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Effectiveness of Sunflower Seed Husk Biochar for Removing Copper Ions from Wastewater: a Comparative Study

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Abstract

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Copper represents one of major hazardous pollutants in wastewater. The aim of this study is the comparison between sunflower seed husk biochar (SSHB) and activated carbon (AC) and sunflower seed husk feedstock (SSHF) in their efficiency of Cu^{2+} removing from aqueous solutions. The removed Cu^{2+} was monitored for various intervals extended to 96 h at 298, 303, and 308 K in batch experiments. Adsorption reactions showed that SSHB was superior in Cu^{2+} removal process at all tested temperatures in comparison with AC and SSHF. Results of surface properties and Fourier transform infrared spectroscopy confirmed the higher surface reactivity of SSHB than AC and SSHF. Both SSHF and AC were affected by time and temperature of reaction in their removal efficiency for Cu^{2+} while SSHB was not affected by these parameters. A deformation observable under a scanning electron microscope and a higher release of dissolved organic carbon from SSHF after the reaction with Cu^{2+} and vice versa in SSHB suggested the electrostatic ion exchange and complex reactions mechanisms for Cu^{2+} removal by SSHF in addition to the physical sorption controlled by surface area and porosity of SSHB. The adsorption kinetics of Cu^{2+} was fitted to pseudo second order equation and obtained results indicate that SSHB is a recalcitrant and a strong biosorbent. Therefore, SSHB can be introduced as a cost-effective and efficient biosorbent for copper removal from wastewaters.

Keywords: adsorption kinetics; biosorbents; charcoal; heavy metals; sunflower biochar; water treatment

Copper metal ions (Cu^{2+}) have become an ecotoxicological hazard of major interest and increasing importance, because of their accumulation in living organisms (Karabulut *et al.* 2000). Cu^{2+} is considered as a common hazardous pollutant in wastewater and is often released by metallurgical, plating, electric circuits, fertilizer, excessive use of Cu-based agrochemicals, and refining industries. Extended oral administration of excess amount of Cu^{2+} may result in liver injury and acute poisoning to the human body (WHO 1971). Maximum acceptable copper concentration in drinking water is less than 3 mg/l (Manahan 1991; Murley 1992).

The traditional techniques for copper ions removal from water and wastewater include adsorption/absorption (Ahmad *et al.* 2010; Bilal *et al.* 2013), ion exchange (Matyjaszewski *et al.* 2000; Madhava Rao *et al.* 2006), and chemical precipitation with various mineral phases such as carbonate (Aziz *et al.* 2001) and oxi-(hydroxides) of iron (Kurniawan *et al.* 2006). Adsorption method is considered as one of the highly efficient and cost-effective processes of removal technologies (Huang *et al.* 1990; Suzuki *et al.* 2005). Among the materials used as biosorbents, activated charcoal is considered one of the common commercial adsorbents for the removal of heavy metals from water and wastewater, but it is classified as one of the concise prices materials (Kurniawan *et al.* 2006).

Biochar, which results from thermo-chemical degradation under limited-oxygen conditions of various

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biomass feedstocks such as crop and forest residues (Lehmann 2007; Li *et al.* 2013), animal manure (Cao *et al.* 2009; Cao & Harris 2010; Ro *et al.* 2010), sewage sludge (Gascó *et al.* 2012; Méndez *et al.* 2012), is a carbon-rich material with reactive surfaces. Currently, it has attracted much attention due to its wide applications in environmental management (Kumar 2010). Recent studies on biochar application as biosorbent for removing heavy metals from aqueous solutions such as Cd^{2+} (Mahmoud *et al.* 2011; Regmi *et al.* 2012; Saleh *et al.* 2014), Pb^{2+} (Kolodynska *et al.* 2012), Cu^{2+}(Tong & Xu 2013), and Zn^{2+} (Chen *et al.* 2011) expanded its importance in the field of contaminants removal from aqueous environments.

The sunflower (*Helianthus annuus*) is one of the most important oil crops. The industrial processing of sunflower seeds leaves husk as a by-product representing a biological waste material. Sunflower husk was used as biosorbent for removing cationic dyes (Soldatkina *et al.* 2009) and various heavy metals (Lyubchik *et al.* 2008; Witek-Krowiak 2012). But scarce information about its use as a biochar for wastewater decontamination (Lyubchik *et al.* 2008; Tikhonova *et al.* 2008) is available. Therefore, the principal objective of this study was to investigate the ability of sunflower seed husk biochar (SSHB) to remove copper ions from aqueous solutions. Additional objectives included (1) the comparison of copper ions removal efficiencies by SSHB with its feedstock (SSHF) and commercially activated carbon(AC), (2) a fundamental understanding of the adsorption process by examining the physical and chemical characteristics of biochar, and (3) the evaluation of the Cu^{2+} removal kinetics.

