



Biochar-assisted Fenton-like oxidation of benzo[a]pyrene-contaminated soil

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Abstract In the present study, the biochar derived from sunflower husks was used as a mediator in the heterogeneous Fenton process. The physical and chemical characteristics were studied in terms of specific surface area, elemental contents, surface morphology, surface functional groups, thermal stability, and X-ray crystallography. The main aim was to evaluate the effectiveness of biochar in a heterogeneous Fenton process catalyzed by hematite toward the degradation of benzo[a]pyrene (BaP) in Haplic Chernozem. The Fenton-like reaction was performed at a pH of 7.8 without pH adjustment in chernozem soil. The effects of operating parameters, such as hematite dosage and H₂O₂ concentrations, were investigated with respect to the removal efficiency of BaP. The overall degradation of 65% was observed at the optimized conditions where 2 mg g⁻¹ hematite and 1.25 M H₂O₂ corresponded to the H₂O₂ to Fe ratio of 22:1. Moreover, the biochar amendment showed an increment in the removal efficiency and promotion in

the growth of spring barley (*Hordeum sativum* distichum). The BaP removal was reached 75 and 95% after 2.5 and 5% w/w addition of biochar, respectively. The results suggested that the Fenton-like reaction's effectiveness would be greatly enhanced by the ability of biochar for activation of H₂O₂ and ejection of the electron to reduce Fe(III) to Fe(II). Finally, the presence of biochar could enhance the soil physicochemical properties, as evidenced by the better growth of *Hordeum sativum* distichum compared to the soil without biochar. These promising results open up new opportunities toward the application of a modified Fenton reaction with biochar for remediating BaP-polluted soils.

Keywords Biochar · Fenton-like reaction · Benzo[a]pyrene · Contaminated soil · Soil properties

Introduction

Soil is one of the major sinks for collecting organic pollutants due to their strong affinity to be absorbed by naturally occurring organic matters (Sazykin et al. 2019). As one of the most widespread organic contaminants, the appearance and accumulation of polycyclic aromatic hydrocarbons (PAHs) have become a significant concern for more than decades (Duan et al. 2015). Only a small fraction of PAHs is

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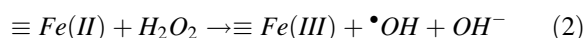
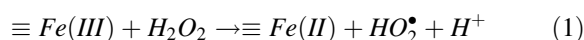
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bioavailable, while a large fraction is sequestered and remained in soil unavailable to microorganisms or degrading agents (Sazykin et al. 2019). Intensifying anthropogenic activities by several industries have worsened the conditions of PAHs accumulation in soil (Abdel-Shafy and Mansour 2016). Due to the mutagenic, carcinogenic, and teratogenic effects on human health, most of PAHs are regarded as a priority pollutant (Abdel-Shafy and Mansour 2016). Among PAHs, benzo[a]pyrene (BaP) has been proven to be highly carcinogenic (G. liang Li et al. 2014). In this context, the implementation of innovative treatment technologies is of the urgent need to alleviate the hazardous risk associated with PAHs (Kuppusamy et al. 2017).

In situ chemical oxidation (ISCO) is known as a widely used technique for abatement PAHs in contaminated soils (Zhang et al. 2019). Fenton and Fenton-like processes are one of the commonly used ISCO techniques that gain popularity as an alternative to conventional PAHs-contaminated soil treatments (Gitipour et al. 2018). The Fenton-like process involves a series of reactions between hydrogen peroxide and heterogeneous type iron aimed at the production of highly powerful hydroxyl radicals ($\cdot\text{OH}$) to decompose organic molecules (Kuppusamy et al. 2017). Recently, this process has emerged as a viable and cost-effective option for remediating PAH-contaminated soils (Usman et al. 2016). Contrary to traditional Fenton reagent oxidation, the Fenton-like is not only limited to acidic pH to exert its highest oxidation ability (Yap et al. 2011). In this regard, several papers highlighted removing PAHs in the contaminated soils by the reaction between solid's Fenton catalysts and H_2O_2 . Among solid activators, hematite (Jorfi et al. 2017), magnetite (Usman et al. 2012), goethite (Kanel et al. 2004), and soil's endogenous iron (Silva et al. 2008) have been successfully used in the Fenton-like oxidation of PAHs-contaminated soils.

