Journal of Anatolian Environmental and Animal Sciences
(*Anadolu Çevre ve Hayvancılık Bilimleri Dergisi*)
DOI: https://doi.org/10.35229/jaes.672951

JAES
Year: 5, No: 2, 2020 (131-137)
AÇEH
Yıl: 5, Sayı: 2, 2020 (131-137)

ARAŞTIRMA MAKALESİ **RESEARCH PAPER**

Adsorption of Copper (II) from Aqueous Solution by Using Carbonized Peanut Hull: Determination of the Equilibrium, Kinetic and Thermodynamic Parameters

Gülşad USLU ŞENEL
Department of Environmental Engineering, Firat University, 23100 Elazig, Turkey

Geliş/Received: *10.01.2020* ***Kabul/Accepted:*** *17.04.2020*

How to cite: **Uslu Şenel, G. (2020).** Adsorption of Copper (II) from Aqueous Solution by Using Carbonized Peanut Hull: Determination of the Equilibrium, Kinetic and Thermodynamic Parameters. *J. Anatolian Env. and Anim. Sciences,* ***5***(2), 131-137.
Atıf yapmak için: **Uslu Şenel, G. (2020).** Karbonize Fıstık Kabuğu Kullanılarak Sulu Çözeltilerden Bakır (II)'nin Adsorpsiyonu: Denge, Kinetik ve Termodinamik Parametrelerin Belirlenmesi. *Anadolu Çev. ve Hay. Dergisi*, **5**(2), 131-137.

*: https://orcid.org/0000-0002-5304-9436

***Corresponding author's:**
Gülşad USLU ŞENEL
Department of Environmental Engineering,
Firat University, 23100 Elazig, Turkey.
✉: guslu@firat.edu.tr
Mobile telephone : +90 (533) 748 35 53
Telephone : +90 (424) 237 00 00/8403

Abstract: In this study, the effect of temperature, pH, initial metal concentration and adsorbent dosage on Cu(II) adsorption onto carbonized peanut hull (PHC) was investigated. Activated carbon was prepared from peanut hull. It was produced by carbonization in carbon dioxide atmosphere at 500°C for 1.0 h. The maximum Cu (II) adsorption capacity was obtained as 168.16 mg/g for 500 mg/L initial Cu (II) at pH = 4.0 and 60 °C. The Freundlich and Langmuir adsorption models were used for the mathematical description of the adsorption equilibrium. The best interpretation for the experimental data was given by the Freundlich isotherm and the maximum adsorption capacity was obtained. Batch adsorption models, based on the assumption of the pseudo-first and pseudo-second order mechanism, were applied to examine the kinetics of the adsorption. Kinetic data fitted the pseudo-second kinetic order model. Thermodynamic functions, the change of free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) of copper adsorption on PHC were calculated as -23.21 kjmol^{-1} (at 60^{o}C), 15.94 kjmol^{-1} and 117.59 kjmol^{-1} K^{-1}, respectively, indicating the spontaneous, endothermic and the increased randomness nature of Cu^{2+} adsorption. The results show that adsorption of Cu (II) on PHC is an.

Keywords: Adsorption, carbonization, equilibrium, kinetic, peanut hull carbon (PHC), thermodynamic.

Karbonize Fıstık Kabuğu Kullanılarak Sulu Çözeltilerden Bakır (II)'nin Adsorpsiyonu: Denge, Kinetik ve Termodinamik Parametrelerin Belirlenmesi

***Sorumlu yazar:**
Gülşad USLU ŞENEL
Firat Üniversitesi, Mühendislik Fakültesi,
Çevre Mühendisliği Bölümü, 23100 Elazig,
Turkey.
✉: guslu@firat.edu.tr
Mobile telephone : +90 (533) 748 35 53
Telephone : +90 (424) 237 00 00/8403

