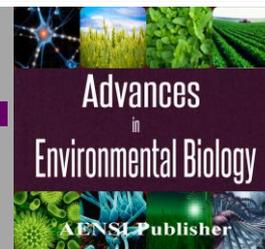




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Removal of Cadmium from Aqueous Solution by Biochars Derived from Peanut Hull and Wheat Straw

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ABSTRACT

The scope of this study was the examining of biochar of peanut hull (PHB) and wheat straw (WSB) in removing cadmium ions (Cd^{2+}) from wastewater. The feedstock of peanut hull (PHF) and wheat straw (WSF) were pyrolyzed at 450 °C for 15 min. The properties of these adsorbents were characterized scanning electron microscopy, fourier transform IR, N_2 adsorption/desorption isotherms, and particle size distribution. Adsorption isotherm of Cd^{2+} onto feedstock and biochar, using batch experiments, was studied for periods extended to 120 hours. Kinetic adsorption data were analyzed using Lagergren pseudo-first-order kinetic model and the pseudo-second-order model. Results showed that biochar was efficient than feedstock in Cd^{2+} removal from aqueous solutions throughout the reaction time. About 94.9 and 98.0 % of Cd^{2+} was removed within the first 15 min of adsorption by PHB and WSB, respectively, and the maximum adsorption was observed after 6 hours of reaction with both biochars. Significant increases in pH values to about 2.24 (PHF) and 1.42 (WSF) unites were observed during the reaction with Cd^{2+} and about 0.17 and 0.24 unit were observed with corresponded biochar sorbents. Measured values of pH in all systems were not exceeding than 8.0 and support the speculation that ion exchange, complex formation and/or diffusion are possible mechanisms controlling the removal process. Values of constants and regression coefficients of kinetic models suggested that pseudo second-order equation can be considered in the present adsorption system and was well fitted in description of removal kinetics of Cd^{2+} by PHB and WSB.

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INTRODUCTION

Water is becoming an increasingly scarce resource in arid and semi-arid countries. The water sector in Egypt is facing many challenges including water scarcity and deterioration of water quality because of population increase and lack of financial resources. Sustainable Egyptian agriculture strongly depends on the country's ability to conserve and manage its water resources. Available conventional water resources are estimated by 56.53 billion cubic meters (BCM) and the 83.0% is consumed in irrigation [1]. The non conventional resources coming from drainage water reuse (4.7 BCM/year) and treated wastewater (0.7 BCM/year). It is expected that the wastewater resource will increase till 2.97 BCM by 2017 [1].

Looking for to economic or cost effective water treatment technologies for removing pollutants becomes one of the major challenges to reuse municipal wastewater in irrigation. Various treatment methods for removing pollutants from wastewater are used. The selection of technologies should be environmentally sustainable, appropriate to local conditions, acceptable to users, and affordable for those who have to pay for them [2]. Adsorption techniques are widely used to remove certain types of pollutants in wastewater treatment processes. Activated carbon has been widely used as an adsorbent for the removal of various pollutants due to its high adsorption capacity. However, it has relatively high operation costs, problems of regeneration, and is difficult to separate from the wastewater after use. Therefore, a number of low-cost adsorbents, derived from crop residues, have been tried for treatment of wastewaters. The alternative adsorbents, such as peanut hull [3, 4], rice husk [5,6,7] and sunflower seed husk have been studied for removing contaminants from aqueous solutions [8].

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The removal of water soluble cadmium species, as one of the major heavy metals, from contaminated water has become a major research attentions due to its toxicological problems to the environment and to human health. Cadmium, which is widely used in the industry, responsible for causing kidney damage, renal disorder, high blood pressure, bone fraction and destruction of red blood cells [9]. According to the WHO standards, the permissible limit for Cd (II) in wastewater is 2 mg/l and the permissible level for Cd(II) in drinking water is 0.003 mg/l [10]. The main anthropogenic pathway through which Cd(II) enters the water bodies is via wastes from industrial processes such as electroplating, plastic manufacturing, metallurgical processes, industries of pigments and Cd/Ni batteries [11].