MATERIAL AND METHODS

Preparation and characteristics of materials. The sunflower seed husk feedstock (SSHF) was collected at local market and extensively washed with tap water to remove soil and dust. Washing process was repeated with distilled water and followed by drying in an oven at 70°C for 24 h. The dried SSHF was transferred into ceramic jars with covers, then transferred into muffle furnace and pyrolyzed at a temperature of 450°C for 15 min under limited O_2 conditions. After cooling to ambient temperature, the produced biochar was weighed to calculate the volatile biomass, then crushed and sieved using a 0.5-mm polypropylene sieve and stored in plastic jars. For comparison, samples of commercial active charcoal (AC) and dried SSHF were also grinded by porcelain mortar and sieved using a 0.5-mm polypropylene sieve and then stored in plastic jars. Figure 1 presents photos of biosorbent samples of sunflower seed husk feedstock and biochar before and after pyrolysis and crushing. Total carbon, nitrogen, hydrogen, oxygen, and sulfur contents in SSHF, SSHB, and AC were determined by a CHNOS analyzer (Elementar, Vario EL, Hanau, Germany).

Surface area. Surface areas of SSHF, SSHB, and AC samples were measured from N_2 isotherms at 77 K using a gas sorption analyzer (Beckman Coulter SA(TM) 3100 Surface Area and Pore Size Analyzer, Beckman Coulter, Nyon, Switzerland). The samples were degassed for 6 h under vacuum at 473 K prior to conducting adsorption measurements. The N_2 adsorbed per g of sample was plotted versus the relative vapour pressure (P/Po) of N_2 ranging from 0.02 to 0.2, and the data were fitted to the Brunauer–Emmett–Teller equation (BET) to calculate surface area. Total pore volume was estimated from N_2 adsorption at P/Po of 0.5. The Barret–Joyner–Halender method was used to determine the pore size distribution from the N_2 desorption isotherms (Park & Komarneni 1998).

Identification of functional groups. Functional group compositional analysis of the SSHF, SSHB, and AC was carried out using Fourier transform infrared (FTIR) spectrometry. The FTIR spectra of the adsorbent were recorded in the range 400–4000 cm^{-1} using an infrared spectrophotometer FT/IR-5300 (JASCO Corp., Tokyo, Japan). A small amount of

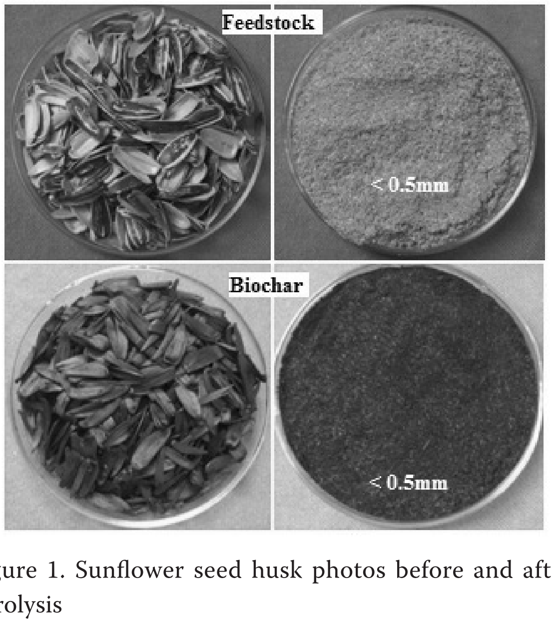

Figure 1. Sunflower seed husk photos before and after pyrolysis

the SSHF, SSHB, or AC samples was mounted on a potassium bromide (KBr) disc which had been previously scanned as a background.

Surface morphology. The surface physical morphologies of SSHF, SSHB and AC were examined by conducting a scanning electron microscopy (SEM) experiments. SEM analysis of samples was performed using a Phillips SEM-505 scanning electron microscope (Phillips, Eindhoven, The Netherlands). The SEM instrument was operated at 300 kV/SE and 50°C inclination. Before analysis, all samples were gold-coated in a sputter-coating unit (Edwards Vacuum Components Ltd., Sussex, UK) for electrical conduction. The micrographs were recorded at various magnification scales using photographic techniques to characterize the morphology of SSHF, SSHB, and AC, which had been dried overnight at approximately 105°C under vacuum before the SEM analysis.

Pre-equilibrium pH measurement. Pre-equilibrium pH of SSHB, SSHF, and AC was determined by transferring a 2.00 g sample of biosorbents into a 125 ml Erlenmeyer flask to which 40 ml of CO_2-free distilled water was added. Flasks were sealed with Parafilm, and then agitated in a horizontal shaker (G24 Environmental Incubator Shaker, New Brunswick Scientific Co., Connecticut, USA) for 48 h at 20, 25, or 30°C. Then the suspensions were filtered using a 0.45 µm Gelman membrane filter and pH of the clear solutions was measured using a pH meter WTW inLab pH/Ion 735 (WTW GmbH, Weilheim, Germany).