Öz: Bu çalışmada, karbonize fıstık kabuğu (PHC) üzerine Cu (II) adsorpsiyonuna sıcaklık, pH, başlangıç metal konsantrasyonu ve adsorban dozajın etkisi araştırılmıştır. Aktif karbon fıstık kabuğundan hazırlanmıştır. PHC, karbon dioksit varlığında 500 ° C'de 1.0 saat süresince karbonizasyon ile üretilmiştir. Maksimum Cu (II) adsorpsiyon kapasitesi, pH = 4.0'de 60 °C'de ve 500 mg/L başlangıç Cu (II) iyon konsantrasyonunda 168.16 mg/g olarak bulunmuştur. Adsorpsiyon dengesinin matematiksel olarak ifadesinde Freundlich ve Langmuir adsorpsiyon modelleri kullanılmıştır. Deneysel veriler için en iyi Freundlich izotermi ile verildi ve maksimum adsorpsiyon kapasitesi elde edildi. Adsorpsiyon kinetiğini incelemek için yalancı birinci ve yalancı ikinci derece düzeneğinin varsayımına dayanan bir seri adsorpsiyon modelleri uygulanmıştır. Kinetik veriler, yalancı ikinci derece kinetik düzen modeline uymuştur. PHC üzerinde bakır adsorpsiyonunun termodinamik fonksiyonları, serbest enerji değişimi (ΔG^o), entalpi (ΔH^o) ve entropi (ΔS^o) değeleri sırasıyla -23.21 kjmol^{-1} (60^{o}C'de), 15.94 kjmol^{-1} ve 117.59 kjmol^{-1} K^{-1} olarak hesaplanmıştır. Cu^{2+} adsorpsiyonu endotermik bir reaksiyondur. Sonuçlar, Cu (II) iyonlarının adsorpsiyonunda PHC kullanımının bir alternative olacağını göstermiştir.

Anahtar kelimeler: Adsorpsiyon, denge, fıstık kabuğu karbonu, karbonizasyon, kinetic, termodinamik.

INTRODUCTION

The water pollution by toxic heavy metals through the discharge of the industrial waste is a world-wide environment problem (Jiang et al., 2009). Heavy metal ions such as cobalt, copper, nickel, chromium and zinc are detected in the waste streams from mining operations, battery manufacturing processes, the production of paints and pigments, ammunition, ceramic and glass industries tanneries, electronics, electroplating and petrochemical industries, as well as in textile mill products (Argun & Dursun, 2008; Dursun, 2006). From the environmental risk and health hazards point of views, one of the most dangerous heavy metals is copper. Copper is heavily used metal in industries such mining and smelting, brass manufacture, electroplating industries, petroleum refining and excessive use of copper based agrichemicals mining. These industries produce much wastewater and sludge containing Cu(II) ions with various concentrations, which have negative effects on the water environment (Demirbaş et al., 2009). Although copper is an essential micronutrient and is required by the body in very small amounts (20-80 μg/kg of body weight per day), excess exposure to copper can cause acute as well as chronic effects (WHO, 2006). Hence, the removal of copper from aques solutions is extremely important.

Heavy metal removal from aqueous solutions has been commonly carried out by several processes: chemical precipitation, solvent extraction, flotation, ion-exchange, electrolytic recovery, membrane filtration, biological process, adsorption, biosorption (Wang et al., 2007; Çetin & Pehlivan, 2007; Giwa & Bello, 2007). Most of these methods are extremely expensive or inefficient, especially for a large amount of solution of relatively low concentrations (Jiang et al., 2009). Adsorption is highly effective and economical method to remove heavy metal ions from aques solutions (Özçimen & Ersoy-Meriçboyu, 2009). Among these processes, the adsorption with the selection of a suitable adsorbent can be an effective technique for the removal of heavy metals from wastewater (Bayat, 2002). The respective and widely used adsorbent material in the adsorption processes is activated carbon. Even though it has a high adsorption capacity, surface area and has a micro porous structure; it is restricted to use due to its relatively high price; high operation costs, and problems with regeneration for the industrial scale applications. This led to a search directed to developing the low-cost and locally available adsorbent materials with the maximum adsorption capacity (Sölener et al., 2008; Dursun et al., 2005; Özer et al., 2007).

The aim of this study is the evaluation of peanut hull carbon an effective, low cost, biomass adsorption media for the removal of metal ions from dilute aqueous waste streams. In order to achieve the aim of developing an effective adsorber, the parameters and mechanisms affective metal ion capture by peanut hull carbon must be identified and the physical and chemical limitations of the proposed technology assessed. A few researches in literature studied on copper binding ability onto PHC and they investigated the effect of pH on adsorption. However there is still lack of the studies focusing on temperature effects on the adsorption of copper (II) onto PHC. In earlier works, peanut hull carbon obtained from different methods to use as an adsorbent was studied for removing heavy metals such as copper (II) (Periasamy & Namasivayam, 1996) and nickel (II) (Gong et al., 2005) ions and dyes (Gong et al., 2005). The present study, deals with understanding of the temperature effects on the biosorption and one of the main objective of the work is to investigate the feasibility of using PHC in the batch model for adsorption of copper (II). The sorption phenomena were expressed by the Langmuir and Freundlich adsorption models and model constants were evaluated depending on temperature. As there is no information about the kinetic analysis of the adsorption of copper (II) by PHC, the experimental data was also analyzed using the pseudo-first and pseudo second-order adsorption kinetic models and kinetic constants were calculated. An understanding of the kinetics of sorption gives useful knowledge for on-site full-scale applications. Since the evaluation of the heat change of the adsorption process is very important for reactor design, the thermodynamics of the adsorption process was also investigated.