In the removal of Cd (II) from wastewater, there is the distinct tendency to replace the costly activated carbons and ion exchangers with various low cost adsorbents, which have high metal binding capacities [12, 13]. Biochar is a pyrogenic carbon-rich material, derived from anaerobic thermal decomposition of biomass [14,15, 16]). The use of biochar as a low-cost sorbent to remove metallic contaminants from aqueous solutions is an emerging and promising wastewater treatment technology, which has already been exhibited in previous studies [17, 18, 19, 20]. Biochars converted from various waste resources (agricultural residues, animal manure, and woody materials) have been tested for their capacity to retain various heavy metals [19, 21, 22], . Biochar is a porous substance, and its physicochemical characteristics are related to pyrolysis conditions and feedstock properties [23, 24, 25]. Among the crop residues, peanut hull and wheat straw are representing about 30% and the Egyptian agricultural sector annually produces 20 MMTyear⁻¹ [26]. Periasamy and Namasivayam [27] showed that activated carbon prepared from peanut hull (PHC) has been used for the adsorption of Cu (II) from aqueous solution. In their comparative study with a coal based commercial granular activated carbon (GAC), they showed that the adsorption capacity of PHC was 18 times larger than that of GAC.

This study was performed to investigate the efficiency of peanut hull and wheat straw biochar and their feedstock on removing cadmium from dilute wastewaters. The parameters that effect on biosorption such as surface characteristics and surface area of biosorbents besides contact time of sorption reaction were investigated.

MATERIALS AND METHODS

2.1. Preparation of feedstock and biochar:

The feedstocks of peanut hull (PHF) and wheat straw (WSF) used in this study were collected from the local markets. The collected materials were extensively washed with tap water to remove impurities and dust, Washing process was repeated with distilled water then dried in an oven at 80 °C for 24 h. Dried feedstocks were splitted into two parts, one part was crushed into powder and sieved by 0.5-mm polypropylene sieve then preserved in the desiccators for analyses. The other part was used for preparing the biochar.

Pyrolysis process was carried out using the method described by Saleh *et al.* (2012) [3] for producing the peanut hull biochar (PHB) and wheat straw biochar (WSB) under the conditions listed in Table (1). After cooling to ambient temperature, the produced biochars were weighted to calculate the volatiles fractions by subtraction from the total amount of feedstock used in pyrolysis (Table 1). Then, biochar samples were washed several times by de-ionized water using vacuum funnels, dried at 105 °C for for 5.0 hours, cooled then crushed and sieved using 0.5-mm polypropylene sieve then stored in plastic bottles.

2.2. Surface characterization:

2.2.1. Surface area:

Surface areas of feedstock and biochar samples were measured from N₂ isotherms at 77 K using a gas sorption analyzer (Beckman Coulter SA(TM) 3100 Surface Area and Pore Size Analyzer). The samples were degassed for 6 h under vacuum at 473 K prior to conducting adsorption measurements. The N₂ adsorbed per g of sample was plotted versus the relative vapor pressure (P/P₀) of N₂ 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 N₂ adsorption at P/P₀ = 0.5. The Barret–Joyner–Halender method was used to determine the pore size distribution from the N₂ desorption isotherms [28].

2.2.2. Functional groups identification:

Functional groups compositional analysis of the PHF, WSF, PHB and WSB was carried out using Fourier transform infra-red spectrometry. Fourier transform infrared (FTIR) spectra of the adsorbent were recorded in the range 400–4000 cm⁻¹ using Shematzu infrared spectrophotometer; model FT/IR-5300, JASCO Corporation, Japan, which had data processing and spectral library search facilities. A small amount of the feedstock or biochar samples was mounted on a potassium bromide (KBr) disc which had been previously scanned as a background.

2.2.3. The surface morphology:

The surface physical morphologies of PHF, WSF, PHB and WSB were examined by conducting a scanning electron microscopy (SEM) experiments. SEM analysis of samples was performed by using a Phillips SEM-505 scanning electron microscope. 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, England) for electrical conduction. The micrographs were recorded at various magnification scales using photographic techniques to characterize the morphology of the feedstocks and the biochars, which were dried overnight at approximately 105 °C under vacuum before SEM analysis.

2.3. Carbon determination:

Total carbon content in PHF, WSF, PHB and WSB was determined by oxidation method (Walkley-Black method) using potassium dichromate solution (0.50 M) and back titration of the excess dichromate by ammonium ferrous sulfate solution (0.50 M) in the presence of ferroin (1,10,0-phenanthroline) indicator [29].

