Simultaneous immobilization of heavy metals in soil environment by pulp and paper derived nanoporous biochars

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Abstract

Background Biochars are the new generation of sustainable soil amendments which may be applied both to fertilize and remediate the impacted soils. The aim of current research has been synthesis and characterization of pulp and paper-derived biochars and determination of their mechanisms in simultaneous immobilization of heavy metals (Cu^{2+} , Pb^{2+} , and Zn^{2+}) within contaminated soil. In a novel attempt, three different solid wastes of Mazandaran Wood and Paper Industries (barks and effluent sludge) were utilized to produce biochars.

Methods The thermogravimetric behavior of the three selected biomasses were initially analyzed and the proper pyrolysis condition has been determined, accordingly. Alterations in surface active groups, before and after the pyrolysis process, have been detected by Fourier transform infrared (FTIR) spectroscopy. Elemental analysis and acid digestion procedure have been employed to measure C, H, N, S, O, and P contents of the biochars. Moreover, porosity and morphological characteristics have been monitored by Brunauer-Emmett-Teller (BET) porosimetry and scanning electron microscopy (SEM). Batch adsorption tests have been designed and carried out. Finally, a set of soil sequential extraction experiments was performed over both amended/unamended soils which together with a post-sorption FTIR analysis, explained the possible competitive immobilization mechanism.

Results Porosimetry study indicated the nanoporosity of the chars and the distribution pattern of adsorbed metals over the char samples. Batch sorption tests suggested remarkable uptake capacity for each char. The results of post sorption tests suggested that Cu is mainly involved in organic bonds of $-\text{NH}_2$, $-\text{OH}$ and $-\text{COOH}$ groups, Pb forms insoluble hydroxide, phosphate or carbonate precipitates, and Zn is mostly engaged in the residual fraction.

Conclusions Accordingly, the bulky wastes are confirmed to have the potential to form sustainable biochar soil amendments.

Keywords Biochar · Heavy metals · Immobilization · Pulp and paper · Soil

Background

In pulp and paper industry, wood as raw material is used for production of pulp, paper, board and many other cellulose-

based products. Regardless of target products such as paper and Kraft liners which are directly sold to publication or packaging industries, a large amount of unwanted by-products are inevitably introduced [1–3]. In Mazandaran Wood and Paper plant, the biggest factory of its kind in the Middle East region, situated in Mazandaran Province, Iran, these unwanted materials include bark residues and effluent treatment sludge which are produced as much as 140 tons per day. Although the company has recently tried to process barks for production of organic fertilizers, effluent sludge is still to be landfilled for disposal. So, there is a lack of proper waste management strategy of these bulky residues.

In recent years, application of low-cost sorbent materials in soil and water cleanup has become a hot research field [4]. This comprises the quest for efficient sustainable adsorbents to be utilized instead of high-performance commercial ones which are usually costly and economically non-feasible [5]. Among these, amending with biochar as a green and

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sustainable approach has been increasingly receiving attention worldwide. Biochar is a charcoal-like porous solid which is the product of biomass pyrolysis in oxygen-depleted environment at rather low temperatures [6]. The product mainly contains surface active groups such as carboxylic, phenolic, hydroxyl, and carbonyl [7]. The physical and chemical properties of biochar depends on the biomass characteristics, treatment processes, and the conditions applied during pyrolysis [8]; however, C-enrichment and high porosity are the two specific properties which influence some remarkable soil characteristics such as cation exchange capacity (CEC), alkalinity, and water/nutrients holding capacity [9]. Nevertheless, before the engineered chars are used as environmental sorbents, a deep knowledge of their sorption mechanisms with respect to different contaminants must be obtained.