Adsorption kinetic studies. A batch adsorption technique was used to conduct the adsorption kinetics of Cu^{2+} onto studied adsorbents. In 1-litre Pyrex double-jacketed reactors containing 0.8 l of 10.0 mmol/l KCl electrolyte solution (prepared by dissolving of 0.5968 g of KCl, BDH AnalaR in 790 ml deionized water), 4.0 g of SSHF, SSHB or AC were added. The suspensions were agitated for 24 h for equilibration before adsorption reaction. 10 ml of 0.12 mol/l copper ions (prepared from copper chloride, $CuCl_2 \cdot 2H_2O$, BDH AnalaR, Poole, UK) were added to the mixture to give an initial concentration of Cu^{2+} equal to 1.5 mmol/l and final solid:solution ratio 1 : 200. The reactions were carried out at 20, 25, and 30°C. The mentioned temperatures were controlled using constant-temperature circulator (Cole Parmer Model 126-02; Cole Parmer, Illinois , USA). At the end of each reaction period, suspension pH was measured using a pH meter (WTW inLab pH/Ion 735, WTW GmbH) and immediately, 50.0 ml of suspension was withdrawn by Nalgene syringe and filtered (using a 0.45 µm Gelman membrane filter). The sample withdrawal intervals were started after 5 min and ended after 96 h of adsorption reaction without replication. Copper metal ion concentrations were measured in the filtrate using a ICP-OES Spectrometer (Thermo iCAP 6000 Series,Thermo Scientific, Loughborough, UK). In another part of the filtrate, concentration of dissolved organic carbon (DOC) was determined by a CHNS analyzer (Elementar, Vario EL, Hanau, Germany).

The adsorbed amount (q_t) of Cu^{2+} was calculated according to the following equation:

$$q_t = \frac{(c_0 - c_t)V}{m} \qquad (1)$$

where:

q_t – adsorbed amount of Cu^{2+} at time t (mg/g)

m – weight of adsorbent (g)

V – volume of solution (l)

c_0, c_t – initial and equilibrium concentrations of ions in the solution, respectively (mg/l)

To estimate the removal kinetics of Cu^{2+} from aqueous solutions by SSHF, SSHB, and AC, pseudo-first-order and pseudo-second-order models were applied. The pseudo-first-order model (Lagergren 1898) is given by:

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \qquad (2)$$

where:

k_1 – pseudo-first-order rate constant (min^{-1})

q_e – adsorption capacity at equilibrium (mg/g)

q_t – amount of metal adsorbed at any time t (mg/g)

On the other hand, pseudo-second order model (Ho 2006) is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

where:

k_2 – pseudo-second-order rate constant (g/mg/min)

The values of q_e, k_1, and k_2 were calculated from the slopes and intercepts of the adsorption curves.

RESULTS AND DISCUSSION

Characterization of biosorbents and active charcoal. Table 1 presents the C and N contents in adsorbents as well as the volatilization, ash content, and biochar yield percentage in SSHB. The pyrolysis of SSHF at 450°C yielded about 59.5% of biochar and about 39%

Table 1. Selected chemical properties of biosorbents and active charcoal used in the study

Element (WT%)	SSHF	SSHB	AC
C	40.00	52.64	71.33
N	1.03	0.91	0.30
C : N	38.80	57.90	237.80
H	5.70	0.70	2.51
O	46.50	21.80	14.11
S	0.32	0.14	0.03
Volatiles after pyrolysis (%)	–	38.99	–
Ash content (%)	–	1.55	–
Biochar yield (%)	–	59.46	–

SSHF – sunflower seed husk feedstock; SSHB – sunflower seed husk biochar; AC – activated carbon; WT – weight

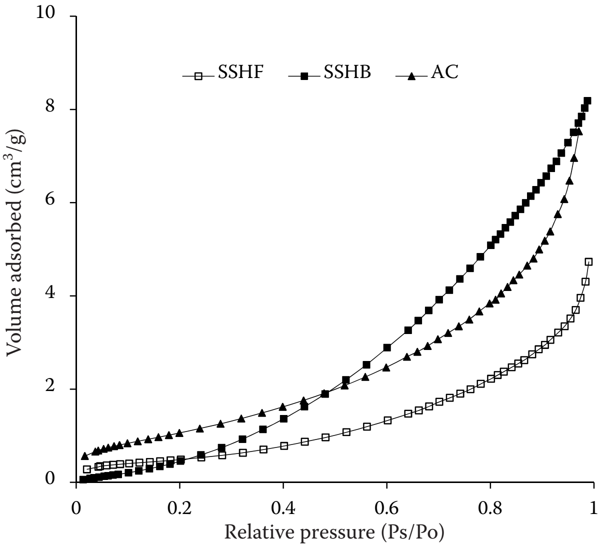

Figure 2. Adsorption isotherms of N_2 at 77 K for carbons derived from sunflower seed husk (SSHF), sunflower seed husk biochar (SSHB), and activated carbon (AC)

of volatile materials. It seems that the temperature and the residence time of pyrolysis control most of biochar properties including the amount of resulted biochar (Lyubchik *et al.* 2008; Downie *et al.* 2009).

