff equation in Eq. (9). According to Van't Hoff equation, the slope and intercept of the plot of ln K_c vs $1/T$ (in Kelvin) are equal to $-\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively (see Fig. 8). The value of the r^2 from Van't Hoff equation plot is found as 0.993. The obtained thermodynamic parameters are submitted in Table 4.

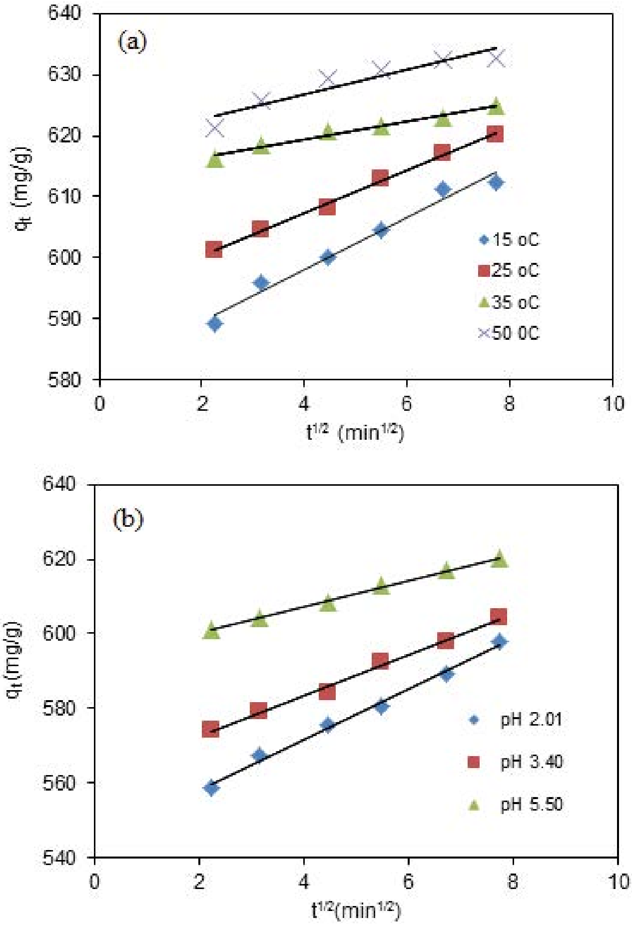

Fig. 7. Intraparticle diffusion plots of the adsorption of Cu^{2+} ions by PSPUF: (a) for different temperatures and (b) for different pH values.

As seen from Table 4, the ΔG° values are determined to be −2,298, −2,495, −2,651, and −2,910 J mol^{-1} for the temperatures of 15°C, 25°C, 35°C, and 50°C, respectively. The negative ΔG° values indicate the spontaneous nature of Cu^{2+} ion adsorption. As seen from these values, the values of ΔG° decreasing with the effect of the rise in the temperature indicate the increase of spontaneous tendency of the adsorption. The values of ΔH° and ΔS° are calculated as 2,682 J mol^{-1} and 17.32 J mol^{-1} K^{-1}, respectively. Herein, the low ΔH° value indicates a physical adsorption. The positive value of ΔS° shows a randomness adsorption of Cu^{2+} ions onto the surface of the PSPUF. A similar trend has been reported for the adsorption of Cu^{2+} ions onto garden grass [49]. On the other side, the similar results to the negative ΔG° and the positive values of ΔH° and ΔS° have been reported for both the adsorption of Fe^{2+} ions onto Calabrian pine bark [7] and the adsorption of a cationic dye methylene blue onto open cell polyether-type PUF [50].

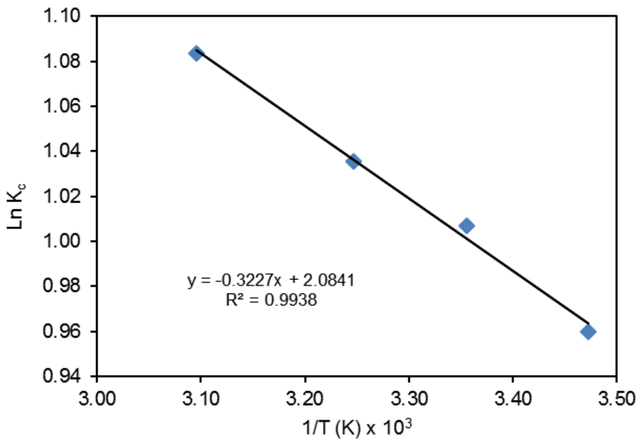

Fig. 8. Van't Hoff graph of the adsorption of Cu^{2+} ions by PSPUF.