Metals such as Cu^{2+} , Pb^{2+} , and Zn^{2+} are the usual pollutants in soils of mine-impacted industrial sites, and their transport in both soil and aquatic environments has become a global dilemma [10]. Similar cases have been reported for soils surrounding Sarcheshmeh Copper Complex, Kerman, Iran [11, 12]. As a remedial approach, application of soil amendments such as biochars during a long-term and cost-effective rehabilitation program may be effective. This has been formerly confirmed in heavy metal contaminated paddy soils by a three-year experiment [13]. Moreover, application of biochar on mine tailings and its effect on substrate modification during phytostabilization of contaminants has been already investigated [14]. The pulp and paper industry introduces huge volumes of different solid residues which are thermally suitable for the charring process; however, detailed description of producing efficient biochars out of these solid wastes and the mechanisms in heavy metal or organic pollutants immobilization by the obtained chars are limitedly investigated so far [15–18]. In our previous work, the performance of such novel biochars in adsorbing the metal ions from aqueous solutions was suggested after limited number of sorption tests [19]; however, the objective of the current work was to produce engineered biochars out of three different pulp and paper residues, fully characterize their physical and chemical properties, and systematically determine their impact in multi-metal impacted soil media, as a novel comprehensive study.

Methods

Chemicals

All the chemical reagents were of analytical grade and were used without further purification. Nitrate salts of Lead (II), copper (II), zinc (II), and potassium, sodium chloride, nitric acid, sulfuric acid, and sodium hydroxide were all purchased from

Table 1 The applied procedure used in soil sequential extraction

Extractant	Equilibrium conditions	Chemical form extracted
0.5 M KNO_3	16 h, 25 °C	Exchangeable
Deionized water	2 h, 25 °C (extract three times and combine data)	Water soluble
0.5 M NaOH	16 h, 25 °C	Organically bound
0.05 M Na_2EDTA	6 h, 25 °C	Oxide or carbonate
4 M HNO_3	16 h, 80 °C	Sulfide

Merck. Na_2EDTA was obtained from Sigma-Aldrich. Distilled, deionized water (DDW) was utilized during all experiments.

Soil sample

Soil sample was synthetically prepared by mixing 50% sand, 35% silt, and 15% kaolinite according to reported mean texture of the polluted soils in vicinity of Sarcheshmeh Copper Mine Complex, Kerman, Iran [20]. The CEC of amended/unamended soil was measured by ammonium acetate method according to EPA method 9080.

Biochar source and preparation

Biomass samples were collected from the waste dump of Mazandaran Wood and Paper plant comprising wood barks of grades 1 and 2, and effluent treatment sludge, coded as W_1 , W_2 , and W_3 , respectively. The samples were air-dried overnight and then subjected to a thermogravimetric analysis (TGA) using a TGA1 device (Mettler Toledo, Switzerland). Accordingly, the biomasses were

Table 2 Organic and inorganic composition of Mazandaran Pulp and Paper effluent sludge

		Klason lignin (15.3%)
Effluent sludge	Organic fraction (60.54%)	Dissolved lignin (1.02%)
		Glucose (22.61%)
		Xylose (17.31%)
		Mannose (0.53%)
		Galactose (3.72%)
		Arabinose (0.05%)
		CaO (24.9%)
		SiO_2 (2.37%)
		MgO (1.89%)
		Al_2O_3 (8.37%)
	Inorganic fraction (39.46%)	Na_2O (0.3%)
		K_2O (0.24%)
		P_2O_3 (0.12%)
		MnO_2 (0.01%)
		TiO_2 (0.002%)

Fig. 1 Thermogravimetric mass loss (solid line) and derivative thermogravimetric mass loss (dashed line) curves of a) W_1 , b) W_2 , and c) W_3

pyrolysed at 600 °C at a temperature rate of 10 °C/min under 3 lit/min nitrogen gas stream for 2 h residence time inside a box furnace (Nabertherm, Germany). The obtained biochars were then left until they reached the ambient temperature, rinsed with DDW, dried at 80 °C in an oven, and finally sieved to <2 mm size fraction.