2.4. Adsorption Isotherm of Cd:

In the present investigation, batch mode of operation was selected in order to measure the progress of Cd²⁺ adsorption isotherm for intervals extended to 96 h. Four grams of oven-dried feedstock or biochar samples (≤ 500 μm particles), as adsorbents, with 750 ml of 0.01M KCl solution as background electrolyte were stirred for 24 hours, as a pre-equilibration period before the reaction with adsorbates. Then 50 of Cadmium chloride (CdCl₂.H₂O, trace metals basis, Aldrich) solution was added to give an initial concentration of 7.784 μmol Cd²⁺ g⁻¹ adsorbent. The mixtures were continuously stirred at 400 rpm at temperature of 30 °C using constant-temperature water path circulator connected to one-liter double-jacketed reaction vessels. Values of pH of suspension system were measured at intervals from time zero to the end of reaction using pH meter WTW (inoLab pH/Ion 735, Germany). At the completion of determined time intervals, the adsorbate and adsorbent were separated by filtration using 0.45μm membrane filter (Gelman Science, MI, USA). The filtrate was acidified by few drops of 4.0 M nitric acid (BDH ANALAR, UK) then Cd²⁺ was measured by ICP-OES Spectrometer (Thermo iCAP 6000 Series, UK). The adsorbed Cd²⁺ was calculated by subtraction of remained Cd²⁺ in solution from the total added Cd²⁺. In another part of filtrate, after 2, 4, and 24 h of reaction, dissolved organic carbon (DOC; Organic matter, contained in a water sample that is soluble and/or colloidal, that can pass through a 0.45-μm filter as defined by USEPA [30] was determined according to the method described by Allison [29].

2.5. Mathematical kinetics procedures:

The adsorption kinetic data of cadmium on the adsorbents studied were analyzed in terms of pseudo-first order and pseudo-second order rate equations. The linearized form of pseudo-first order rate equation is given as [31]:

$$\log(q_t - q_e) = \log q_e - k_1 t / 2.303 \quad (1)$$

Linearized form of pseudo-second order rate equation is given as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (2)$$

Where q_t and q_e (mg/g) are adsorbed Cd²⁺ at time t (h) and equilibrium (e), k_1 (1/h) and k_2 (g/(mg.h)) are the rate constants for the pseudo-first-order and pseudo-second-order adsorption kinetics, respectively.

RESULTS AND DISCUSSION

3.1. Characterization of bio-adsorbent:

Table (1) illustrated that pyrolysis of PHF and WSF at 450 °C for 15 minutes condensate the carbon content in biomass and more than 50% of initial weights were lost as volatile gases (58.72 – 60.12 % from PHF and WSF, respectively). Carbon content increased from 31.18 and 26.24% to 55.00 and 43.64% in PHB and WSB, respectively. The obtained results slightly varied than those mentioned in similar studies. But that variation is accepted because the pyrolysis temperature, heating rate and residence time play an important role in carbon condensation during biochar production and consequently biochar carbon content. For example, the results obtained by Ahmed *et al.* [4] showed that C content was 68.27 and 83.76% for peanut hull biochar produced at 300 and 700 °C, respectively, for residence time of 3 hours. Whereas the carbon content of wheat straw biochar was 69.62% when the temperature of pyrolysis was 525 °C and residence time was 2 hours [32]. One the other hand, the slow or fast rate of heating temperature increments possibly will play another role in carbon condensation. The high biochar C content resulted from mentioned studies Ahmed *et al.*, [4] and Bruun *et al.*, [32] for peanut and wheat straw biochars, respectively was accompanied with low heating rate (7.0 and 6.0 °C/min., respectively) whereas, in the current study, the high heating rate (25.0 °C min⁻¹) produced low biochar C content (Table 1). Therefore, regardless the type of feedstock, not only the pyrolysis temperature and residence time but also heating rate will affect the ultimate C content of biochar.

3.1.1 Specific Surface Area:

Previous studies have suggested that temperature plays an important role in affecting biochar surface area through controlling the creation of pores and creaking in the biochars basal-structural sheets [33, 34]. Heating the samples of PHF and WSF for 15 minutes on 450 °C under limited oxygen conditions increased the surface area about 2 times in both materials (Table 2). On the other hand, the distribution percentage of the pore volume and pore area increased about 10 % in the range below 20 nm for PHB whereas only 8.5% increase in pore volume was observed in WSB. The pyrolysis heating conditions (heating rate, temperature level and time residence on that level) control the resulted values of surface area, pore volume and pore area [35, 36].