Surface area and pore analysis. The Brunauer–Emmett–Teller (BET) specific surface area (SSA_{BET}), total pore volume (V_p), and pore volume distribution for SSHF, SSHB, and AC are given in Table 2. Pyrolysis of SSHF at 450°C approximately doubled the pore volume and the newly-formed pores in the range of meso- and macropores increased by about 91% and the micropores increased by about 266% compared to the values measured before pyrolysis. Thermochemical transformation of SSHF into SSHB led to the values of surface area and pore volume similar to those of AC biosorbent, but the formation of micropores in SSHB tended to be higher than in AC (Table 2). Figure 2 presents adsorption isotherms of type II for the studied SSHF, SSHB, and AC carbons, which exhibit a smoothed lap and a small up-rise at high relative pressures with varying degrees of slope in the higher range. Adsorption in micropores does not go on by successive build-up of layers as disclosed by the BET model. However, the BET method has been used for microporous adsorbents owing to its simplicity and reasonable predictions (Giles & Trivedi 1969; Girgis *et al.* 2011).

Table 2. Basic parameters of surface area and porous structures for sunflower seed husk feedstock (SSHF), sunflower seed husk biochar (SSHB), and activated carbon (AC)

Sorbent source	SSA_{BET} (m^2/g)	V_p	$V_{mes+mac}$	V_{mic}
			(mm^3/g)	
SSHF	1.782	6.5	5.06	1.09
SSHB	3.850	12.4	9.68	3.99
AC	3.964	13.9	11.33	2.86

SSA_{BET} – the Brunauer–Emmett–Teller specific surface area; V_p – total pore volume; mes – mesoporous; mac – macroporous; mic – microporous

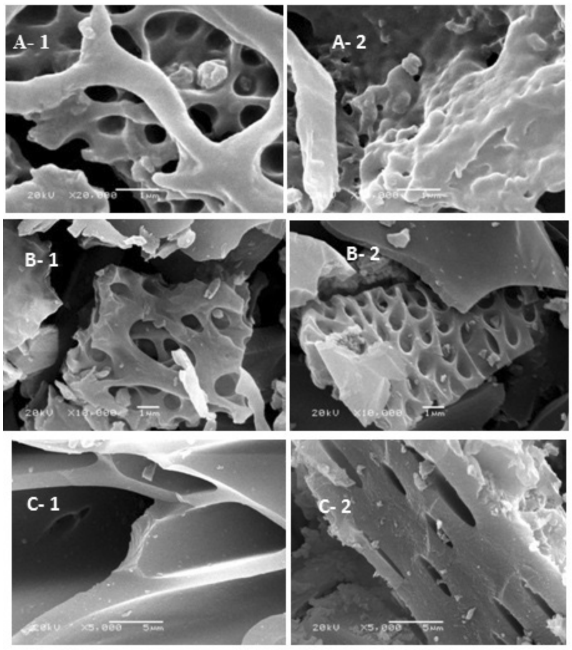

Figure 3. Scanning electron micrographs (SEM) of sunflower seed husk (SSHF) (A), sunflower seed husk biochar (SSHB) (B), and activated carbon (AC) (C) before (1) and after (2) the removal reactions of Cu^{2+} ions from aqueous solutions at 25°C

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Surface properties. The surface structure of SSHF, SSHB, and AC was analyzed by SEM before and after Cu^{2+} adsorption (Figure 3). The textural and morphological structure examination of SSHF particles can be observed from the SEM photographs at 500× magnification (Figure 3A-1). This figure reveals that the surface of SSHF is rough. After Cu^{2+} adsorption, a significant change was observed in its structure (Figure 3A-2). The clear structure of observed voids of feedstock before the reaction was blocked and/or deformed after the reaction, whereas a minor softening was observed on the edges of pores of biochar and charcoal samples after the reaction with Cu^{2+} (Figure 3 B-1, B-2, C-1, and C-2). The sharp changes observed in the porous structure of SSHF rather than those observed in SSHB and AC (Figure 3) may be attributed to various mechanisms of Cu^{2+} removal among the studied biosorbents.