Equilibrium modeling in a batch system: Adsorption is a well-known equilibrium separation process for wastewater treatment. Adsorption isotherms are the equilibrium relationships between the concentrations of adsorbed metal and metal in solution at a given temperature. The well-accepted adsorption isotherm models of Freundlich and Langmuir have successfully described Cu (II) adsorption isotherms.

The well-known expression of the Langmuir model is given by Equation (1)

$$q_{eq} = \frac{q_{\max} K C_{eq}}{1 + K C_{eq}} \qquad (1)$$

where K is the adsorption equilibrium constant including the affinity of binding sites (L mg^{-1}), C_{eq} and q_{eq} are unadsorbed metal ions in solution and adsorbed metal ions on the sorbent at equilibrium, respectively. q_{max} is the maximum amount of metal ion per unit weight of adsorbent to from a complex monolayer on the surface (mg g^{-1}) (Langmuir, 1916).

The empirical Freundlich equation based on sorption on a heterogeneous surface is given by Equation (2)

$$q_{eq} = K_F C_{eq}^{1/n} \qquad (2)$$

where K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the sorbent, respectively (Freundlich, 1906; Tewari, 2006).

Kinetic Modelling: The capability of pseudo-first order and pseudo-second order kinetic models were examined in this study. The pseudo-first order equation of Lagergren is generally expressed as follows (Lagergren, 1998):

$$\frac{dq}{dt} = k_1(q_{eq} - q) \tag{3}$$

where q is adsorbed dye quantity per gram of sorbent at any time (mg g^{-1}), k_1 is the rate constant of pseudo-first order sorption (min^{-1}). The integrated form of the differential equation becomes,

$$\log(q_{eq} - q) = \log(q_{eq}) - \frac{k_1}{2{,}303}t \tag{4}$$

The pseudo-second order kinetic rate equation is expressed as (Ho & Mckay, 1999):

$$\frac{dq}{dt} = k_2(q_{eq} - q)^2 \tag{5}$$

where k_2 is the rate constant of pseudo-second order sorption (g mg^{-1} min^{-1}). For the same boundary conditions the integrated form of Equation (5) becomes

$$\frac{t}{q} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}}t \tag{6}$$

The second order rate constant can be determined from the intercept of the linearized pseudo-second order rate equation.

Thermodynamics of adsorption: In engineering practice, entropy and Gibbs free energy factors should be considered in order to determine what processes will occur spontaneously. The Gibbs free energy change ($\Delta G°$) can be determined using equilibrium constant (The Langmuir constant K_b) (Equation 7)

$$(\Delta G°) = - RT \ln K_b \tag{7}$$

where R is the universal gas constant (8.314 J $mol^{-1}K^{-1}$) and T is the absolute temperature (K), K_b is the equilibrium constant (The Langmuir constant) (Ho & Mckay, 1999; Kara, 2003). The higher negative value of the Gibbs free energy reflects a more energetically favourable adsorption. The equilibrium constant can be used in the Van't Hoff equation to determine the enthalpy ($\Delta H°$) and entropy change of biosorption ($\Delta S°$) as a function of temperature.

$$lnK_b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{8}$$

MATERIALS AND METHODS

Preparation of peanut hull carbon (PHC): Raw peanut hull material used in this study was obtained from a local market in Elazig, Turkey. It was extensively washed with top water to remove soil and dust, sprayed with distilled water than the raw peanut hulls were prepared by air-drying to environmental equilibrium moisture in the lab on shallow trays at room temperature followed by grinding and sieve analysis. It was grounded and sieved to 50-100 mesh size (0.34-0.15 mm) to separate the material into discrete particle size ranges. Then, powder of peanut hull (25 g) was placed in a horizontal ceramic tube furnace and heated up to 500 ^oC at a rate of 5 ^oC/min. It was left at this temperature to thermally decompose to porous carbonaceous materials for 1 h and than allowed to cool to room temperature in carbon dioxide atmosphere carbon production yield from peanut hull was %25.

Physical and Chemical Characterized of Adsorbent: Characterization of the peanut hull was performed by infrared spectroscopy (IR) and by determination of the BET surface area.

