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Co-conversion of Industrial Biowaste Mixtures by Hydrothermal Method and Application to Cu^{2+} Adsorption

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ABSTRACT

In present work, a novel carbonaceous product (HPSHC) was obtained by hydrothermal co-carbonization (co-HTC) of hazelnut and peanut shells (HS and PS). HS and PS were mixed at a mixing ratio of 1:1 by mass and subjected to co-HTC treatment at 220°C for 6 hours' reaction time. The physicochemical characteristics of the produced HPSHC such as atomic carbon content, mass yield, higher heating value and energy density were determined. In addition, attenuated total reflectance-fourier transform infrared spectroscopy (ATR-FTIR) was taken to determine the surface functional groups and scanning electron microscopy (SEM) images were taken to highlight the surface morphology. HPSHC was utilize as a sorbent sample in copper ions (Cu(II)) adsorption. The rate and equilibrium parameters of the system were calculated by kinetic and isotherm modeling of the adsorption. Kinetic studies showed that the adsorption was consistent with the pseudo-second order kinetic model, and isotherm studies showed that it was obeyed the Langmuir model. A theoretical maximal uptake capacity (q_m) was calculated 39.90 mg/g. In addition, as a result of thermodynamic calculations using equilibrium constants, it was observed that the adsorption of Cu(II) on HPSHC is a spontaneous and endothermic process.

Keywords: Co-hydrothermal carbonization, Cu(II), Hazelnut shell, Peanut shell, Isotherm, Kinetic

Endüstriyel Biyoatık Karışımının Hidrotermal Yöntemle Birlikte Dönüşümü ve Cu^{2+} İyonları Adsorpsiyonuna Uygulanması

ÖZ

Mevcut çalışmada, fındık ve fıstık kabuklarının birlikte hidrotermal karbonizasyonu (ko-HTK) ile karbon esaslı yeni bir ürün (HPSHC) elde edildi. Fındık ve fıstık kabukları kütlece 1:1 karışma oranında karıştırılıp 220 °C sıcaklıkta 6 saat reaksiyon süresinde ko-HTK işlemine tabi tutuldu. Üretilen HPSHC'nin atomik karbon içeriği, kütle verimi, üst ısıl değer ve enerji yoğunluğu gibi fizikokimyasal karakteristikleri belirlendi. Ayrıca yüzey fonksiyonel gruplarını belirlemek için fourier transform kızılötesi spektrumu (FTIR) ve yüzey morfolojisini aydınlatmak için taramalı elektron mikroskop (SEM) görüntüleri alındı. HPSHC sulu çözeltiden bakır iyonları (Cu(II)) adsorpsiyonunda adsorplayıcı olarak kullanıldı. Adsorpsiyonun kinetik ve izoterm modellemesi yapılarak, sisteme ilişkin hız ve denge parametreleri hesaplandı. Kinetik çalışmalar, adsorpsiyonun yalancı-ikinci dereceden kinetik modeli ile uyumlu olduğunu ve izoterm çalışmaları ise Langmuir adsorpsiyon izotermine uygunluğunu gösterdi. HPSHC için maksimum Cu(II) adsorpsiyon kapasitesi (q_m) 39.90 mg/g olarak hesaplandı. Ayrıca denge sabitleri kullanılarak yapılan termodinamiksel hesaplamalar sonucu, HPSHC üzerinde Cu(II) adsorpsiyonunun kendiliğinden ve endotermik bir süreç olduğu gözlemlendi.