Table 4
Thermodynamic parameters of the adsorption of Cu^{2+} ions onto PSPUF

T (°C)	K_c	$\Delta G°$ (J mol^{-1})	$\Delta H°$ (J mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})
15	2.61	−2,298	2,682	17.32
25	2.74	−2,495		
35	2.81	−2,651		
50	2.96	−2,910		
pH				
2.01	2.40	−2,170		
3.40	2.49	−2,226		
5.50	2.73	−2,495		

Moreover, the thermodynamic parameters were also estimated for different pH values (see Table 4). The values of $\Delta G°$ are determined as −2,170, −2,226, and −2,495 J mol^{-1} for the pH values of 2.01, 3.40, and 5.50, respectively. As seen in Table 4, the values of $\Delta G°$ decreasing with a rise in pH indicate the increase of spontaneous tendency of the adsorption as in the temperature effect.

4. Conclusions

The conclusions of research works based on all of the experimental findings can be expressed as follows:

- The PSPUF could be utilized as a new adsorbent and as an alternative to activated carbon in metal removal due to its very high affinity to Cu^{2+} ions.
- A contact time of 60 min was determined for maximum adsorption at various pHs and temperatures.
- The adsorption of Cu^{2+} ions onto the PSPUF increased with a rise in pH and temperature.
- SEM image, FTIR analysis, and kinetic results indicated a surface adsorption of Cu^{2+} ions onto the PSPUF.
- Kinetic results indicated that the adsorption of Cu^{2+} ions onto the PSPUF was consistent with the pseudo-second-order model and the intraparticle diffusion model.
- The thermodynamic results showed that the adsorption of Cu^{2+} ions onto the PSPUF was spontaneous, physical, and random.
- From the distribution coefficient values, it was seen that the adsorption of Cu^{2+} ions onto the PSPUF occurred via extraction from aqueous solution.

References

[1] B. Acemioğlu, Adsorption of congo red from aqueous solution onto calcium-rich fly ash, J. Colloid Interface Sci., 274 (2004) 371–379.
[2] M. Dogan, M. Alkan, Adsorption kinetics of methyl violet onto perlite, Chemosphere, 50 (2003) 517–528.
[3] Y.S. Ho, G. McKay, Kinetic models for the sorption of dye from aqueous solution by wood, Trans. IChemE, 76B (1998) 183–191.
[4] B. Acemioğlu, M.H. Alma, Sorption of copper (II) ions by pine sawdust, Holz. Roh. Werkst., 62 (2004) 268–272.
[5] A.E. Ofomaja, Y.S. Ho, Effect of temperatures and pH on methyl violet biosorption by Mansonia wood sawdust, Bioresour. Technol., 99 (2008) 5411–5417.
[6] A. Şen, H. Pereira, M.A. Olivella, I. Villaescusa, Heavy metals removal in aqueous environments using bark as a biosorbent, Int. J. Environ. Sci. Technol., 12 (2015) 391–404.
[7] B. Acemioğlu, Removal of Fe(II) ions from aqueous solution by Calabrian pine bark wastes, Bioresour. Technol., 93 (2004) 99–102.
[8] B. Acemioğlu, M.H. Alma, Removal of Cu(II) from aqueous solution by Calabrian pine bark wastes, Fresenius Environ. Bull., 13 (2004) 585–590.
[9] B. Acemioğlu, M.H. Alma, A.R. Demirkıran, Removal of Zn(II) and Pb(II) ions by Calabrian pine bark wastes, J. Chem. Soc. Pak., 26 (2004) 82–89.
[10] B.H. Hameed, Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent, J. Hazard. Mater., 162 (2009) 344–350.
[11] N. Feng, X. Guo, Characterization of adsorptive capacity and mechanisms on adsorption of copper, lead and zinc by modified orange peel, Trans. Nonferrous Met. Soc. China, 22 (2012) 1224–1231.
[12] L. Kule, B. Acemioğlu, E. Baran, Kinetics, thermodynamics and isotherm studies of malachite green adsorption by modified orange peel, Int. J. Chem. Technol., 1 (2017) 58–66.
[13] B.H. Hameed, M.I. El-Khaiary, Removal of basic dye from aqueous medium using a novel agricultural waste material: pumpkin seed hull, J. Hazard. Mater., 155 (2008) 601–609.
[14] Y.S. Ho, G. Mckay, Sorption of dye from aqueous solution by peat, Chem. Eng. J., 70 (1998) 115–124.
[15] Y.S. Ho, G. Mckay, The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat, Can. J. Chem. Eng., 76 (1998) 822–827.
[16] R. Gündoğan, B. Acemioğlu, M.H. Alma, Copper(II) adsorption from aqueous solution by herbaceous peat, J. Colloid Interface Sci., 269 (2004) 303–309.
[17] N. Kılıç, J.A. Ballantine, Magnitudes of back diffusion during long-term diffusive sampling of volatile organic compounds using Carbotrap and Chromosorb 106, Turk. J. Chem., 24 (2000) 131–140.
[18] A. Gürses, Ç. Doğar, M. Yalçın, M. Açıkyıldız, R. Bayrak, S. Karaca, The adsorption kinetics of the cationic dye, methylene blue, onto clay, J. Hazard. Mater., 131 (2006) 217–228.
[19] M. Uğurlu, Adsorption of a textile dye onto activated sepiolite, Microporous Mesoporous Mater., 119 (2009) 276–283.
[20] A. Vanaamudan, N. Pathan, P. Pamidimukkala, Adsorption of reactive blue 21 from aqueous solutions onto clay, activated clay, and modified clay, Desal. Wat. Treat., 52 (2014) 1589–1599.
[21] O. İnel, A. Aşkın, Adsorption of monovalent cationic dyes on some silicates, Turk. J. Chem., 20 (1996) 276–282.
[22] B. Acemioğlu, Batch kinetic study of sorption of methylene blue by perlite, Chem. Eng. J., 106 (2005) 73–81.