The surface active groups typical of the biosorbents before and after the removal of Cu^{2+} are listed in Table 3. As a raw material, SSHF is made up of polymers of ligno-cellulose (mainly hemicelluloses, cellulose, and lignin) having surface active groups (hydroxyl, carboxyl, amine, carbonyl, etc,) in their structures that are capable to bind copper ions and other heavy metals. In the spectrum of the SSHF, the peaks of OH groups bound with the hydrogen bond, CH bonds in methyl and methylene groups, O-H stretching; NH_3^+ and carboxyl groups characterizing aromatic compounds are found. Similar spectra were found for sunflower seed husks studied by Soldatkina *et al*. (2009). Therefore, the results in Table 3 show that the ligno-cellulosic composition of SSHF was capable to form complexes with Cu^{2+}. On the other hand, the values of FTIR spectra of SSHB (Table 3) showed the bands located at 3419, 2351, 1581, 1391 and 830 cm^{-1}, which correspond mainly to the presence of N-H, stretched O-H (hydroxyl), -NH (amine), asymmetric C-H, and aromatic C-C

Table 3. Functional surface groups and FTIR wave numbers of sunflower seed husk feedstock (SSHF), sunflower seed husk biochar (SSHB), and activated carbon (AC) before and after the reaction with Cu^{2+} in aqueous solutions

Functional groups	Wave number (cm^{-1})	
	$- Cu^{2+}$	$+ Cu^{2+}$
SSHF		
C-H bend alkenes (tri-substituted)	604.64	600.78
C-H alkyl halides	1057.88	1057.88
C-H asymmetric deformation; C-C aromatic	1266.18	1265.22
N-H bend (amines)	1403.12	1402.15
O-H (hydroxyl)	1633.59	1628.77
Alkynes, C≡C, and ether	2178.45	2165.91
CH (methyl and methylene), O-H (stretching vibrations)	2920.99	2918.10
OH alcoholic and phenol, NH (stretching vibrations)	3399.30	3417.63
SSHB		
C-H bend alkenes (tri-substituted)	830.3	828.37
C-H alkyl halides	nd	1260.39
C-H asymmetric deformation; C-C aromatic	1391.54	1391.54
N-H bend (amines)	1581.52	1587.31
O-H (stretching vibrations)	2351.06	2352.03
OH alcoholic and phenol, NH (stretching vibrations)	3419.56	3423.41
AC		
alkyl halide stretch (e.g. C-Cl)	510.14	482.17
C-H aromatic	781.12	nd
C-N stretch (aliphatic amines)	1072.35	1053.06
O-H bend (carboxylic acids)	1438.80	1432.05
C=C stretch (aromatic ring)	1599.84	1588.27
OH alcoholic and phenolic, NH (stretching vibrations)	3419.56	3417.63

nd – not detected

and alkenes C-H functional groups, respectively. The FTIR spectrum of AC showed bands approximately similar to those of biochar. Slight shifts were observed in FTIR bands of the studied biosorbents after sorption reaction with copper ions (Table 3).

Adsorption kinetics of Cu. The adsorption of Cu^{2+} on biosorbent surfaces is illustrated in Figure 4 where SSHB shows a strong capability to remove most Cu^{2+} within the first 5 min of the batch reaction, whereas about 63.06–78.76% and 74.15–81.00% of copper were removed by AC and SSHF, respectively, in the same period along with the tested temperature range. Then gradual increases in Cu^{2+} removal by AC and SSHF with the reaction time were observed and reached 96.94–99.34% and 85.74–89.40%, respectively, after 96 h of reaction. Time independence of Cu^{2+} removal by SSHB may reflect dissimilarity in retention mechanisms followed by biochar and those pursued by feedstock and active carbon. According to the metal ion adsorption by surface-active materials, Cu^{2+} removal can be achieved by electrostatic interaction with negatively charged surface functional groups (cation exchange), specific metal–ligand complexation involving surface functional groups of biosorbents, interactions between metals and aromatic C of biosorbents and/or physical sorption controlled by surface area and porosity (Biniak *et al.* 1997; Joseph *et al.* 2010; Uchimiya *et al.* 2010). Significant changes in pH values were observed with the progress of removal reactions (Table 4). Under the slightly acidic conditions of SSHF-Cu aqueous system, pH increased with increasing Cu^{2+} removal and similar trend was observed with AC and extended to slightly basic conditions.