Anahtar Kelimeler: Birlikte-hidrotermal karbonizasyon, Cu(II), Fındık kabuğu, Fıstık kabuğu, İzoterm, Kinetik

INTRODUCTION

As a result of rapid developments in global industrial technologies, copper (Cu(II)) ions are frequently used in the manufacture of semiconductors [1], batteries [2] and electronic components of machines [3]. Some of the industrial waste from this processing industry inevitably results in the release of Cu(II) into the ecological environment. Due to its high toxic potential, environmental persistence, non-biodegradability and bioaccumulation, aquatic system contamination from copper (Cu(II)) ion causes severe ecological environment and body function disorders [4]. After Fe(II) and Zn(II) ions, Cu(II) is the third most abundant transition metal in the human body [5]. When Cu(II) exceed the normal limit, they can accumulate in human cells and cause many dangerous diseases like Wilson and Alzheimer diseases or cancer [6]. For this reason, the US

Environmental Protection Agency specifies that the Cu(II) concentration in drinking water should be less than 20 µM [7]. Therefore, it is of great importance to develop new types of materials that can effectively remove Cu(II) ions from wastewater. Different methods like ion exchange [8], redox [9], chemical precipitation [10] and adsorption [11] are used to remove Cu(II) from wastewater. Among these, the adsorption technique attracts great interest owing to its easy applicability, high purification efficiency and low cost [12].

Hydrothermal carbonization (HTC) of biomass wastes attracts great attention due to the environmental and energy crisis that has increased its impact in recent years. HTC, a thermochemical conversion process of wet biomass to hydrochar, a solid product with high added value, is a low-cost technique [13]. Owing to the presence of oxygen-containing functional groups on its surface, hydrochar is an effective sorbent material for pollution removal. Since oxygen-containing functional groups on the surface play a key role in removing pollutions through surface complexation, electrostatic interaction, and ion exchange [14]. Co-hydrothermal carbonization (co-HTC) technique, in which carbonization stage is applied to more than one feedstock simultaneously, has recently attracted the attention of researchers. This method is applied to improve the resulting hydrochar product properties such as carbon content and fuel quality increase or decrease in ash content relative to the single hydrothermal carbonization product [15].

In this research, a new hydrochar was prepared by co-hydrothermal carbonization of hazelnut and pistachio shells. Next, the obtained HPSHC was implemented in copper Cu(II) ions elimination process. Physicochemical properties of HPSHC were characterized by spectroscopic techniques such as FTIR, SEM and elemental analysis. Cu(II) sorption process was searched including kinetics and isotherms studies, and the impact of several agents on the sorption performance of HPSHC, containing solution pH, temperature and equilibrium-contact time were investigated.

MATERIALS and METHODS

Biomass and Chemicals

Hazelnut and pistachio shells (HS and PS) were obtained from the hazelnut processing factory in Ordu and the peanut processing factory in Gaziantep, respectively. Both raw materials were thoroughly cleaned with distilled deionized (DI) water and air-dried for 12 h. After drying, feedstocks were crushed in a pulverizer for 60 sec and sieved at <200 µm to obtain a homogenous HS and PS powder mixture. The chemicals used in this study were $CuSO_4.5H_2O$, NaOH, HCl and C_2H_5OH of analytical purity and purchased from Sigma-Aldrich.

HPSHC production

The co-HTC process of HS and PS was performed in a high-pressure reactor with a volume of 100 mL (Fytronix, FYHT-8000, Turkey). A mixture of 50 mL DI water and 5 g biomass (2.5 g of HS and 2.5 g of PS) was transferred to the hydrothermal reaction system to keep the biomass/water ratio 1:10. The biomass-water mixture was kept in an autoclave at 220 ºC for 6 h and the hydrothermal product was collected by vacuum filtration, washed several times with DI water and dried in electrical oven at 80 °C for 12 h.

Characterization of HPSHC

The synthesis yield (*SY*), higher heating value (*HHV*) and energy yield (*EY*) of HPSHC were calculated according to the following formulas:

$$SY\ (\%) = \frac{mass\ of\ hydrochar}{mass\ of\ feedstock} \times 100 \tag{1}$$

$$HHV = 0.3491\ C\% + 1.1783\ H\% + 0.1005\ S\% - 0.1034\ O\% - 0.015\ N\% - 0.021\ ash\% \tag{2}$$