[23] N. Dizge, C. Aydiner, E. Demirbas, M. Kobya, S. Kara, Adsorption of reactive dyes from aqueous solutions by fly ash: kinetic and equilibrium studies, J. Hazard. Mater., 150 (2008) 737–746.

[24] M. Mukhopadhyay, S.B. Noronha, G.K. Suraishkumar, Kinetic modeling for the biosorption of copper by pretreated *Aspergillus niger* biomass, Bioresour. Technol., 98 (2007) 1781–1787.

[25] B. Acemioğlu, M. Kertmen, M. Digrak, M.H. Alma, F. Temiz, Biosorption of crystal violet onto *Aspergillus wentii* from aqueous solution, Asian J. Chem., 22 (2010) 1394–1402.

[26] J.Y. Farah, N. El-Guendy, L.A. Farahat, Biosorption of astrazone blue basic dye from an aqueous solution using dried biomass of *Baker's yeast*, J. Hazard. Mater., 148 (2007) 402–408.

[27] A. Ergene, K. Ada, S. Tan, H. Katırcıoğlu, Removal of remazol brilliant blue R dye from aqueous solutions by adsorption onto immobilized *Scenedesmus quadricauda*: equilibrium and kinetic modeling studies, Desalination, 249 (2009) 1308–1314.

[28] A.İ. Vaizogullar, A. Balcı, İ. Kula, M. Uğurlu, Preparation, characterization, and adsorption studies of core@shell SiO_2@CeO_2 nanoparticles: a new candidate to remove Hg(II) from aqueous solutions, Turk. J. Chem., 40 (2016) 565.

[29] H. Mittal, V. Parashar, S.B. Mishra, A.K. Mishra, Fe_3O_4 MNPs and gum xanthan based hydrogels nanocomposites for the efficient capture of malachite green from aqueous solution, Chem. Eng. J., 255 (2014) 471–482.

[30] A. Kara, B. Acemioğlu, M.H. Alma, M. Cebe, Adsorption of Cr(III), Ni(II), Zn(II), Co(II) ions onto phenolated wood resin, J. Appl. Polym. Sci., 101 (2006) 2838–2846.

[31] V.S.K. Lo, A. Chow, Extraction of tin by the use of polyurethane foam, Talanta, 28 (1981) 157–160.

[32] A.S. Khan, A. Chow, Determination of arsenic by polyurethane foam extraction and X-ray fluorescence, Talanta, 31 (1984) 304–306.

[33] E.A. Moawed, A.B. Farag, M.F. El-Shahat, Separation and determination of some trivalent metal ions using rhodamine B grafted polyurethane foam, J. Saudi Chem. Soc., 17 (2013) 47–52.