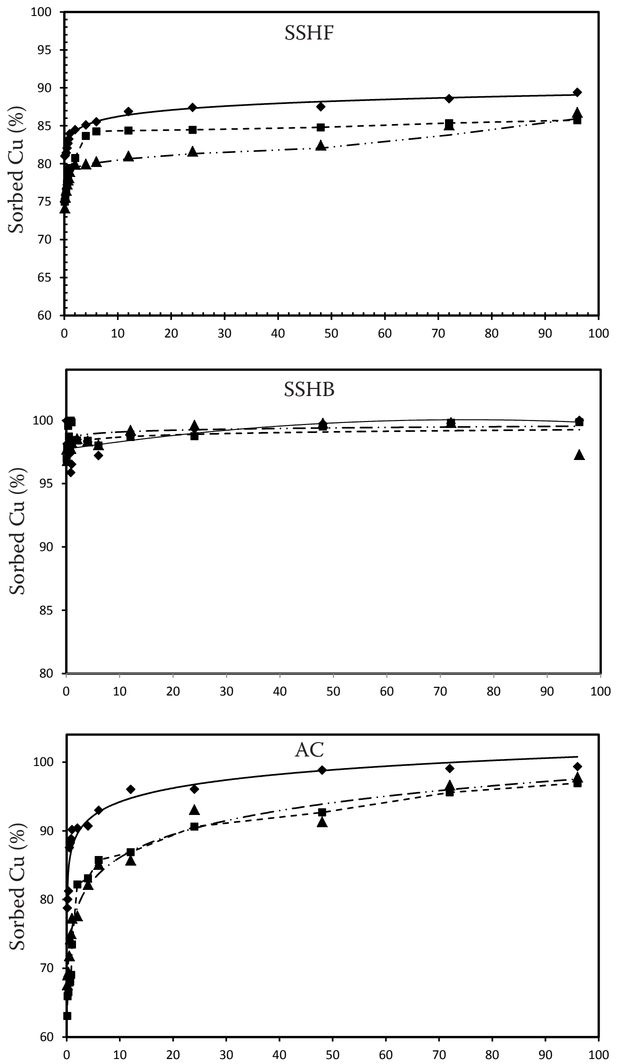

Figure 4. Adsorption of Cu^{2+} ions from aqueous solutions on sunflower seed husk feedstock (SSHF), sunflower seed husk biochar (SSHB), and activated carbon (AC) as a function of time and temperature

On the other hand, Cu^{2+} removal from aqueous solution by SSHB, relatively, was not associated with pH changes. The present results reflect the occurrence of possible various mechanisms, which may control the removal process of Cu^{2+} depending on the sorbent surface characteristics and changes in functional groups configuration.

The presence of copper ions in aqueous solutions containing SSHF biosorbent led to the increase of DOC concentration and vice versa in those containing SSHB and AC (Figure 5). These results indicate that formation of water soluble complexes between Cu^{2+} and DOC tended to increase with the raw feedstock and decreased with pyrolyzed ones. Thus, it was reflected on the higher Cu^{2+} removal efficiency from aqueous solutions by SSHB than by SSHF (Figure 4).

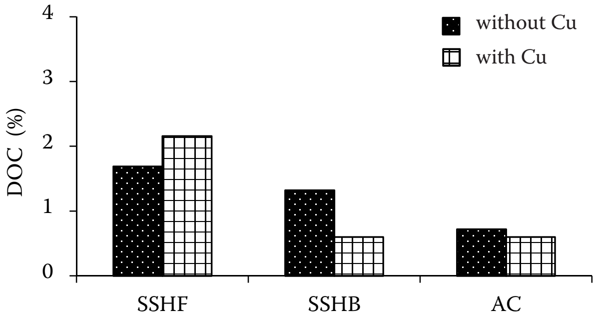

Figure 5. Dissolved organic carbon (DOC) released from sorbent materials after 96 h of agitation in aqueous solutions in the absence or presence of copper ions
SSHF – sunflower seed husk feedstock; SSHB – sunflower seed husk biochar; AC – activated carbon

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Table 4. Changes in pH of sorbent/sorbate mixtures of sunflower seed husk feedstock (SSHF), sunflower seed husk biochar (SSHB), and activated carbon (AC) during Cu^{2+} adsorption at various temperatures (in °C)

Reaction time (h)	SSHF			SSHB			AC		
	20	25	30	20	25	30	20	25	30
Pre-equilibrium	7.25	7.15	6.99	9.07	9.00	8.96	8.79	8.76	8.55
0.083	5.24	5.23	4.99	6.37	6.39	6.07	6.32	6.33	6.17
0.17	5.28	5.07	4.98	6.30	6.26	5.80	6.26	6.34	6.27
0.33	5.22	4.98	4.8	6.40	6.13	5.92	6.14	6.42	6.36
0.50	5.26	4.89	4.83	6.45	6.13	6.11	6.10	6.50	6.47
0.67	5.58	4.97	4.78	6.49	6.13	6.17	6.28	6.57	6.57
0.83	5.41	4.76	4.95	6.70	6.13	6.23	6.28	6.65	6.62
1.00	5.54	4.76	4.97	6.66	6.25	6.28	7.13	6.73	6.54
2.00	5.32	4.82	4.90	6.79	6.18	6.36	6.90	6.75	7.29
4.00	4.74	4.79	5.11	6.75	6.39	6.16	6.53	6.85	7.04
6.00	4.80	4.82	5.04	6.61	6.3	6.48	6.71	7.15	7.12
12.00	4.86	4.84	5.14	6.75	6.72	6.65	7.06	7.29	7.42
24.00	4.87	4.94	5.13	6.77	6.8	6.81	7.16	7.53	7.55
48.00	4.93	5.21	5.30	6.90	6.99	6.69	7.17	7.84	7.59
72.00	5.38	5.15	5.29	7.40	7.19	6.81	7.33	7.61	7.60
96.00	5.45	5.15	5.32	8.15	7.21	6.68	8.40	7.45	7.63