$$EY = MY \times \frac{HHV_{hydrochar}}{HHV_{feedstock}} \tag{3}$$

The ATR-FTIR spectrum was recorded in the 450-4000 cm^{-1} wavelength region to perform the qualitative analysis of the functional groups in sorbent surface. The morphological structure pristine and Cu(II)-loaded hydrochar were investigated with scanning electron microscopy (SEM). The fundamental elemental composition of feedstocks and HPSHC were analyzed instrumentally, and percentage of O was calculated by subtraction technic (O%= 100%-C%-H%-N%-S%-Ash). Fixed carbon (FC), volatile matter (VM), moisture (M) and ash content (A) analyzes of hazelnut and pistachio shells and HPSHC were made according to China GB/T212-2008 standard test.

Adsorption Studies

pH, kinetic and isotherm experimental studies were carried out to investigate Cu(II) adsorption on HPSHC. All experimental studies were carried out with 0.1 gram of HPSHC, each experiment was repeated twice and calculations and models were made with average values. For the investigation of pH effect on sorption process, pH values were set ranging from 2 to 6, at 293 K with 100 ppm. To observe the adsorption kinetics of copper ions, the batch tests were analyzed with temperatures ranging from 293 to 333 K under the optimal working pH (pH:5) and initial concentration of 100 ppm. Supernatants (15 mL) were collected at different contact time intervals (5-360 min). Isotherm experiments were carried out at different concentrations (50-400 ppm) and temperatures (293-333 K) for 10 h. After sorption, heavy metal ion concentration was detected by Atomic Adsorption spectrophotometer (AAS). Each experiment was repeated at least two times. The rate constants for the HPSHC-Cu(II) system were calculated by two models namely pseudo-first order (PFO) [16] (Eq. 4) and pseudo-second order (PSO) [17] (Eq. 5) kinetic equations:

$$log(q_e - q_t) = log q_e - \frac{k_{ads,1}}{2.303} t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_{ads,2} q_e^2} + \frac{t}{q_e} \quad (5)$$

where q_e, q_t, $k_{ads,1}$, and $k_{ads,2}$ represent adsorption uptake at equilibrium (mg/g), adsorption uptake at time t (min) (mg/g), rate constant of PFO (1/min), and rate constant of PSO ((g/(mg.min)), respectively.

The isotherms of Langmuir [18] (Eq. 6) and Freundlich [19] (Eq. 7) were analyzed for adsorption system and parameters of equilibrium were calculated:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (6)$$

$$log\, q_e = log\, K_F + \frac{1}{n} log C_e \quad (7)$$

where C_e is equilibrium concentration of Cu(II) (mg/L), b Langmuir constant representing energy of adsorption (L/mg) and q_m represents maximum adsorption capacity of the adsorbent (mg/g). K_F ((mg/g)(L/mg)$^{1/n}$) is the equilibrium constant of Freundlich and n is the heterogeneity factor. In addition, Langmuir's constant b is used in Eq. (8) to determine the equilibrium factor R_L:

$$R_L = \frac{1}{1 + b\, C_0} \quad (8)$$

where C_o (mg/L) is the initial concentration of metal ion. The R_L value indicates the type of sorption either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($R_L < 1$) or irreversible ($R_L = 0$).