Fourier transforms infrared spectroscopy (FT-IR) was used to determine the vibration frequency changes in the functional groups in the peanut hull. The spectra of PH were measured by on FTIR spectrometer within the range of 500-4000cm^{-1} wave number. The infrared spectrum of raw PH and PHC were obtained with Mattson 1000 FTIR spectrometer with a pellet of powdered potassium bromide and sample.

Surface area is related to the adsorption capacity of an adsorbent. The BET surface area was determined from nitrogen isotherms using a Micromeritics Flow Sorb II-2300 Surface Area Analyzer.The measured BET surface area for PHC was 41.3 m^2g^{-1}.

The BET surface area was determined from nitrogen adsorption isotherms using a Micromeritics Flow Sorb II-2300 Surface Area Analyzer. The BET surface area of PHC was measured as 41.3 m^2g^{-1}. The infrared spectrum of raw peanut hull and PHC were obtained with a Mattson 1000 FTIR spectrometer with a pellet of powdered potassium bromide and sample.

Chemicals: Metal ion solution was prepared by dissolving 1.0 g/L of stock metal ion solution, which was obtained by dissolving a weight quantity of nitrate salts of the metal (Merck). The pH of the each solution was adjusted to the required value with dilute of concentrated HNO_3 and NaOH solutions before mixing with the PHC. While there was no significant changes observed on pH in the equilibrium, the uptake pH was assumed constant during the experiments. The concentration of residual Cu (II) ions in the adsorption media were determined by using an atomic adsorption spectrophotometer (UNICAM, 929).

Adsorption studies: Copper (II) adsorption studies were performed at various initial concentrations and temperatures at constant 150 rpm shaking glass flasks of 0.25 L containing of 0.1 L copper (II) ion solution at desired concentration including 0.5 g peanut hull carbon using a rotabit shaker from Selecta. Samples 5 mL were taken from mixture during stirring at predetermined time intervals for determining the residual Cu (II) ion concentration in the solutions. Before analysis, samples were filtered by using blue type whatman filter paper and supernatant fluid was analyzed for the remaining metal ions. All the experiments were carried out in duplicates and average values were used for further calculations. For isotherm studies, a series of flask containing (0.1 L Cu (II) ion solution in the range of 25-500 mg/L were prepared. The weighed amount of 0.5 g PHC was added to each flask and then the mixtures were agitated at constant temperature of 20, 40 and 60 ^{o}C. These experiments were carried out at a constant pH of 4.0 for duration 24 h.

RESULTS AND DISCUSSION

Adsorption of copper (II) ion onto peanut hull was investigated as a function of pH, temperature, adsorbent dosage and initial Cu (II) ion situation in a batch stirred reactor in this study. The kinetics and equilibrium results were given as units of adsorbed metal ion concentration at equilibrium result ($C_{ad,eq}$: mg/L), adsorbed metal ion quantity per gram at PHC end unadsorbed metal ion concentration (q_{eq}, g^{-1}, C_{eq}, mg/g, respectively and adsorption yield (Ads%= 100x(C_o-C_{eq}/C_o)).

FTIR analysis: The presence of functional groups depends on the treatment procedure of the sample. Figure 1 shows the FT- IR spectrum raw material and peanut hull carbon in the spectroscopic region 4000-500 cm $^{-1}$. The first peak is centered 3900 cm^{-1}. In the spectra of the carbon materials the band of stretching OH vibrations (3600-3100 cm^{-1}) is due to carbon surface hydroxyl and amino groups. The second broad peak at 1700 cm^{-1} has been assigned to the carboxyl stretching. The decreasing intensity of adsorption band of carboxyl groups at 1700 cm^{-1} may be attributed to the destruction of carboxyl groups during the treatment of peanut hull.

Effect of pH on Cu (II) adsorption: The pH of an aqueous solution is an important controlling parameter in the process of adsorption. The effect of pH on the adsorption capacity of copper (II) ion by PHC was evaluated within the pH range of 2-5.5. Removal of copper (II) ions increases with increasing solution pH and a maximum value was reached at an equilibrium pH of around pH 4 at 100 mg/L initial copper (II) ion concentrations. Experiments were carried out up to pH value of 6 due to the fact that metal precipitation occurred at higher pH values. At very low pH values (pH=2-3), copper (II) ion adsorption was found to be very low due to competition between H_3O^+ and copper (II) ions for the adsorption sites. In addition when the pH increases, there is a decrease in positive surface charge, which results in a lower electrostatic repulsion between the positively charged metal ion and the surface of PHC, favoring adsorption. Loading of copper (II) ions onto PHC also found to increase till pH 4, remained constant till pH 5 and beyond pH 6 hydroxide precipitations took place, which in addition to adsorption contributes to the removal of metal ion.