In a heterogeneous Fenton catalytic system, iron mainly exists in the form of Fe(III) (Zhu et al. 2019). Heterogeneous Fenton's reaction begins with reacting surface Fe(III) with H_2O_2 at circumneutral pH to produce hydroperoxyl radical ($\text{HO}_2\cdot$) and Fe(II), as presented by Eq. (1) (Zhu et al. 2019). In the next step (Eq. (2)), the formed Fe(II) can be oxidized by H_2O_2 to regenerate more powerful $\cdot\text{OH}$ through Eq. (2) compared to $\text{HO}_2\cdot$. In the traditional heterogeneous

Fenton reaction, the reaction rate of Eq. (1) is much slower than that of Eq. (2), meaning Fe(II) is quickly consumed but slowly regenerated. Therefore, the Fenton-like reaction would slow down due to the low reduction rate of Fe(III) by H_2O_2 (Eq. 1). In this regard, the acceleration of the redox cycling of Fe(III)/Fe(II) and promotion efficiency of the utilization of H_2O_2 are the core issues that must be addressed to build more effective heterogeneous Fenton reactions.



One way to address the issue associated with the rate-limiting step is combining heterogeneous Fenton catalysts with electron-rich materials (Yan et al. 2017). As a potential solution to accelerate the redox cycling of Fe(III)/Fe(II), biochar can be applied as a means of redox mediators (Zhu et al. 2019). Biochar is a carbon-rich material derived from biomass pyrolysis of a variety of feedstock sources under low O_2 conditions (Chen et al. 2014; Xie et al. 2015). The biochars redox property has been applied in numerous cases whereby substantial amounts of electrons are either accepted, donated, or mediated (Chacón et al. 2017). Previous studies have shown the enhancement of biochar in the Fenton reaction. In this regard, the study of Y. Wang et al. (2019) proved that biochar could transform Fe(III) to Fe(II) in the Fenton-like oxidation catalyzed by iron minerals (Y. Wang et al. 2019). Yan et al. (2017) reported a single electron from biochar surface-bound C–OH to H_2O_2 could enhance Fenton-like oxidation of trichloroethylene by nZVI/biochar composite (Yan et al. 2017). However, most of the previous studies about the redox properties of biochar focused on the removal of pollutants in an aqueous solution. Its application as the mediator to enhance the Fenton-type systems has not been documented inside the soil, thus creating a need to fill the knowledge gap.

Another feature of biochar is the potential to influence soil fertility and the activity of the microbial community and plant growth (Beesley et al. 2011; Gorovtsov et al. 2019). This aspect of its application may serve as a tool for the restoration of the degree of changes occurring in the soil. The addition of chemical oxidants derived from Fenton-like reaction could impact other soil characteristics leading to a global loss of fertility in surface soils (Laurent et al. 2012).

Thus, it is anticipated the biochar would have the potential to reduce the implication of the Fenton-like process in compliance with the revegetation goal.

In the present study, the effectiveness of the biochar-assisted Fenton-like reaction catalyzed by hematite at circumneutral pH was assessed toward the degradation of BaP in Haplic Chernozem. The biochar was physically mixed into the soil aimed to 1) mediate the electron transfer process for the enhanced degradation of BaP and 2) minimize the adverse effects of the Fenton-like reaction to soil properties. Finally, a model experiment using spring barley (*Hordeum sativum* distichum) was carried out to assess the revegetation ability of the soil after the Fenton-like reaction. The *Hordeum sativum* distichum was selected since it regards as one of the most important food grain crops (Minkina et al. 2018) and is widely recommended as a bioindicator according to the ISO 11,269–1 standard (ISO 11, 269–1 2012).

Materials and methods

Materials

The sunflower husks were used as raw materials for biochar production. The sunflower husks were kindly provided by a local company in the Rostov region, Russia. All used chemicals were purchased from Sigma-Aldrich Company. Benzo[a]pyrene (BaP) was used in this study in solvents, including acetonitrile (99.9%, analytical grade) and deionized water. Hydrogen peroxide (H₂O₂, 30%) and hematite (α -Fe₂O₃, the particle size of fewer than 5 μ m) were used as received.