RESULTS and DISCUSSION

Characterization of HPSHC

Elemental analysis, fuel properties and proximate analysis

Elemental analyzes of the raw materials (HS and PS) and HPSHC hydrochar produced by the co-HTC technique were carried out to evaluate the change in elemental compositions and the data obtained are shown in Table 1. The content of elemental carbon in HPSHC is higher than that of HS and PS, which is due to the carbonization and hydrolysis reactions that take place during the co-hydrothermal treatment. Also, the decreases of H and O in HPSHC compared to HS and PS are because of decarboxylation, dehydration and condensation reactions that occur through co-HTC process [20]. In addition, the fact that the H/C and O/C atom ratios of HPSHC are lower than the raw biomasses show that the co-hydrothermal process increases the aromatization in the structure. The contents of ash (A), volatile matter (VM) and fixed carbon (FC) in materials are also presented in Table 1. The ash contents of HS and PS decreased by 52% and 60%, respectively, during the co-HTC treatment. During the HTC process, ash as an inorganic component is mostly inactive, so the reaction and decomposition of the biomass components allows the inorganic structures to easily pass into the liquid phase [21]. When the contents of VM and FC are examined, reducing in VM and rising in FC values are determined after co-HTC for both biomasses. The reduce in VM and the rise in FC are attributed to the condensation and polymerization reactions that occur through co-HTC treatment [22]. According to the data in Table 1, the HHVs of the HS and PS increased after co-HTC treatment and reached 20.12 MJ/kg. In addition, fuel ratios increased by 0.53 and 0.45, respectively, to 0.84 for HS and PS. The increase in HHVs is due to both the increase in %C and the decomposition of cellulose and hemicellulose. That is, after the co-HTC reaction, the contents of ash and volatile matter in raw materials decrease, and hemicellulose and cellulose, which have HHVs ranging from 16.81 to 18.6 MJ/kg, are decomposed at temperatures around 180 ºC and 220-230 ºC. As a result, components with higher HHV remain in the structure of the hydrochar and increase HHV [23]. Considering the mass and energy yield values, it was calculated as SY: 75.45% and EY: 81.24%, respectively.

Table 1. Physicochemical characteristics of HS, PS and HPSHC

Sample ID	HS	PS	HPSHC
%C	48.46	44.75	51.85
%H	5.661	5.705	5.404
%N	0.458	0.292	0.362
%S	-	0.068	-
%O	44.37	47.93	41.88
H/C	1.40	1.53	1.25
O/C	0.69	0.84	0.61
HHV (MJ/kg)	18.97	17.36	20.12
M(%)	10.62	4.73	4.93
A(%)	1.05	1.26	0.50
VM(%)	57.64	64.62	51.29
FC(%)	30.69	29.39	43.28
FR	0.53	0.45	0.84

Morphological characteristics

The surface structures before and after sorption were characterized by SEM technique (Figure 1). From Figure 1, surface of HPSHC is morphologically different from each other before and after loading with copper ions. Before adsorption, the HPSHC surface has an irregular structure, which will increase and ease the sorption of Cu^{2+} to HPSHC surface. After loading with Cu^{2+}, changes on the HPSHC surface approve the sorption of copper ions.