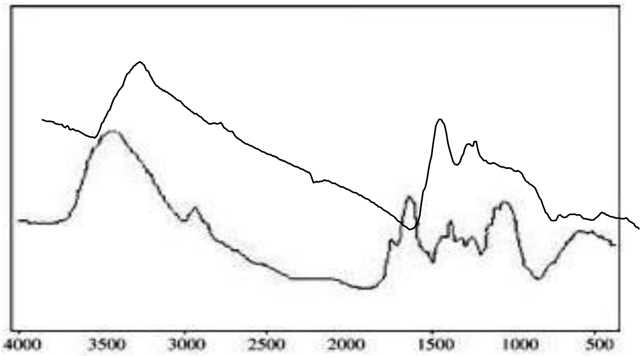

Figure 1. The IR spectrum of the peanut hull.

Effect of temperature Cu (II) adsorption: The effect of temperature Cu (II) uptake capacity onto PHC was studied at 100 mg/L initial metal ion concentration. The variation of equilibrium uptake with temperature was given in Table 1. Results given in Table 1 clearly showed that initial sorption of Cu (II) ion occurred very rapidly and reach equilibrium in 100 min for 100 mg/L initial Cu (II) ion concentrations at 20, 40 and 60^{o}C studied. Figure 2 shows that the adsorption of Cu (II) ions onto PHC as a function of contact time at all temperatures. Adsorption studies were carried out for 24 h and it was observed that, the amount of adsorbed Cu (II) increased linearly with time at the beginning of adsorption. A larger amount of Cu (II) ions were removed in the first 10. min of contact time and the equilibrium was established in 30-60 min at the and of a rapid adsorption for all temperatures studied. After an equilibrium time of 120 min, no more Cu (II) was adsorption. The optimum adsorption temperature for Cu (II) was determined to be 60 ^{o}C. It was shown that the removal of copper (II) ions increased with increasing temperature up to 60 ^{o}C. The adsorption of Cu (II) was endothermic, thus extend of adsorption increased with increasing temperature. The maximum Cu (II) adsorption yields and desorption yields were determined as 60.20 %, 68.44 % and 83.56 % and 80.73 %, 95.52 % and 99.88 % at 25 mg dm^{-3} initial copper (II) ion concentration for 20, 40 and 60 ^{o}C, respectively (Table 1).

Effect of initial metal ion concentration on Cu (II) adsorption: The effect of initial copper (II) ion concentration on the sorption capacity onto PHC was investigated at different temperatures and pH 4.0. The equilibrium uptake capacities of the PHC increased with increasing initial metal ion concentration up 500 mg/L because the initial Cu (II) concentration provides an important driving force to overcome mass transfer resistances between the adsorbent and adsorption medium. Higher sorption capacities were obtained at higher initial concentrations for copper (II) ion at all temperatures (Table 1). Increasing the metal ion concentration generally caused a decrease in the adsorption yield and maximum copper (II) ions adsorption yield determined as 83.56% an initial concentration 25 mg/L at 60 °C. At higher concentrations, the ratio of initial number of metal ions to the available sites of adsorption became fewer and the saturation of the sorption sites was observed so adsorption yields decreased.

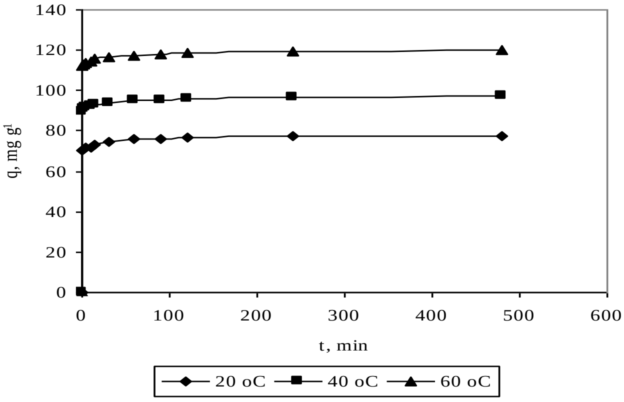

Figure 2. Copper (II) adsorption curves at given conditions.