Table 1: Pyrolysis conditions and carbon content in feedstock and biochar of peanut hull and wheat straw.

Property	Peanut Hull		Wheat straw	
	Feedstock	Biochar	Feedstock	Biochar
Pyrolysis conditions				
Temp. increment, deg. Min ⁻¹	-	25.00	-	25.00
Max. temp., °C	-	450.00	-	450.00
Residence time, min.	-	15.00	-	15.00
Volatiles, %	-	60.12	-	58.72
Solids, %	-	39.88	-	41.28
Total carbon, %	31.180	55.000	26.240	43.640

Table 2: Pore analysis and specific surface area for the feedstock and biochar of peanut hull and wheat straw.

Properties	Peanut hull		Wheat straw	
	Feedstock	Biochar	Feedstock	Biochar
BJH pore volume distribution				
< 20.0 nm	24.20	34.95	54.71	63.11
20 - 80 nm	45.25	41.01	31.17	26.54
> 80.0 nm	30.27	24.06	14.12	10.32
BJH pore area distribution				
< 20.0 nm	68.04	79.18	90.22	89.60
20 - 80 nm	24.98	16.90	8.28	9.41
> 80.0 nm	7.00	3.92	1.48	1.00
BJH total pore size (mL.g ⁻¹)	0.01	0.01	0.02	0.02
BET specific surface area (m ² .g ⁻¹)	1.00	1.90	2.54	4.56

3.1.2 FTIR analysis:

The chemical structure of the adsorbent is of vital importance in understanding the adsorption process. However, FTIR technique is an important device to recognize the features of functional groups. The FTIR spectra of the peanut and wheat straw before and after pyrolysis were used to determine the vibrational frequency changes in the functional groups through the transformation from feedstock (raw chemical structure state) to biochar (carbon-enriched and aromatized structure state). The obtained FTIR spectra revealed that the PHF contained more bands than the PHB (Fig. 1), indicating that the surface functional groups of peanut hulls experienced chemical changes during thermal activation. The wide band at about 3394.48 cm⁻¹ for PHF was assigned to the OH stretching vibration of the hydroxyl groups including hydrogen bonding [37]. The charring process led to form a broad peak of OH group at about 3398.34 cm⁻¹ due to the degradation of cellulosic material. The intense peak at 2925.81 cm⁻¹ for PHF was attributed to the C-H stretching vibration [38], which moved out for the PHB (Fig. 1), indicating that the hydrogen element was removed to a large extent after thermal activation. The peaks positioned at 2160.13 cm⁻¹, 1633.59 cm⁻¹, 1411.8 cm⁻¹ and 1261.36 cm⁻¹ in the spectra of the PHF also demonstrated that the peanut hull contained large amounts of lingo-cellulosic material, as lignin was a complex amorphous polymer which was constructed by alkynes group, carbon-carbon bonds and ether link. After pyrolysis, the peaks located at 1591.16 cm⁻¹ and 1402.15 cm⁻¹ attributing to carbonyl C=O stretching vibration and to -COOH symmetric stretching vibration, respectively [39, 40], were present for PHB, which possibly due to the withdrawal of H element and OH groups from the aromatic rings during the heat treatment. The absorption peak at 1122.49 cm⁻¹ indicated the existence of C=O bond in carboxylic groups [41]. The peaks around 599.82 cm⁻¹ of PHF spectrum and around 781.12 and 615.25 cm⁻¹ of PHB represent C-H aromatic and alkyl bend. Also, it can be interpreted as Si-O-Si and Si-H reactive groups.

The FTIR spectra of WSF (Fig. 1) showed that the dominant peaks in the region between 3994.300 and 2918.1 cm⁻¹ are due to stretching vibrations of CH and OH. The major peak at 1631.67 cm⁻¹ in the WSF is attributed to either the acetyl and uronic ester groups of the hemicelluloses or the ester connection of carboxylic group of the ferulic and p-coumeric acids of lignin and/or hemicelluloses [42, 43]. This peak moved out completely in the thermally treated materials (Fig. 1, WSB spectrum) because of the elimination of most hemicelluloses and cellulose from the feedstock. The peak at 1373.22 cm⁻¹ in the WSF represents the C=C stretch of aromatic rings of lignin [42, 43, 44]. This peak was moved to 1384.79 cm⁻¹ by high intensity in WSB (Fig. 1, WSB spectrum) which deduce more condensation and tendency on the way to lignin formation. The peak at 1245.93 cm⁻¹ for the WSF - which disappeared in the FTIR spectra - reflects C-H asymmetric

deformations [43]. The peak at 1054.99 cm^{-1} of the WSF was splitted into two peaks at 1101.28 and 792.69 cm^{-1} after the thermal activation (WSB) and all of which are due to C–O stretching [44]. From the spectral analysis, we can denote to that FTIR appears importance of both organic and inorganic groups located on feedstock and biochar surfaces and the pyrolysis process imposes to more occurrences of inorganic (resistant) surface groups on biochar.