Surface area, elemental, FTIR analyses, and scanning electron microscopy

Nitrogen adsorption isotherms at 77 K were applied to determine the surface area of each biochar by Belsorp mini II (BelJapan, Japan) using the Brunauer, Emmett, and Teller (BET) isotherm. For this, each sample was degassed at 120 °C for 15 h, in advance. Furthermore, a CHNS/O analysis has been carried out using an ECS 4010 device (Costech, Italy) for each char. Assessment of the active surface functional sites in samples was conducted using a Nexus 670 apparatus (Thermo Nicolet, USA).

A LEO 1450 VP scanning electron microscope was employed to study the morphological characteristics of raw biomasses, and chars before and after the sorption process.

Immobilization of Cu^{2+} , Pb^{2+} , and Zn^{2+} by biochar in soil

Synthetic rain water (SRW) was prepared by adding a diluted sulfuric/nitric acids mixture (60/40 w/w) to DDW until pH=4.2 according to EPA method 1312. 10 g of the soil sample amended with 10% char ($w_{\text{char}}/w_{\text{soil}}$) was equilibrated in SRW (20 g/L) for 24 h by an end-over-end agitator. The equilibrium pH was recorded (Metrohm 827 pH lab, Switzerland) and then Cu, Zn, and Pb salts were added to the system for the ultimate concentration of 4 mM. The agitation process was continued for another 24 h and after measuring the final pH, the slurry was centrifuged, the supernatant was filtered, and the aqueous phase was sent for AAS analysis (Varian, Australia). The contaminated soil was rinsed with DDW, oven-dried at 80 °C, and kept for further analyses.

Soil sequential extraction

A portion of the contaminated soil (both amended and unamended) was subjected to sequential extraction experiment in order to determine the speciation of heavy metals. The sequential extraction method was performed

Table 3 Elemental composition of the three chars

Char name	C (%)	H (%)	N (%)	S (%)	O (%)	P (%)	Ash (%)	O/C	H/C
B ₁	77.74	1.92	0.66	0.55	11.15	0.134	8.53	0.1434	0.0247
B ₂	47.69	1.47	0.89	—	18.41	0.133	31.54	0.3860	0.0308
B ₃	19.10	1.49	0.67	0.70	25.64	0.0028	53.1	1.342	0.0780

Table 4 CEC comparison of unamended/amended soils

Soil sample	Unamended	Amended with 10% w/w biochar		
		SB ₁	SB ₂	SB ₃
CEC (meq/100 g)	6.3	7.4	8.91	9.8

according to Sposito [21] where 2 g of the soil sample is sequentially mixed with 25 g extractant and shaken end-over-end in a HDPE tube according to Table 1.

After extraction the suspension was centrifuged and the resulting supernatant solution was filtered. The concentration of each metal in the obtained solution was determined by AAS. In case of each extraction step, standard solutions for the metals were prepared in a background solution of the corresponding extracting reagents.

Data availability All data generated or analyzed during this study are included in this published article.

Results

Characterization

Like any other bark sample, W₁ and W₂ are generally composed of lignin, cellulose and hemicellulose (with associated glucose, galactose, mannose, arabinose, and mannose sugars) [22]. Moreover, the composition of Mazandaran pulp and paper effluent sludge (W₃) is given in Table 2.

The three feedstocks were subjected to thermal analysis. Result of TGA done over the three biomasses is illustrated in Fig. 1.