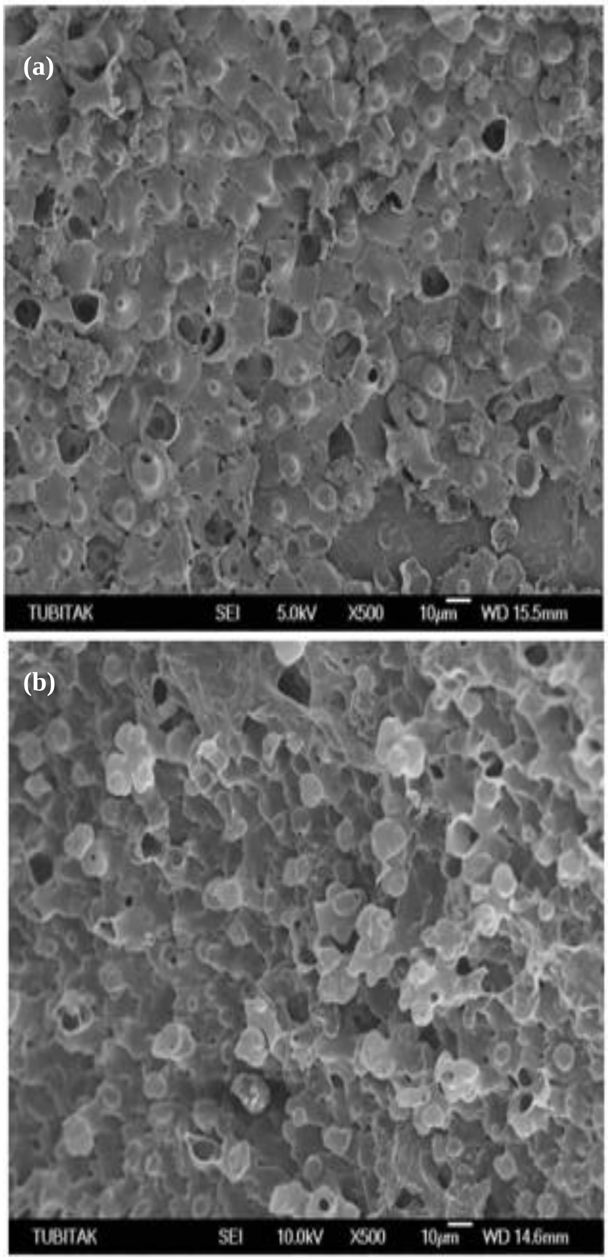


Figure 1. Morphology of HPSHC (a) and (b) Cu^{2+}-loaded HPSHC

FTIR analysis

FTIR spectra was presented to analyze the functional groups of HPSHC in Figure 2. The FTIR peak located at 3500-3000 cm^{-1} assigned to functional group of -OH vibration. The absorption peaks at between 3000 and 2500 cm^{-1} corresponded to the stretching vibrational functional group of to aliphatic $-CH_n$. The peaks between 1750 and 1500 cm^{-1} belong to -C=O groups originating from ketone and amide structures in the HPSHC. The presence of peak at 1650 cm^{-1}, related that the vibration of -C=N group at surface. The bands appearing at 1000 and 950 cm^{-1} are due to the aromatic C-H out-of-plane bending vibrations. Additionally, the vibrational peaks observed at 1500 and 1450 cm^{-1} confirm the presence of carboxylic groups in the structure.

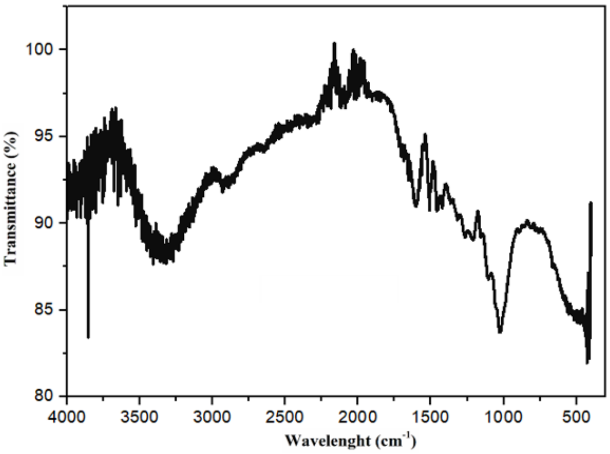


Figure 2. FT-IR spectra of HPSHC

Cu(II) ion adsorption results

Influence of pH

pH is a crucial parameter, which influence the sorption period. Therefore, the effect of solution pH was examined in the range of 2.0-6.0, and the results are presented in Figure 3. As observed in Figure 3, the Cu(II) sorption capacity of hydrochar occurs at pH 5. At low pH, sorption ability of HPSHC was low. The main reason is that the abundant H^+ at low aqueous pH can strongly fight with Cu(II) ions for the same sorption sites of HPSHC. Since the mobility of heavy metal ions is lower than that of H^+, proton orientation towards adsorption sites is greater. Additionally, when pH is lowered, the functional groups on the HPSHC surface become positively charged, which prevents the positively charged metal cations from approaching the surface [24]. Since metal precipitation occurs at pH values higher than 5, pH 5 was selected as the optimal pH for further experiments.