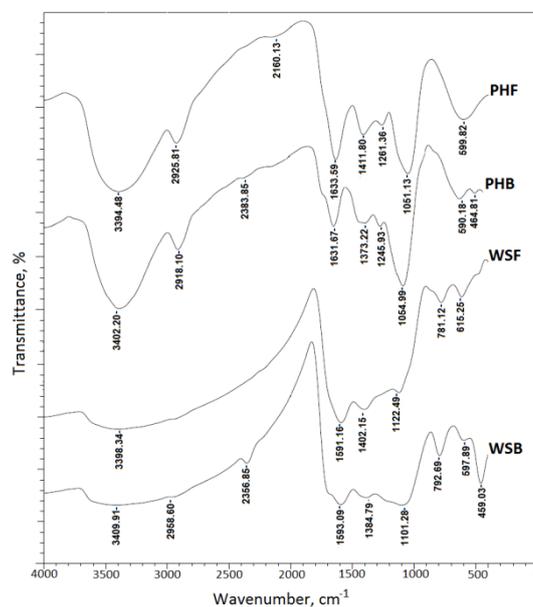


Fig. 1: FTIR spectra of the feedstock and biochar of peanut hull and wheat straw obtained by pyrolysis at $450\text{ }^{\circ}\text{C}$ for 15.0 minutes.

3.1.3. Scanning Electron Image analysis:

SEM images of the feedstock and biochar of peanut hull and wheat straw were taken to investigate the effect of anaerobic thermal decomposition on the change in their structure (Figure 2A-D). The morphology of molten surfaces of PHF and WSF images (Fig. 2A and C) may possibly reflect some surface complexation between cadmium ions and the active groups of low-molecular weight constituents of hemicelluloses and cellulose and subsequent deformation of native structural surfaces. Also, the thermal decomposition of chemical bonds and the melting of some compounds can break the fibers of the feedstock [45]. A porous surfaces were observed in biochar images (Fig. 2B (PHB) and D (WSB)) which resulted from biomass losses in the form of volatiles (about 60.12% from peanut hull and 58.72% from wheat straw as listed in Table 1).

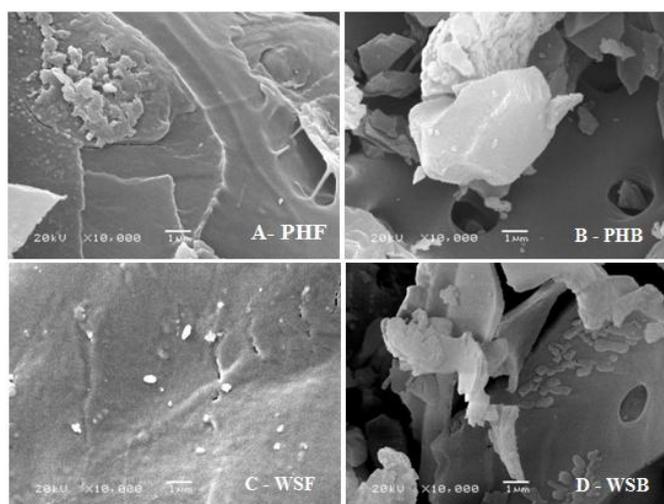


Fig. 2: The images of scanning electron microscope representing the changes and voids formation on the surface of feedstock and biochar samples of peanut hull (A and B) and wheat straw (C and D).