The conceptual model of biochars is reported to be a heterogeneous blend of heat-treated biopolymers with N, O and S functional groups being substituted within the pure graphitic sheets [23–25]. Oxygen content of chars plays a significant role in determining its surface chemical behavior such as surface pH, which is an important driver for chemical reactions and degradation potential. Moreover, the amount of carbon determines the position of biochar within the Black C

Fig. 2 SEM micrographs showing the original porous structures of a) W₁, b) W₂, and c) W₃

Fig. 3 EDS maps of Cu, Zn, and Pb distribution on a) B₁, b) B₂, and c) B₃

spectrum thereby the chemical and thermal stability of biochars [23, 26]. Thus, elemental analysis is necessary to be conducted as part of any biochar study. The obtained chars (B₁, B₂, and B₃) were analyzed for C, H, N, S, and O content

(Table 3). Moreover the total P content of each char was measured by acid digestion procedure according to Kuo method [27,28]. The ash content (comprising S) of each char was calculated by [29]. Table 4 carries the

Fig. 4 Nitrogen gas adsorption-desorption isotherms at 77 K on biochars

Fig. 5 Pore volume distribution of biochars

measured CEC values in case of unamended/amended soil samples measured by sodium acetate procedure proposed by Bower et al. [30].

SEM micrographs are shown in Fig. 2. Moreover, Fig. 3 carries post-sorption EDS metal distribution map on each char. The total surface areas of B₁, B₂, and B₃

are determined as 272.49, 94.795 and 113.22 m²/g, respectively. Nitrogen adsorption-desorption isotherm for B₁, B₂, and B₃ is given in Fig. 4. The BJH pore volume distribution is also depicted in Fig. 5.

Figure 6 presents FTIR spectra related to each biomass and its corresponding biochar.

Fig. 6 Comparison of FTIR spectra in feedstock and derived chars: a) W₁-B₁, b) W₂-B₂, and c) W₃-B₃

Fig. 7 Residual amount of Cu^{2+} , Pb^{2+} , and Zn^{2+} in solution after 24 h (20 gL^{-1} char amended 10% w/w soil in SRW, initial concentration of each metal: 4 mM)

Immobilization of Cu^{2+} , Pb^{2+} , and Zn^{2+} by Biochar in soil

In this part of study, the ability of biochars to immobilize a mixture of Cu, Pb, and Zn in soil was assessed through batch experiments. Results of batch equilibrium tests with amended/unamended soils (Fig. 7) shows that the unamended soil (S) has the least attenuation capacity of all (31.95% Pb^{2+} and 37.70% Zn^{2+} , and 9.5% Cu^{2+}). However, the soil amended with 10% B₁ (SB₁) was able to immobilize Cu^{2+} by 29.18%, Pb^{2+} by 85.52%, and Zn^{2+} by 70.52%. B₂ when used at 10% AA rate as the soil amendment (SB₂) sorbs 19.26% Cu^{2+} , 61.39% Pb^{2+} , and 55.7% Zn^{2+} . Finally, soil amended with 10% B₃ (SB₃), was able to immobilize 11% Cu^{2+} , 51.37% Pb^{2+} , and 39.65% Zn^{2+} .

To better understand the metals speciation within the amended soil, the contaminated soil obtained from the batch sorption tests was subjected to a sequential extraction procedure (Table 1). The basis of this method is that KNO_3 and deionized water are displacing agents for the species weakly sorbed or held on ion-exchange sites [21], NaOH extracts the organically-bound metals [21], EDTA is able to release species chemisorbed on or associated with carbonates and oxides [31, 32], and finally, HNO_3 is able to release the species bound to sulfides or more refractory residual [33].

Table 7 presents the amount of metal extracted by each extractant during the sequential experiment. In order to assess the adsorption mechanisms more accurately, a FTIR analysis was performed over the post-sorption solid fraction of batch tests collected from the previous section.

Figure 8 demonstrates the results of FTIR analysis performed on the char samples.