Site description and soil sampling

The sample was taken from the upper layer (0–20 cm). The soil was classified as Haplic Chernozem according to World Reference Base for Soil Resources (FAO 2016). The site is called Persianovsky Steppe Nature Reserve, located in the Rostov region (southern of the Russian Federation). After sampling, the fresh soils were transferred into a laboratory, air-dried, and filtered through a 1-mm sieve. The soil was characterized by the following physical and chemical properties: pH 7.8 ± 0.1 , organic carbon content $3.4 \pm 0.2\%$, cation exchange capacity

37.1 ± 3.1 mM(+)/100 g, CaCO₃ $0.1 \pm 0.04\%$, physical clay $53.1 \pm 2.1\%$.

Biochar preparation and characterizations

Biochar derived from sunflower husks. The raw materials were loaded into a home-mode slow pyrolyzer. The primary raw materials were slowly pyrolyzed on a heating rate of 15 °C min⁻¹ and then held at 500 °C for 45 min. Thereafter, the vessel allowed to cool down to room temperature, and the obtained biochar was unloaded.

The obtained biochar was characterized to reveal elemental contents, specific surface area, surface morphology, and surface functional groups. The element measurement of biochar was determined using a C, H, N elemental analyzer (TOC-L CPN Shimadzu, Japan). The specific surface area of biochar was measured from the low-temperature N₂ adsorption method using an ASAP 2020 analyzer. The surface area of biochar was also visualized by laser scanning confocal microscopy using a 3D scanning laser microscope (Keyence VK-9700) with a 408 nm violet laser wavelength. A field emission scanning electron microscope (SEM, Carl Zeiss EVO-40 XVP) was applied to study the surface morphology in detail. X-ray diffraction (XRD) measurement was carried out on a Bruker D2 Phaser diffractometer in the range from 20° to 90° with a step of 0.01°. The Cu anode material was used as the detector (LYNXEYE/SSD160). The XRD's sample was preliminarily crushed and applied to the measuring cuvette as a dry powder. Fourier transform infrared spectroscopy (FTIR) was measured using an FSM-1202 spectrometer in transmission mode with a DTGS detector to investigate the presence of functional groups. The spectrum was acquired in the range from 4000 to 400 cm⁻¹ with a resolution of 4 cm⁻¹ and 100 scans. Thermogravimetric analysis (TGA, NETZSCH STA 449F5) was recorded with a rate of 25 °C min⁻¹ to investigate functional groups and thermal stability, respectively.

Fenton-like procedure

The soil was artificially spiked with a BaP to form a final concentration of 100 μ g kg⁻¹. The batch series of the Fenton-like reaction was started after 24 h incubation. Specifically, 50 g of contaminated soil

was mixed with hydrogen peroxide (H₂O₂, 30%) and hematite without pH adjustment. The corresponding H₂O₂ (0–2 molarity (M)) and hematite (04 mg g⁻¹) were added slowly while the soil was mixed gently by a spatula. The soil to water ratio was kept constant at 1:0.5 for all experiments. This study was conducted on an unsaturated level (soil: water ratio = 1:0.5) to hold Haplic Chernozem at its natural water holding capacity. It should be noted that the molarity of H₂O₂ was calculated according to the final volume of 25 mL. The soil was humidified to keep the same condition within the whole spectrum of the experiment.

The same procedure was followed for biochar-assisted Fenton-like reaction. Before the Fenton-like experiment begun, biochar at two different doses of 2.5 and 5% w/w was applied to the contaminated soil. All Fenton experiments were carried out in triplicates.

After 48 h of the reaction, a 10% aqueous solution of Na₂SO₃ was added to terminate the Fenton-like reaction. The withdrawn samples were collected for further analysis. The effectiveness of the process was expressed by BaP removal efficiency by the following formula:

$$\text{BaP removal (\%)} = \frac{C_{\text{final}} - C_{\text{initial}}}{C_{\text{initial}}} \times 100 \quad (3)$$

where C_{initial} and C_{final} are the measured concentration of BaP at the beginning and the end of the reaction, respectively.

Preliminary revegetation assessment

Spring barley (*Hordeum sativum* distichum) was chosen to assess the revegetation ability of the soil after the Fenton-like reaction. The leftover soils were seeded with the test culture. Planting was performed under identical conditions of natural light for all variants of the model experiment. Irrigation was applied with distilled water based on the calculated irrigation rate of *Hordeum sativum* distichum in a given volume of soil. The incubation took place at a temperature ranged between + 20 and 22 °C within 2 months.