Effect of the adsorbent dosage on the adsorption of Cu(II): The effect of adsorbent dosage on the removal of copper (II) ion at C_o= 100 mg/L was studied. While other experimental conditions were kept constant as the adsorbent concentration was varied 0.5 to 2.5 g/L. The influence of adsorbent dosage in percentage adsorption and equilibrium uptake is depicted in Figure 3. It is clear that copper (II) ion uptake increased with increasing adsorbent dosage from 0.5 to 2.5 g/L, as the percentage of copper (II) ions removal yield decreased from 60.09 to 34.16 %, as the number of binding sites would be increased, but the adsorption of copper (II) ion per unit weight of adsorbent decreased from 120.18 to 68.32 mg/g of adsorbent. This is because of the availability of more and more binding sites for complexation of copper (II) ions. Adsorption sites remain unsaturated during the adsorption reaction. This is due to the fact that as the dosage of adsorbent is increased, there is less commensurate increase in adsorption resulting from the lower adsorptive capacity utilization of the adsorbent. The decrease in adsorption capacity can be explained with the reduction in the effective surface area.

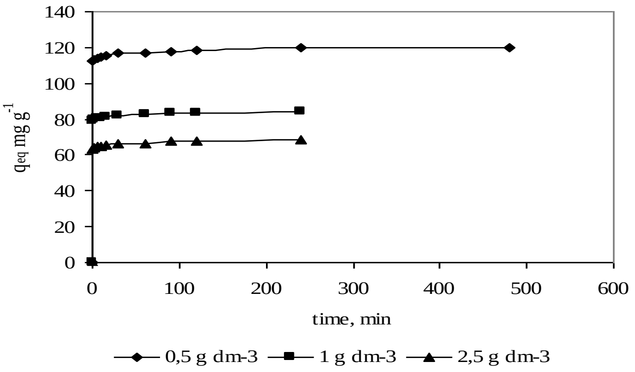

Figure 3. Influence of adsorbent dosage in adsorption yield and equilibrium uptake (C_o= 100 mg L^{-1}, pH= 4.0, T= 60 °C, X: 0.5 g L^{-1}, agitation rate= 150 rpm).

Table 1. The equilibrium uptake capacities adsorption yields and desorption yields obtained at different initial concentrations and temperatures.

C_o mg dm^{-3}	20°C			40°C			60°C		
	q_{eq}, mg g^{-1}	% Ad.	% Des.	$q_{eq,}$mgg-^{1}	% Ad.	% Des.	q_{eq}(mgg^1)	% Ad.	% Des.
25	30.10	60.20	80.73	34.22	68.44	95.52	41.78	83.56	99.88
50	42.92	42.92	79.68	48.38	48.38	95.05	76.24	76.24	99.45
75	58.60	39.07	76.96	75.66	50.44	94.52	99.54	66.36	99.28
100	77.44	38.72	75.43	97.18	48.59	93.89	120.18	60.09	99.10
200	99.58	24.89	75.37	110.56	27.64	93.21	175.62	43.91	98.55
300	137.12	22.85	73.23	149.18	24.86	92.53	242.18	40.36	98.15
500	168.16	16.82	72.79	184.38	18.44	92.14	381.16	38.12	95.02

Determination of equilibrium parameters: The equilibrium adsorptions isotherms are very important for the design of adsorption systems since they represent how the metal ions are partitioned between the adsorbent and liquid phases at equilibrium as a function of metal ion concentration. Various isotherm equations were well known and two different isotherms were selected in this study, which are the Langmuir and Freundlich isotherms. The linearized Langmuir and Freundlich adsorption isotherms of copper (II) ions obtained at the temperatures 20, 40 and 60 °C. The Langmuir and Freundlich adsorption constants evaluated from the isotherms and correlation coefficient are given in Table 2. As observed from the Table 2, the isotherms appeared to follow Freundlich model more closely than the Langmuir model at all the temperatures studied. The Langmuir equation is based on a monolayer adsorption by the adsorbent with the same energy of active sites. The surface of this material was expected to have nearly homogenous sites for adsorption, so a much better fit was obtained. The experimental data indicate that the amount of Cu (II) sorbed increased from 117.99 to 212.88 mg/g with increase in temperature from 20 °C to 60°C. The other Langmuir constant, K indicates the affinity for the binding of Cu (II).The higher value of K found at 60°C showed strong bonding of Cu (II) to the PHC at this temperature. The Freundlich isotherm is an empirical equation employed to describe heterogeneous system. The Freundlich isotherm model exhibited a good fit to the experimental sorption data since the r^2 values were 0.99, 0.98 and 0.99 at 20, 40 and 60°C. The Magnitude of K_F and n of the Freundlich isotherm constants showed the tendency of Cu (II) uptake from the adsorption medium with high capacity of PHC especially at 60°C. The highest K_F value was determined as 21.49 at this temperature. All n values were found high enough for adsorption.

Table 2. Isotherms constants for Cu (II) ion adsorbed on PHC.