Discussion

Results of TGA analysis (Fig. 1) show that the initial mass loss in case of the two bark samples (W₁ and W₂) was approximately 10% and mainly due to the moisture evaporation. This stage is the only mass loss and constitute as big as 50% in case of the sludge sample (W₃). Next, devolatilization and thermal decomposition were responsible for other mass losses (approximately 70% and 50% in case of W₁ and W₂ respectively). Two obvious peak values in DTA curves of Fig. 1a, b confirms these two steps. The characteristic thermal decomposition of hemicellulose, cellulose and lignin are reported to be 200–350, 320–400, and 250–550 [34, 35]. According to these behaviors, the pyrolysis conditions were selected as 600 °C at a heating rate of 10 °C/min and 2 h residence time for each biomass. The pyrolysis process at this temperature, leads to a higher recalcitrant character of the char by degrading

Fig. 8 FTIR spectra before and after co-sorption of Cu, Zn, and Pb, in case of a) B₁, b) B₂, and c) B₃

Table 5 Mean pore diameter/ total pore volume values obtained from BET analysis

Char name	Mean pore diameter (nm)	Total pore volume (cm ³ /g)
B ₁	1.9842	0.1352
B ₂	3.1915	7.5635×10^{-2}
B ₃	6.5383	0.1851

the main biopolymers and increasing the number of aromatic compounds [36].

The results indicate considerable amount of carbon in B₁ (77.74%) in comparison with the other two chars (47.69 and 19.10% in case of B₂ and B₃ respectively).

The presence of nutrients such as nitrogen and phosphorus makes the obtained biochars attractive amendment not only to immobilize the metal contaminants, but also to achieve greater soil fertility [37]. Using the results of elemental analysis, the O/C and H/C ratios may be calculated, both of which are indicators used to predict the stability of biochar in the soil environment [38]. Carbon content of chars is believed to be inert and contribute to refractory soil organic matter. However, as mentioned earlier, there is a spectrum for biochars in terms of stability and their resistance to microbial degradation [23]. This can be predicted by the O/C ratio. In this regard, the half-life of B₁, B₂, and B₃ in soil system, are estimated to be more than 1000, within (100–1000), and less than 100 years, respectively [23]. Moreover, lower H/C ratio presents higher resistance to degradation [39, 29]. Amount of volatile materials is also an important physicochemical property to be considered when characterizing the biochar [40]. The latter may be calculated with respect to the results of TGA. According to Enders et al. [29], all three chars (B₁, B₂, and B₃) may be considered as having high carbon sequestration potential (volatile material < 80%, O/C < 0.2 or H/C < 0.4), with B₁ being the best fitting within the limits.

Moreover, the O/C ratio may be related to cation exchange capacity and presence of oxygenated groups on the biochar [23, 41]. According to Table 4, Addition of biochar to the soil clearly enhances the CEC value with the order B₃ > B₂ > B₁ which is in agreement with their O/C ratios.

SEM micrographs show porous texture for the initial bio-masses with pore diameters up to several hundred nanometers (Fig. 2); however, BET analysis proves the nanoporosity in case of the three resulting chars (Table 5). EDS metal distribution maps for each char (Fig. 3) indicate that Cu, Zn, and Pb ions are mainly sorbed in pore areas. Generally, the biochar surface area depends on the treatment temperatures and the post-treatment with chemicals enhances the microporosity of biochars [42]. According to IUPAC classification of adsorption isotherms, B₁ follows a mixture of type I and IV, while B₂ and B₃ may be classified as type IV isotherms. The interaction between sample surface and adsorbate in types I and IV isotherms are usually relatively strong and the sorbent samples are classified as a combination of microporous (up to 2 nm) and mesoporous (2–50 nm). According to the classification made, various data could be derived using different analytical methods such as t-plot, Barrett-Joyner-Halenda (BJH), and Micropore analysis (MP) (Table 6). These data shows that microporosity in B₁ is higher than the other two char samples whereas B₃ is the most significant biochar in terms of mesoporosity.

Sorption tests from aqueous solution [19] showed that all three chars have higher affinity for Cu ions, while Zn and Pb ions are on the second and third ranks, respectively. Moreover, B₁ has shown the highest immobilizing effect as it leads to lower values of residual metal ions in the solution [19]. The overall performance of the amended soils are in total agreement with their behavior within aqueous solution [19] as SB₁ > SB₂ > SB₃ in terms of affinity towards metal ions.