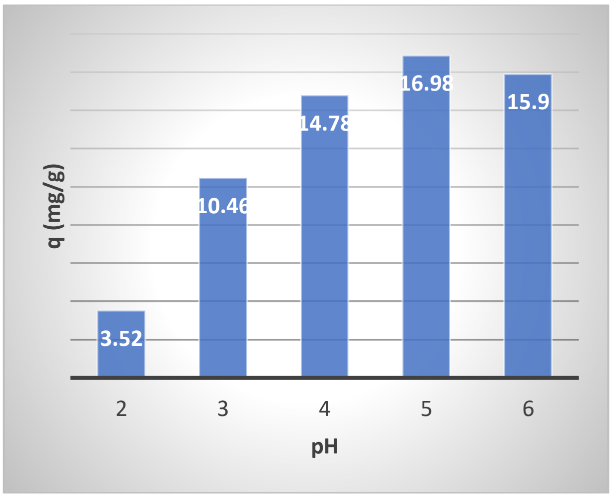


Figure 3. Influence of solution pH on Cu(II) adsorption performance

Studies on adsorption kinetic

In order to make kinetic modeling, the experimental data were evaluated in Eq. 4 and Eq. 5, and plots of PFO and PSO models were obtained (Figure 4a-b). PFO and PSO rate constants were determined from the slope values of these linear graphs. The suitability of the model was investigated by calculating the $q_{e,cal}$ values from the intercept values and comparing them with the experimental q_e ($q_{e,exp}$) values. The parameters and correlation coefficients (R^2) determined for both kinetic models are reported in Table 2. From Table 2, Cu(II) sorption on HPSHC complies with the PSO kinetics, considering the R^2 values. In addition, the closeness of $q_{e,cal}$ values and $q_{e,exp}$ values for the PSO model confirms this situation.