T (°C)	Langmuir Model			Freundlich Model		
	q_{max}	K	R^2	K_F	n	R^2
20	117.99	0.032	0.90	9.67	2.09	0.99
40	133.19	0.040	0.86	14.49	2.33	0.98
60	212.88	0.069	0.86	21.49	2.40	0.99

Kinetic parameters of adsorption: Various kinetic models namely the lagergren's pseudo-first order, pseudo-second order and intraparticle diffusion models have been used for the validity with the experimental at adsorption process for Cu (II) onto PHC. With the average shaking speed of 150 rpm, it was assumed to offer no mass transfer resistance to the overall adsorption process. The values of various kinetic parameters are tabulated in Table 3. The results showed that, the correlation coefficient for the pseudo-first order kinetic model obtained 20-60°C was very low and they increased with increasing temperature. The theoretical $q_{eq,cal}$ values found from this model did not give reasonable values especially at low temperature so pseudo-first order model could not describe the adsorption results of Cu (II) onto PHC.

The values of second order adsorption rate constant, k_2, were calculated. Theoretical and experimental q_{eq} and correlation coefficients are also given Table 3. In the view of these results, it can be said that the pseudo-second order kinetic model provided a good correlation for the adsorption of Cu (II) onto PHC in contrast to the pseudo-first order model.

Tablo 3. Change of the pseudo- first and second order reaction rate constants with temperature.

T, °C	$q_{eq,exp}$ (mg g^{-1})	First order kinetic model			Seconder order kinetic model		
		k_1 (dm^{-3} min ^{1})	$q_{eq,cal}$ (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	$q_{eq,cal}$ (mg g^{-1})	R^2
20	77.44	0.023	9.017	0.83	0.019	77.52	0.99
40	97.18	0.015	9.090	0.61	0.015	97.20	0.99
60	120.18	0.014	9.175	0.59	0.012	120.18	0.99

Determination of thermodynamic parameters: Thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) can be estimated by using equilibrium constants changing with temperature. The value of ΔG° for the adsorption of Cu (II) onto PHC at different temperature (20, 40 and 60°C) is given in Table 4. The magnitude of ΔG° increased with the rise in temperature. Gibs free energy values for the adsorption process were obtained as -18.55, -20.49 and -23.21 kJmol^{-1} for the temperatures 20, 30 and 60 °C, respectively. The K values increased with increasing temperature. The negative value of ΔG° confirms the feasibility of the process and the spontaneous nature of adsorption of Cu (II) onto PHC. ΔH° for the adsorption of Cu (II) onto PHC was found to be 15.94 k J mol^{-1} while ΔS° was 117.59 k J mol^{-1}K^{-1}. The positive value of ΔH° suggested the endothermic nature of adsorption, while positive values of ΔS° reflect the affinity of Cu (II) for sorbent used. In addition, positive value of ΔS° shows the increasing randomness at the solid/liquid interface during the sorption of Cu (II) on selected sorbent.

Table 4. The thermodynamic constants of adsorption obtained PHC.

T, °C	K (dm^{-3} mg^{-1})	-ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1}mol^{-1})
20	7.618	18.55		117.72
40	7.839	20.49	15.49	116.05
60	8.385	23.21		117.59

CONCLUSION

PHC is an effective adsorbent for the removal of Cu (II) from aqueous solution. The results indicated that adsorption capacity of the adsorbent was considerably affected by initial pH, temperature and initial Cu (II) concentration. The optimum pH value was determined to be 4.0. It was found that Cu (II) adsorption increased with temperature up to 60°C and initial Cu (II) ion concentration up to 500 mg/L. The Langmuir and Freundlich adsorption equations were used to expiries adsorption phenomenon of the Cu (II). The Freundlich isotherm model at those optimum conditions best defined the equilibrium data. The PHC can be used as an effective low-cost agricultural waste adsorbent for the removal of Cu (II) with its adsorption capacity of 120.18 mg/g at 60°C. The kinetics of Cu (II) adsorption onto PHC was examined using the pseudo-first and pseudo-second order kinetic models. The results indicated that the pseudo-second order equation provided the best correlation of the sorption data. The thermodynamic constants of adsorption were also evaluated. The negative value of ΔG° confirms the spontaneous nature adsorption process. The positive value of ΔS° showed the increased randomness at the solid-solution interface during adsorption and the positive value of ΔH° indicated the adsorption process was endothermic. It can be concluded that the PHC would be useful for the economic treatment of wastewater containing Cu (II) to use on agricultural by-product such as peanut hull as an adsorbent.