Before addition of metals, the alkaline condition of the suspension and release of OH[−] anions, enables the precipitation through formation of hydroxide phases [43, 44]. Moreover, existence of P element in the composition of biochars may lead to formation of insoluble phosphates [45]. After addition of metals, for each char investigated, a dramatic pH decrease was observed (from 9.67–9.76 to 5.28–5.37) which suggests considerable CEC of chars and the release of exchangeable protons as a result of divalent metals sorption. Yet, the exchangeable fraction is only a limited part of the total amount of metals sorbed [44]. Another mechanism involved maybe the replacement of divalent metals with original cations in chars (e.g. sodium and calcium) which is also usually

Table 6 Analysis data obtained from the nitrogen adsorption isotherm

Char name	External specific surface area (m ² /g)	Micropore area (m ² /g)	Micropore width (nm)	Micropore volume (cm ³ /g)	Micropore distribution peak (nm)	Mesopore distribution peak (nm)	Mesopore volume (cm ³ /g)	Mesopore area (m ² /g)
B ₁	3.6346	283.2654	0.8855	0.1262	0.35	1.21	5.0116×10^{-2}	56.734
B ₂	10.309	88.746	0.9913	4.4258×10^{-2}	0.50	1.21	4.8259×10^{-2}	34.734
B ₃	42.357	79.883	2.4852	9.9879×10^{-2}	0.90	1.21	0.1744	98.962

Table 7 Results of soil sequential extraction procedure

Extractant	S			SB ₁			SB ₂			SB ₃		
	Extracted metals (%)											
	Cu ²⁺	Pb ²⁺	Zn ²⁺	Cu ²⁺	Pb ²⁺	Zn ²⁺	Cu ²⁺	Pb ²⁺	Zn ²⁺	Cu ²⁺	Pb ²⁺	Zn ²⁺
0.5 M KNO ₃ & deionized water	nd	0.70	17.34	nd	nd	0.98	6.13	0.39	0.10	0.23	0.11	nd
0.5 M NaOH	nd	0.055	0.091	69.91	14.2	0.16	57.34	25.60	4.21	52.49	39.68	3.81
0.05 M Na ₂ EDTA	99.00	82.04	6.57	11.17	85.04	5	0.5	70.32	25.2	39.24	59.4	24.50
4 M HNO ₃	nd	17.2	76	18.92	nd	93.67	36	3.6	70.53	8.0	0.77	71.66

nd means “not detected”

negligible [46]. The sorptive interaction between *d*-electrons in metal and aromatic π -electrons in biochars [47], and formation of metal complexes with O, N, P, S containing functional groups are the other possible mechanisms [44].

According to the soil sequential extraction results, in unamended soil (S), copper is mainly present in oxide or carbonate form, whereas, in amended soils (SB₁, SB₂, and SB₃), most of copper was extracted by NaOH which means Cu ions are mainly sorbed on the organic fraction of the soil. In both amended/unamended cases, practically, the major amount of zinc was found in the residual fraction of the soil. Moreover, lead is mainly accumulated in oxide/carbonate sites. In all cases, only trace amounts of each metal were detected in the exchangeable fraction denies the physical sorption phenomenon. Instead, metals would make chemical bonds with the active functional groups present on the surface of biochars.

In the post sorption FTIR spectra, changes in vibration patterns indicate the development of new bonds and alteration of surface functional configuration. In the post-sorption spectra for all three chars, there are obvious changes for C=C, C=O, O-H, and C-H stretching. Moreover, the P-bearing functional groups in B₃ are somehow amplified. These observations when merged with the results of soil sequential extraction process (Table 7), substantially confirm the possible formation of metal complexes with carboxyl (-COOH) and hydroxyl (-OH) functional groups of biochars, and also formation of insoluble metal phosphates and hydroxides. These mechanisms are in agreement to those dominant in the sorption from the aqueous environment [19].