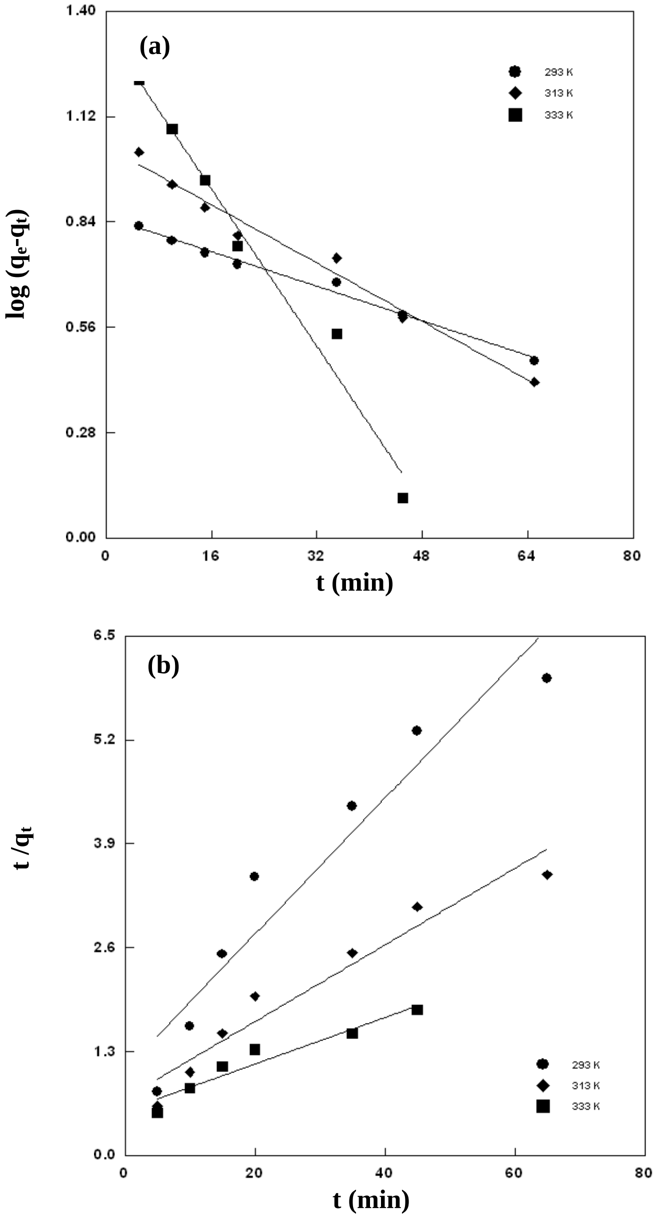


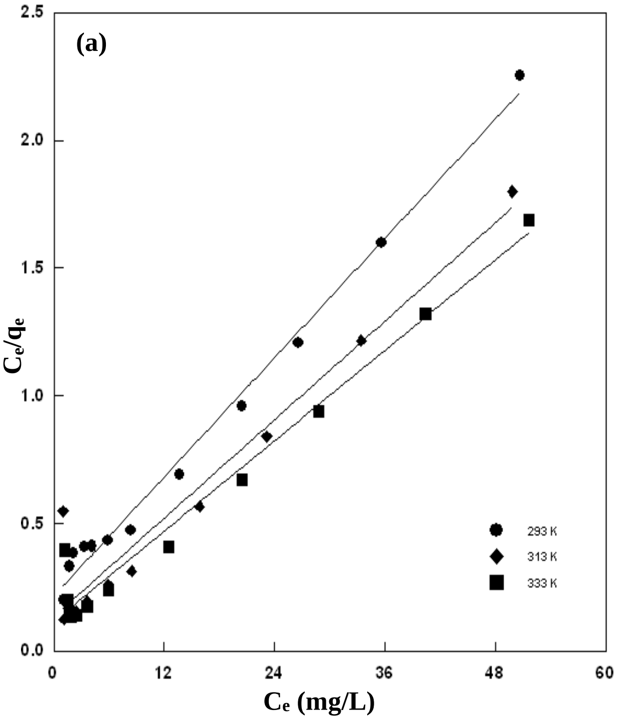
Figure 4. Sorption kinetic fitting results for Cu(II) uptake onto HPSHC; Linear fitting curves from PFO (a) and PSO (b) models

Table 2. Kinetic parameters related to Cu(II) adsorption on HPSHC surface at different temperatures

Temperature (K)	PFO				PSO		
	$q_{e,exp}$	$q_{e,cal}$	$k_{ads,1}$	R^2	$q_{e,cal}$	$k_{ads,2}.10^3$	R^2
293	12.50	9.42	0.0176	0.9742	12.02	2.04	0.9858
313	17.40	11.57	0.0229	0.9854	16.95	4.48	0.9917
333	23.50	20.48	0.0544	0.9882	22.79	5.12	0.9924

Studies on adsorption isotherm

The results obtained from the sorption experiments were evaluated in the model equations of Langmuir and Freundlich and the plots of these isotherm models were obtained (Figure 5a-b). From the slope and intercept values of these plots, the isotherm parameters were calculated. In addition, the R^2 for both models correlation coefficients were also calculated and all data were collected in Table 3. As observed in Table 3, the R^2 of the Langmuir is higher than the R^2 of the Freundlich isotherm. This shows that Cu(II) sorption on HPSHC fits sorption isotherm of Langmuir. This compatibility indicates that the sorption active centers on HPSHC surface show a uniform distribution. The maximal sorption uptake value calculated from the Langmuir isotherm model was determined as 39.90 mg/g. Also, R_L calculated with the help of Langmuir equation dispersion factor is in the range of 0.0750-0.0570. This shows that Cu^{2+} sorption on HPSHC is favorable.