On the other hand, the released amounts of DOC from biosorbents may be attributed to the biodegradability and recalcitrance nature of SSHF, SSHB, and AC, respectively. The surface deformation after interaction with Cu^{2+} (as seen in SEM of Figure 3-A1 and A2) might approve the existence of DOC–Cu^{2+} complexation mechanism (Fitts *et al.* 1999; Alcacio *et al.* 2001). These authors concluded that sorption of metal ions under weakly acidic conditions of organic wastes (as shown for SSHF biosorbent in the current study) can be explained by electrostatic interactions and/or by formation of ternary surface complexes,

Table 5. Kinetic parameters for Cu^{2+} adsorbtion on biosorbents at various temperatures

Biosorbent (°C)	Kinetic model					
	Pseudo-first-order			Pseudo-second-order		
	q_e	k_1	R^2	q_e	k_2	R^2
SSHF						
30	0.00031	0.0010	0.651	3597.126	0.00386	1.000
25	0.00034	0.0010	0.745	3546.100	0.00199	0.999
20	0.00033	0.0010	0.445	3533.569	0.00616	1.000
SSHB						
30	0.00033	0.0006	0.405	3816.788	0.00458	0.999
25	0.00027	0.0002	0.087	3745.324	0.00356	0.999
20	0.00027	0.0003	0.252	3802.280	0.00532	0.999
AC						
30	0.00035	0.0030	0.454	3846.149	0.00113	0.999
25	0.00052	0.0080	0.589	3703.816	0.00049	0.999
20	0.00059	0.0100	0.490	3703.816	0.00052	0.999

SSHF – sunflower seed husk feedstock; SSHB – sunflower seed husk biochar; AC – activated carbon; q_e – adsorption capacity at equilibrium; k_1 – pseudo-first-order rate constant; k_2 – pseudo-second-order rate constant; R^2 – correlation coefficient in which metal ions (Cu^{2+}) are associated to organic surfaces by coordination to degradable surface formed by organic compounds (mainly hemicellulose- and cellulose-derived DOC). This type of ion removal (feedstock-DOC-Cu) is fragile and simply biodegradable with time progressing. In contrast, a further decrease in DOC released from SSHB reacted with Cu^{2+} was observed and revealed a strong retention of Cu^{2+} with carbon-rich and aromatic surfaces. This result may represent another kind of surface retention mechanisms (only lignin-derived DOC). As shown in Figure (5), the changes in DOC of AC, before and after the reaction with Cu^{2+}, were non-significant; therefore, its influence on Cu^{2+} removal is expected to be negligible.

The values of adsorption capacity (q_e, mg/g), rate constants (k_1 and k_2, min^{-1}, of the pseudo-first-order and pseudo-second order models, respectively), and correlation coefficients (R^2) for Cu^{2+} adsorption kinetics on studied biosorbents are listed in Table 5. The values of correlation coefficient for the pseudo-second-order model in all the tested biosorbents are relatively higher than those for the pseudo-first-order kinetic model. Moreover, experimental q_e values are very close to those calculated for the pseudo-second-order kinetic model. Therefore, the obtained results implied that the adsorption of Cu^{2+} by all tested biosorbents could be best explained by the pseudo-second-order model (Figure 6).

Effect of temperature on Cu^{2+} removal. To determine the effect of temperature on Cu^{2+} adsorption, the experiments were conducted at 298 K, 303 K, and 308 K. The Cu^{2+} adsorption percentage of the biosorbents of SSHF and AC clearly increased with temperature (Figure 4), but temperature did not affect Cu^{2+} adsorption by SSHB. Thermodynamic parameters such as changes in Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) were calculated to help understanding the mechanisms involved in Cu^{2+} removal. The following equations are used for obtaining these parameters:

$$\Delta G^{o} = -RT\ln (Ko) \tag{4}$$

$$\ln Ko = \Delta S^{o}/T - \Delta H^{o}/RT \tag{5}$$

where:

R – gas constant (8.314 J/mol/l)
T – absolute temperature (K)
Ko – ratio of Cu^{2+} concentration on adsorbent at equilibrium to the remaining concentration of Cu^{2+} in the solution at equilibrium (l/mol)

The values of $\Delta H°$ (kJ/mol) and $\Delta S°$ (J/mol/K) can be calculated from the slope and intercept of the linear plot of ln Ko versus $1/T$, respectively. The thermodynamic parameters describing Cu^{2+} adsorption onto the SSHF, SSHB, and AC are given in Table 6. Values of $\Delta G°$ were negative for all tested biosorbents indicating that adsorption might occur spontaneously (Zhang *et al.* 2011; Kołodyńska *et al.* 2012). The positive values of $\Delta H°$ indicated that the removal reactions were endothermic and irreversible (Stephen & Sulochana 2002; Dave *et al.* 2009). Also, the positive values of $\Delta S°$ suggest high degrees of disorderliness at the solid solution interface during the removal pro-