3.2. Adsorption Isotherm:

Figure 3 shows that increasing the contact time cause an increase in both the amount of adsorbed Cd^{2+} per mass unit of biochar (or feedstock) and Cd^{2+} removal percent. The adsorption isotherm process of Cd^{2+} on biochar samples was characterized by a strong increase during the first five minutes of contact and about 94.90 and 97.97% of Cd^{2+} was removed by PHB and WSB, respectively. Then, it was followed by a slow increase until reaching a state of equilibrium (Fig. 3). In comparison with the corresponded feedstock adsorbents, Cd^{2+} adsorption was 77.74 and 79.84% within the first five minutes. In the case of biochar adsorbents, adsorption equilibrium is reached faster (one hour) than feedstocks (2 h for WSF and 4-6 h for PHF). The increase in Cd^{2+} adsorption by biochar was also observed (98.9% by PHB and 99.2% by WSB) along with the studied reaction periods. However, that trend was contrary in the Cd^{2+} - feedstock reaction system where amounts of adsorbed ions by PHF and WSF decreased after 6 and 24 hr, respectively, (Fig. 3). These results revealed that using the feedstocks in Cd^{2+} removal for extended periods more than 2 h may possibly not succeed in comparing with pyrolyzed matter (biochar). These results of adsorbed Cd^{2+} may be related to the increase in surface area and the formation of micropores of biochar than those observed in feedstock (see Table 2). Numerous studies showed similar results for Cd^{2+} removal from aqueous solutions by peanut and wheat straw biochars [46, 47, 48, 49].

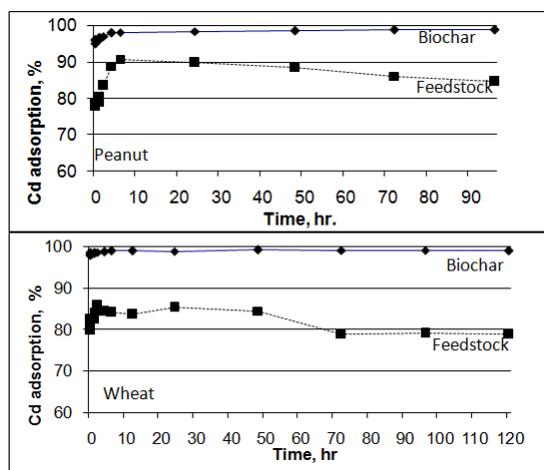


Fig. 3: Cadmium ions removal (%) by the feedstock and biochar of peanut hull and wheat straw as a function of contact time.

The pH is one of the major parameters in the adsorption isotherm. It affects the properties of adsorbent surfaces reactivity and the ionization and speciation of the adsorbates. After the pre-equilibration for 24 h (shaking with 0.01 M KCl electrolyte), the values of suspension pH for feedstock and biochar were 5.50 (PHF), 5.58 (WSF), 7.61 (PHB) and 7.48 (WSB). The pH changes during the adsorption reaction of Cd^{2+} with adsorbents are illustrated in Fig. (4). According to the Medusa software and HYDRA database (Hydrochemical Equilibrium Constant Database, Royal Institute of Technology, Sweden), as pursues from the speciation distribution of the metal ions at the initial concentration 1×10^{-3} M, or less, cadmium is occurred as free ions in the pH range equal 1.0-8.0 then, at higher pH, the ions begin to hydrolyze and precipitation occurs. Adsorption reactions of Cd^{2+} on feedstock and biochar samples showed an increase in suspension pH until the end of reaction (120 hours). The adsorption onto feedstocks was associated with considerable pH increases about 2.2 and 1.42 unites for PHF and WSF, respectively, more than the initial values (Fig. 4). While, a slightly pH increases accompanied the Cd^{2+} adsorption onto biochars (0.17 and 0.24 unit for PHB and WSB, respectively). In all cases and throughout the reaction intervals, the obtained results demonstrated that maximum values of pH were below 8.0 except for PHB after 120 h of reaction where pH was 8.09. Consequently, mechanisms such as precipitation might not be included in these systems and ion exchange, complex formation and/or diffusion are expected responsible for Cd^{2+} removal by studied adsorbents [20, 50,51]. Therefore the maximum adsorption of Cd^{2+} was achieved at a pH of equal 6.45 onto PHF (0.793 mg/g), 6.37 onto WSF (0.751 mg/g), 7.86 onto PHB (0.865 mg/g) and 7.61 to WSB (0.868 mg/g).