REFERENCES

Argun, M.E. & Dursun, S. (2008). A new approach to modification of natural adsorbent for heavy metal adsorption. *Bioresearch Technology*, ***99***, 2516-2527.

Bansode, R.R., Losso, J.N., Marshall, W.E., Rao, R.M. & Portier, R.J. (2004). Pecan shell-based granular activated carbon for treatment of chemical oxygen demand (COD) in municipal wastewater. *Bioresource Technology*, ***94***, 129-135.

Bayat, B. (2002). Comparative study of adsorption properties of Turkish fly ashes. I. The case of nickel(II), copper(II) and zinc(II). *Journal of Hazardous Materials, **95**(3), 251-273*.

Cetin, S. & Pehlivan, E. (2007). The use of fly ash as a low cost, environmentally friendly alternative to activated carbon for the removal of heavy metals from aqueous solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects. **298***(1-2), 83-87.

Demirbaş, E., Dizge, N. & Kobya, M. (2009). Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon. *Chemical Eng. J*, ***148***, 480-487.

Dursun, A.Y. (2006). A comparative study on determination of the equilibrium, kinetic and Thermodynamic parameters of adsorption of copper (II) and lead (II) ions onto pretreated *Aspergillus niger*. *Biochem. Eng. J*, ***28***, 187-195.

Dursun, G., Çiçek, H. & Dursun, A.Y. (2005). Adsorption of phenol from aqueous solution by using carbonised beet pulp**.** *Journal of Hazardous Materials*, ***125***(1-3, 17), 175- 182.

Freundlich, H.M.F. (1906). Uberdie adsorption in lasungen. *J. Phys. Chem.*, ***57***, 385-470.

Giwa, O.S. & Bello, I.A. (2007). Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. *Biochem. Engin. J.*, ***36***(2), 174-181.

Gong, R., Li, M., Yang, C., Sun, Y. & Chen, J. (2005). Removal of cationic dyes from aqueous solution by adsorption on peanut hull**.** *Journal of Hazardous Materials.* ***121***(1-3), 247-250.

Gong, R., Sun, Y., Chen, J., Liu, H. & Yang, C. (2005). Effect of chemical modification on dye adsorption capacity of peanut hull**.** *Dyes and Pigments.* ***67***(3), 175-181.

Ho, Y.S. & Mckay, G. (1999). Pseudo-second order model for sorption processes, *Process Biochem.*, ***34***, 451-465.

Jiang, Y., Pang, H. & Bing, L. (2009). Removal ofg copper (II) ions from aqueous solution by modified bagasse. *J of Hazardous*, ***164***, 1-9.

Kara, M., Yüzer, H., Sabah, E. & Çelik, M. (2003). Adsorption of cobalt from aqueous solution onto seplolite. *Water Research*, ***37***, 224-232.

Lagergren, S. (1998). Zur theorie der sogenannten adsorption geloster stoffe, Kungliga Svenska Vetenkapsakademiens, handlingar. 24, 1–39.

Langmuir, I. (1916). The constitution and fundamental properties of solids and liquids. *J Am Chem Soc.*, ***38***(11), 2221-95.

Özçimen, D. & Ersoy-Meriçboyu, A. (2009). Removal of copper from aqueoussolutions by adsorption onto chestnut shell and garpeseed activated carbons. *J. of Hazardous.* ***168***, 1118-1125.

Özer, D., Dursun, G. & Özer, A. (2007). Methylene blue adsorption from aqueous solution by dehydrated peanut hull. *J. of Hazard. Mater*, ***144***, 171-179.

Periasamy, K. & Namasivayam, C. (1996). Removal of copper (II) by adsorption onto peanut hull carbon from water and copper plating industry wastewater**.** *Chemosphere*, 32(4), 769-789.

Sölener, M., Tunali, S., Özcan, A.S., Özcan, A. & Gedikbey, T. (2008). Adsorption characteristics of lead (II) ions onto the clay/poly (methoxyethyl)acrylamide (PMEA) composite from aqueous solutions. *Desalination*, ***22****3*, 308-322.

Tewari, N., Vasudevan, P. & Guha, B.K. (2005). Study on biosorption of Cr (VI) by Mucor hiemalis, Biochemical Eng. J. 23, 185-192.

Wang, H.J., Zhou, A.L., Peng, F., Yu, H. & Chen, L.F. (2007). Adsorption characteristic of acidified carbon nanotubes for heavy metal Pb (II) in aqueous solution. *Materials Science and Engineering: A. 466*(1-2), 201-206.

WHO. (2006). Guidelines for Drinking-Water Quality: Incorporating First Addendum, 1,. Recommendations, third ed., World Health Organization, Geneva.