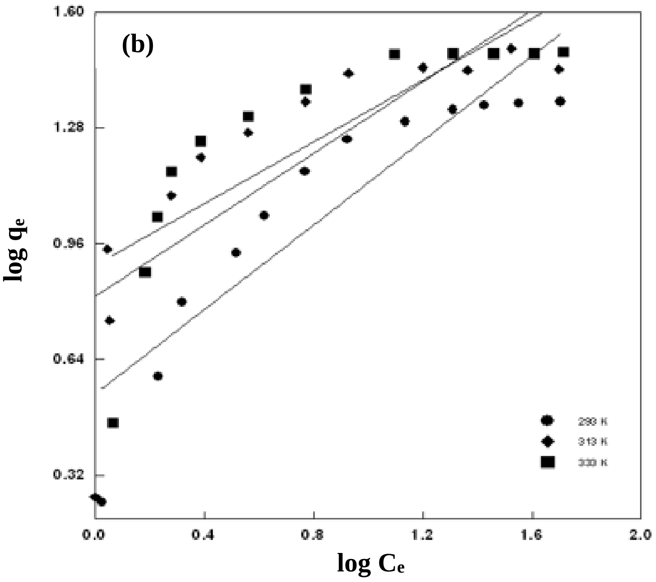


Figure 5. Isotherms of adsorbing Cu(II) onto HPSHC with the fitting curves by Langmuir (a) and Freundlich (b) models

Table 3. Parameters of isotherms for Cu(II) adsorption onto HPSHC

Temperature (K)	**Langmuir**				**Freundlich**		
	q_m	b	R_L	R^2	K_F	$1/n$	R^2
293	28.54	0.1245	0.0750	0.9988	4.52	0.5945	0.9657
313	34.45	0.2257	0.0605	0.9947	5.67	0.4816	0.9741
333	39.90	0.2648	0.0570	0.9956	6.94	0.4117	0.9712

Adsorption thermodynamics

Thermodynamic evaluation of HPSHC toward copper ions was carried out using the Van't Hoff equation formulated by Eq. 9 below:

$$In\ K_C = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (9)$$

where K_C is the thermodynamic equilibrium constant, T (K) is temperature, and R (8.314 J/mol K) is the universal gas constant. Standard enthalpy change (ΔH^o) and change in the entropy (ΔS^o) values were determined from the slope and the intercept between ln K_C-$1/T$ plot, using Eq. 9. In addition, Gibb's free energy (ΔG^o) for all three temperatures was calculated from the equation given by Eq. 10:

$$\Delta G^0 = -RTInK_C \quad (10)$$

From the thermodynamic values, which were calculated by isothermal equation listed in Table 4, Cu(II) sorption process on hydrochar is spontaneous (ΔG^o values are negative) and an endothermic (ΔH^o value is positive). Besides, the positive entropy change ΔS^o (63.50 kJ/molK) confirms the strong interaction between metal ions and sorbent surface.

Table 4. Thermodynamic parameters of Cu(II) ions adsorption on HPSHC surface

T (K)	**ΔG^0 (kJ/mol)**	**ΔH^0 (kJ/mol)**	**ΔS^0 (kJ/molK)**	**R^2**
293	-2.1741	19.22	63.50	0.9952
313	-4.2062			
333	-5.8573			

CONCLUSION

In this study, a new hydrochar was produced by using the co-hydrothermal carbonization technique in which more than one raw material is processed together. Hazelnut and pistachio shells were mixed in equal proportions (1:1) by mass and carbonized at 220 °C for 6 h. The obtained HPSHC hydrochar has a mass yield of 75.45%, an energy density of 81.24% and a HHV value of 20.12 MJ/kg. HPSHC was employed as a sorbent for Cu^{2+} removal from water. The impact of pH over Cu(II) sorption of HPSHC was explored and it was observed that the highest adsorption amount was reached in acidic conditions (pH:5). Temperature dependent kinetic and isotherm experiments were performed and experimental data were evaluated in widely used kinetic and isotherm equations. According to the result, Cu^{2+} sorption obeyed to the PSO kinetic model and the Langmuir isotherm with the monolayer adsorption capacity of 39.90 mg/g. Thermodynamic study identified the adsorption is spontaneous and endothermic process. In addition, FTIR analysis showed that the HPSHC surface is suitable for Cu(II) ions adsorption in terms of functional groups. SEM images taken before and after adsorption also verified the sorption period. Present work revealed the capability of using cost-efficient HPSHC produced with an environmentally friendly technology as an alternative sorbent for copper ions adsorption.

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