Regarding to the adsorption Cd^{2+} onto feedstocks, after 2.0 h (PHF) and 24.0 h (WSF) of the reaction, adsorbed amounts of Cd^{2+} were decreased (Fig. 3) and this trend was associated with increasing in the concentration of dissolved organic carbon (DOC) released to solutions as illustrated in Fig. (5). These results suggested that the biodegradation process of the feedstock during the adsorption reaction might be effective and subsequent slightly facilitate the adsorbed Cd^{2+} to return to solution. The high rate of DOC released from feedstock more than biochar (Fig. 5) was expected and may be owing to occurrence of cellulose and hemicellulose fractions beside lignin in feedstock comparing to only lignin in biochar. On the other hand, and as

shown from FTIR results (Fig. 1), the pyrolysis process lead to increase the aromatic/aliphatic ratio in biochar than those in feedstock [52]. These thermal transformed forms (biochar) are recalcitrant structures and not available to microbes (low and stable concentration of DOC) rather than feedstock.

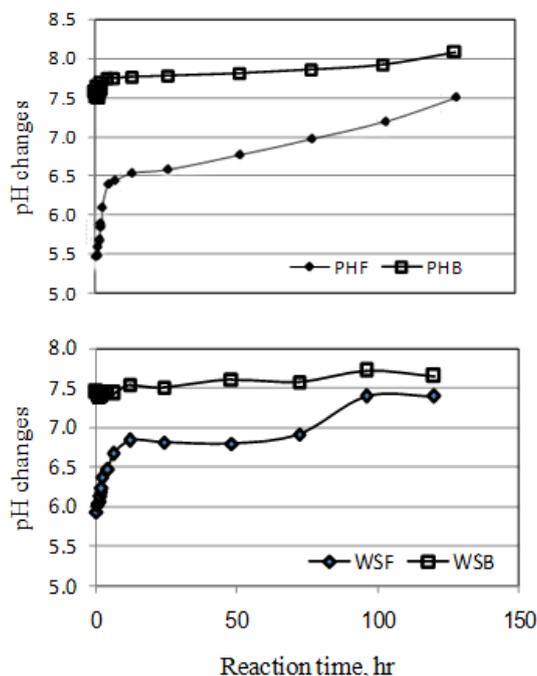


Fig. 4: pH changes during Cd²⁺ removal by feedstock and biochar of peanut hull and wheat straw.

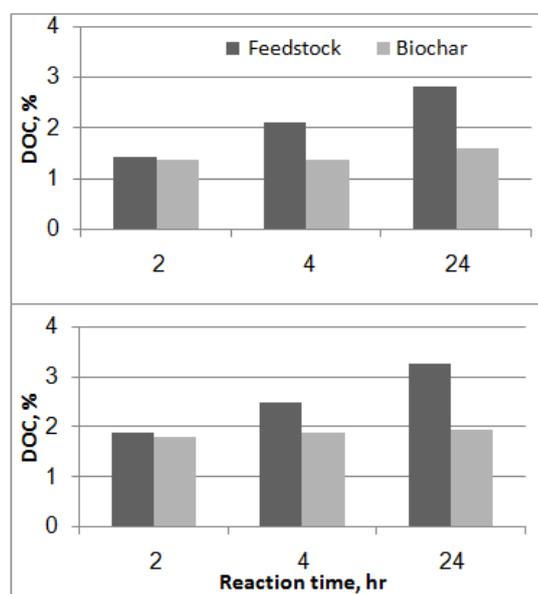


Fig. 5: Dissolved organic carbon (DOC) released during the removal process of Cd²⁺ from aqueous solution by feedstock or biochar of peanut hull and wheat straw.

3.3. Adsorption Kinetics:

The experimental data were tested with pseudo-first order and pseudo-second order kinetic models in order to understand the kinetics of Cd²⁺ removal. According to equations 3, The linear plots of value $\log[(q_e - qt)/q_e]$ against time t can give the pseudo-first-order adsorption rate constant k_1 and q_e can be calculated from the slopes and intercept, respectively. The corresponding values of k_1 , q_e and R^2 for all tested times are presented in Table 3. As can be seen from the results, the correlation coefficients were low ($R^2 < 0.90$). Also q_e values calculated from the plots were lower than the experimental data. Consequently, it may investigate that high concentration

of Cd^{2+} removal by the feedstock and biochar of peanut hull and wheat straw did not follow pseudo-first-order equation. On the other hand, higher orders rate kinetic models should be applied to test the validity. According to equation 4 of pseudo-second-order model, plotting t/q_t versus t (as shown in Fig. 6), rate constant k_2 and q_e were determined from the slope and intercept of the plot, respectively. The values k_2 , q_e and R^2 are given in Table 3. The calculated q_e values show a very good agreement with the experimental values with R^2 values exceeding 0.999. This indicates that the pseudo-second-order kinetic model describes well Cd^{2+} removal using PHF, WSF, PHB and WSB under the current conditions of this study. The higher values of slopes obtained from curves of pseudo-second order model implied that cadmium ions transferred from bulk solution to feedstock and biochar surfaces was faster.