[34] A.S. Khan, W.G. Baldwin, A. Chow, Extraction of monovalent and divalent cations by polyether-based polyurethane foam, Anal. Chim. Acta, 146 (1983) 201–209.

[35] M.H. Bilir, N. Sakalar, B. Acemioğlu, E. Baran, M.H. Alma, Sorption of remazol brilliant blue R onto polyurethane-type foam prepared from peanut shell, J. Appl. Polym. Sci., 6 (2013) 4340–4350.

[36] S.G. Dmitrienko, O.A. Siviridova, L.N. Pyatkova, V.M. Senyamin, Polyurethane foams as solid chromogenic reagents for diffuse reflectance spectroscopy, Anal. Bioanal. Chem., 374 (2002) 361–368.

[37] B.H. Hameed, D.K. Mahmoud, A.L. Ahmad, Sorption equilibrium and kinetics of basic dye from aqueous solution using banana stalk waste, J. Hazard. Mater., 158 (2008) 499–506.

[38] G. Bayramoğlu, M.Y. Arica, Biosorption of benzidine based textile dyes "Direct blue 1 and Direct red 128" using native and heat-treated biomass of *Trametes versicolor*, J. Hazard. Mater., 143 (2007) 135–143.

[39] S. Khamparia, D.K. Jaspal, *Xanthium strumarium* L. seed hull as zero cost alternative for Rhodamine B dye removal, J. Environ. Manage., 197 (2017) 498–506.

[40] B. Acemioğlu, A. Samil, M.H. Alma, R. Gündoğan, Copper(II) removal from aqueous solution by organosolv lignin and its recovery, J. Appl. Polym. Sci., 89 (2003) 1537–1541.

[41] R. Djeribi, O. Hamdaoui, Sorption of copper(II) from aqueous solutions by cedar sawdust and crushed brick, Desalination, 225 (2008) 95–112.

[42] A. Chow, W. Branagh, J. Change, Sorption of organic dyes by polyurethane foam, Talanta, 37 (1990) 407–412.

[43] R. Werbowesky, A. Chow, Extraction of azo dyes by polyurethane foam, Talanta, 43 (1996) 263–274.

[44] L.C. Zhou, Y.F. Li, X. Bai, G.H. Zhao, Use of microorganisms immobilized on composite polyurethane foam to remove Cu(II) from aqueous solution, J. Hazard. Mater., 167 (2009) 1106–1113.

[45] S. Soriano, R.J. Cassella, Solid-phase extraction of Cu(II) using polyurethane foam and eriochrome black t as ligand for its determination in waters by flame atomic absorption spectrometry, J. Braz. Chem. Soc., 24 (2013) 1172–1179.

[46] M.K. Moftakhar, M.R. Yaftian, S. Nahaei, A.A. Zamani, Application of polyurethane foam loaded with a schiff base ligand for determination of trace amounts of copper in water samples by flame atomic absorption spectroscopy, J. Korean Chem. Soc., 58 (2014) 283–288.

[47] S. Azizian, M. Haerifar, H. Bashiri, Adsorption of methyl violet onto granular activated carbon: equilibrium, kinetics and modeling, Chem. Eng. J., 146 (2009) 36–41.

[48] W.S. Tan, A.S.Y. Ting, Alginate-immobilized bentonite clay: adsorption efficacy and reusability for Cu(II) removal from aqueous solution, Bioresour. Technol., 160 (2014) 115–118.

[49] M.A. Hossain, H.H. Ngo, W.S. Guo, T. Setiadi, Adsorption and desorption of copper(II) ions onto garden grass, Bioresour. Technol., 121 (2012) 386–395.

[50] E.E. Baldez, N.F. Robaina, J. Ricardo, R.J. Cassella, Employment of polyurethane foam for the adsorption of methylene blue in aqueous medium, J. Hazard. Mater., 159 (2008) 580–586.

[51] S. Zhu, C.L.P. Wang, V.B. Chen, Removal of Cu(II) from aqueous solution by agricultural by-product: peanut hull, J. Hazard. Mater., 168 (2009) 739–746.

[52] H. Benaïssa, M.A. Elouchdi, Biosorption of copper (II) ions from synthetic aqueous solutions by drying bed activated sludge, J. Hazard. Mater., 194 (2011) 69–78.