Conclusions

Three various biochars were produced through oxygen-limited pyrolysis of Mazandaran Pulp and Paper Industry waste materials. As the very first step, a TGA was performed in case of each selected biomass suggesting the feasible parameters of the pyrolysis process. Next, the resulting chars were subjected to a thorough physical/chemical

characterization and their potential to be used as green sorbents in soil rehabilitation was assessed. The BET results unveiled the mixed micro-mesoporosity of the chars along with high surface area (B₁ had higher surface and mesopore area). Moreover, according to the calculated O/C and H/C ratios, all three biochars exhibit high efficiency in carbon sequestration and are less reactive in biodegradation. Each char improved both the cation exchange capacity and soil alkalinity, in a 10% w/w char/soil mixture. Moreover, the sorptive performance of the obtained chars as an amendment to metal-contaminated soil confirmed that B₁ is the most effective biochar and all three biochars had the same affinity towards the metal ions (Cu > Zn > Pb). The governing mechanisms in immobilization was evaluated by conducting a combined FTIR analysis/soil sequential extraction experiment. The results implied that in a multi-metal polluted soil, Cu is mostly involved in organic bonds with -NH₂, -OH and -COOH groups, Pb is mainly engaged in the insoluble hydroxide, phosphate or carbonate phases, and Zn is predominantly attached to the residual more refractory fraction. In general, the three biochars produced out of Mazandaran Pulp and Paper residues found effective in immobilization of heavy metals in contaminated soils, nevertheless enhancement of their sorptive properties may require some pre-treatments before their successful progress towards commercialization.

As annotated on the figure, bands at 2904 and 2940 cm⁻¹ represent the -CH₃ and -CH₂ groups, respectively, confirming the presence of long-chain aliphatics [44, 48]. Minor band at 1057 cm⁻¹ are assigned to aliphatic C-O-C group existing in cellulose whereas band at 1130 cm⁻¹ arises from the stretching vibrations of C-O bonds in ether [44, 49]. The band at 1070 cm⁻¹ represents the P-O bond of P-containing groups [44, 50, 51]. The band near 1650 cm⁻¹ is assigned to C=O stretching of amides [44, 48]. Minor band at 1443 cm⁻¹ arises from CH₂ scissoring [44]. Band at 1626 cm⁻¹ is assigned to aromatic C=C and C=O stretching [44, 49] and the one at 876 cm⁻¹ is assigned to γ -CH of furan. In Fig. 6c, the vibration at nearly 1050 cm⁻¹ is attributed to the Si-O bond in the mineral fraction of the effluent sludge. Generally, bands within (3200–

3400 cm^{-1}) represent hydroxyl groups [36, 44] while (1580–1600 and 3000–3050 cm^{-1}) indicate aromatic groups both of which is diminished after pyrolysis at 600 °C. The same has happened to aliphatic C–H stretching (2850–2950 cm^{-1}). However, the representative peaks for aromatic carbon appeared more clearly, such as C–H stretching (800–900 and 3000–3050 cm^{-1}), C=C (1380–1450 cm^{-1}), C–C, and C–O stretching (1580–1700 cm^{-1}) [36]. This proves the fact that the charring process modifies the functional group, changing the ratio of aliphatic C and aromatic C groups [36, 41].

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Authors' contributions HA was the main investigator, prepared the samples and performed the analyses, AKD supervised the study. MA and BA were the advisors to the study. All authors read and approved the final manuscript.

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Compliance with ethical standards

Competing interests The authors declare that they have no competing interests.

Consent for publication Not applicable.

Ethics approval and consent to participate Not applicable.

Abbreviations AAS, atomic Absorption Spectrometry; BJH, Barrett-Joyner-Halenda; MP, Micropore

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