Table 3: Parameters of pseudo-first-order and pseudo-second-order kinetics models for Cd^{2+} adsorption onto peanut hull and wheat straw feedstocks and biochars.

Adsorbent		Pseudo-first order			Pseudo-second order		
		q_e	K_1	R^2	q_e	K_2	R^2
Feed Stock	PHF	9.0×10^{-3}	1.9×10^{-3}	0.1820	149.5	-45×10^{-3}	0.9988
	WSF	8.51×10^{-3}	1.2×10^{-3}	0.4400	138.5	-19×10^{-3}	0.9988
Biochar	PHB	6.1×10^{-3}	0.6×10^{-3}	0.5380	172.9	0.147	0.9999
	WSB	8.5×10^{-3}	1.2×10^{-3}	0.4200	173.6	1.106	0.9999

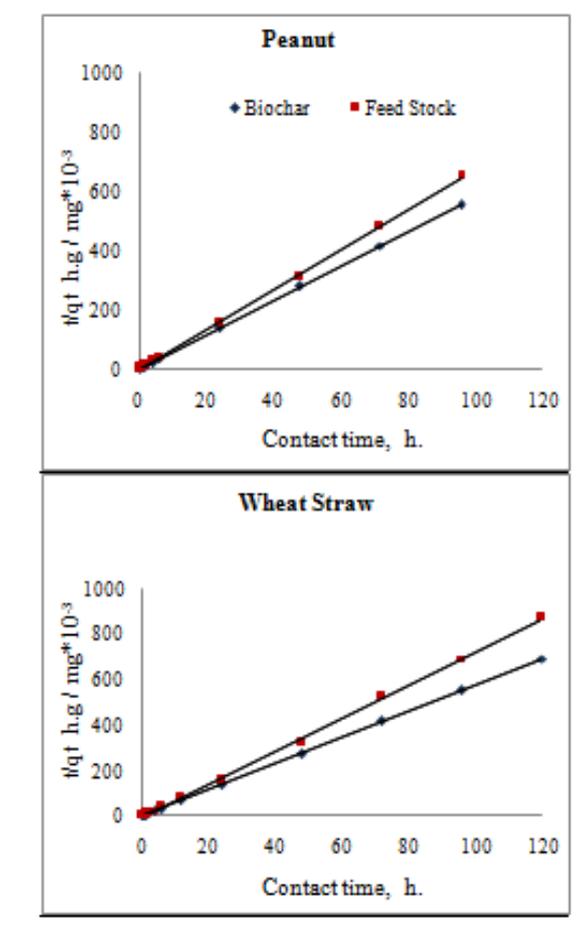


Fig. 6: Pseudo-second-order plot for Cd^{2+} adsorption onto feedstock and biochar of peanut hull and wheat straw.

Conclusion:

The adsorption isotherm efficiencies of cadmium (II) ions on the feedstock and biochar of peanut hulls and wheat straw were investigated as a function of the contact time under laboratory conditions. The results indicated that:

- The biochars of peanut hull and wheat straw produced PHF and WSF at $450\text{ }^{\circ}\text{C}$ for 15 min. were characterized by higher carbon content, BET surface area, porous structures and aromatic active groups than their native forms (feedstocks).
- The PHB and WSB sorbents were effective to remove $\text{Cd}(\text{II})$ ions from aqueous solution than their feedstock along with the investigated times.

- The changes in pH values of suspensions during the reaction of all studied sorbent with Cd²⁺ suggested that the ion exchange, complex formation and/or diffusion mechanisms can be investigated to govern and control Cd²⁺ removal from aqueous solutions.
- The lower efficiencies of Cd²⁺ removal by PHF and WSF than their biochar may be related to those materials are appeared to biodegradation during the removal reaction. The results of released amounts of DOC from feedstock and Cd²⁺ removal decrease can be indicators for degradation.
- The adsorption kinetics of Cd²⁺ removal was best described by pseudo-second order model with R² values exceeding 0.999.

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