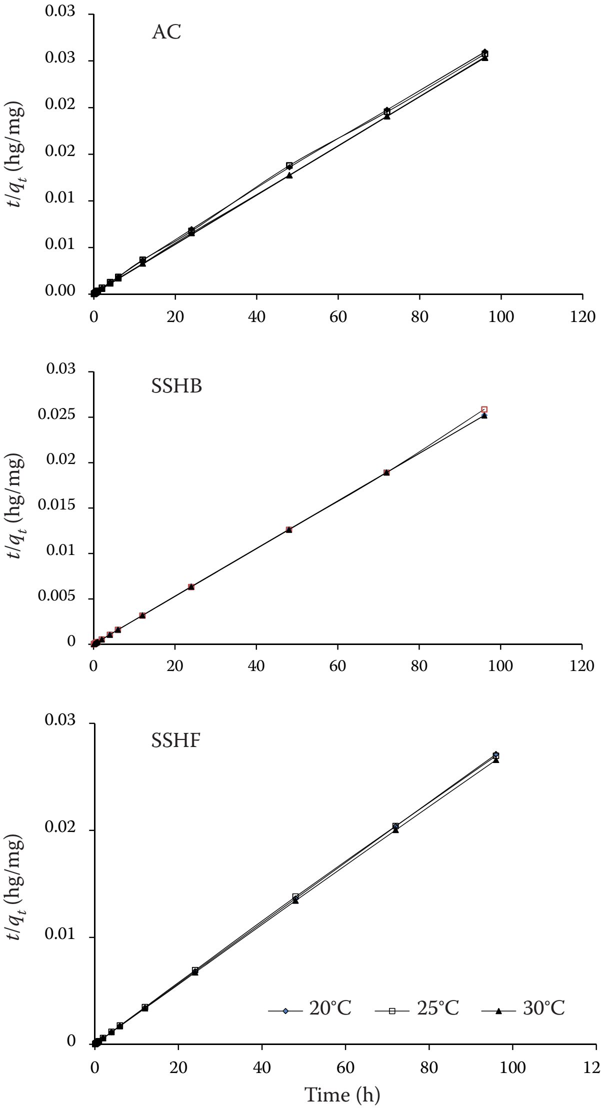

Figure 6. Pseudo-second-order plot for Cu^{2+} removal kinetics by sunflower seed husk feedstock (SSHF), sunflower seed husk biochar (SSHB), and activated carbon (AC) at different temperatures

Table 6. Thermodynamic parameters for the removal of Cu^{2+} on sunflower seed husk (SSHF), sunflower seed husk biochar (SSHB), and activated carbon (AC) from aqueous solutions

Biosorbent	$\Delta G°$ (kJ/mol)			$\Delta S°$ (J/mol/K)	$\Delta H°$ kJ/mol)
	298 K	303 K	308 K		
SSHF	–1.636	–1.476	–2.297	0.870	2.083
SSHB	–7.650	–6.926	–7.416	2.720	5.000
AC	–4.121	–4.054	–3.997	1.050	8.110

$\Delta G°$ – Gibbs free energy; $\Delta H°$ – enthalpy; $\Delta S°$ – entropy

cess of copper ions by the biosorbents. On the other hand, it reflects the affinity of the adsorbents for Cu^{2+} and suggests some structural changes in adsorbate and adsorbent. The elevated adsorption capacity of SSHF and AC at higher temperatures may be due to the enlargement of the pore size and/or activation of the adsorbent surfaces and increase in mobility of metal ions (Dave *et al.* 2009).

CONCLUSION

The comparative study of Cu^{2+} removal from aqueous solutions by SSHF, SSHB, and AC revealed that SSHB presented a strong affinity and higher capacity to remove Cu^{2+} in comparison to its raw feedstock and commercial active charcoal derived from tree woods. The presented tools of reaction characterization (surface properties, FTIR, and SEM) supported that SSHB had physicochemical properties (recalcitrant porous surfaces and mostly carbon-rich aromatic molecules), which controlled the removal process of Cu^{2+} from aqueous solutions in short periods (few minutes). The increase of reaction temperature enhanced Cu^{2+} removal only by SSHF and AC and had no effect on the removal reaction by SSHB. The pseudo-second-order kinetic model was much closed to represent the removal kinetics of Cu^{2+} rather than the pseudo-first-order model.

In conclusion, the results of the current work support the SSHB as a cost-effective biosorbent for Cu^{2+} removal from contaminated aqueous environments. Further researches are needed to explore the effectiveness of using SSHB for Cu^{2+} removal in the presence of other metal ions, organic ligands, and associated anions such as occurring in actual municipal and/or industrial wastewater.

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