Analytical methods

The analytical methods employed in this study was briefly addressed in the following sentences. The physical clay, organic carbon content, and cation

exchange capacity were measured according to the method suggested by Black et al. (1965) (Black et al. 1965), Vorobyova (2006) (Vorobyova 2006), ISO 23,470 (ISO 23, 470 2011), respectively. The soil pH was measured in the soil/water suspension (1/5) (Wilke 2005). For BaP extraction from soil samples, alkaline saponification was followed based on the procedure described in our previous works (Sushkova et al. 2017; Sushkova, Deryabkina, et al. 2018a, b).

Statistical analyses

The existence of a statistically significant difference among measurements was probed using a one-way analysis of variance (ANOVA) followed by Fisher's least significant difference ($p < 0.05$). All statistical analyses were processed using OriginPro (version 9.0.0 SR2 OriginLab Corporation, USA).

Results and discussion

Biochar characterizations

The results of C, H, N, O elemental analysis and specific surface of area are provided in Table 1. The produced biochar showed 69.5, 2.8, 3.3, and 14.7% for the proportion of C, N, H, and O, respectively. These results are relatively in an analogous range with biochar derived from lychee biochar (Jun et al. 2020), date palm biomass (Elnour et al. 2019), and apple tree branches (Zhao et al. 2017). The calculation of surface area with the Brunauer–Emmett–Teller (BET) method resulted in 290 m² g⁻¹. Based on the BET, the produced biochar showed a relatively high surface area as compared to the literature (Ahmad et al. 2014).

Figure 1a presents the light-optical microscopic image of biochar. As shown, the surface of biochar after pyrolyzed became rough with many ups and downs. The surface morphology of biochar was also analyzed by SEM (Figs. 1b and 1c). The SEM images demonstrated that the biochar sample was heterogeneous on morphological composition. As shown in Fig. 1b, the particles exhibited a rough surface with cylindrical cavities extending along the surface. Figure 1c showed a body with numerous fractures, and pores ranged between 1–2 μm wide. Moreover, it was apparent that the biochar featured irregular and porous surfaces.

Table 1 The measured elemental contents and specific surface area of biochar

Content of elements (%)				Ash (%)	Specific surface area (m ² g ⁻¹)
C	N	H	O*		
69.5	2.8	3.3	14.7	9.7	290

*O content was estimated by mass difference: (100 - (C + N + H + Ash))

Figure 2a presents the XRD spectrum of biochar. The spectrum pattern suggested that some inorganic phases were formed within the C matrix of biochars. As shown, it contained the characteristic peaks at $2\theta = 24.40^\circ$ and 30.57° corresponded to the quartz and calcite phase of biochar, respectively (Kim et al. 2011; F. Li et al. 2016). These observations could be due to the carbonation of Ca oxide during the pyrolysis process (Song et al. 2019). Calcite crystalline XRD peak was also observed at 42.67° (Yang et al. 2015).

The FTIR spectrum of the biochar is shown in Fig. 2b. The infrared spectra exhibited the different functional groups, which were specified by several main peaks at 3400, 2922, 1565, and 1128 cm⁻¹. The intensity of a broad peak at 3400 cm⁻¹ was represented the stretching vibration of O–H groups (Zolfi Bavariani et al. 2019). An aliphatic C–H stretch is observed at 2922 cm⁻¹, confirming that the cellulose is not entirely carbonized during pyrolysis (Chia et al. 2012). Moreover, it could arise from the characteristic C–H stretching vibration of the alkyl structure of the aliphatic group (Elnour et al. 2019). The stretching vibrations of the aliphatic –C = C– appeared at 1565 cm⁻¹ (Elnour et al. 2019). C–O–C skeletal vibrations can be seen at 1128 cm⁻¹ (Wu et al. 2016).

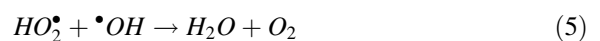
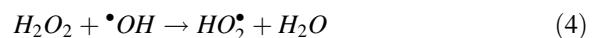
The thermal decomposition of biochar under an air atmosphere is displayed in Fig. 2c. The decay began with losing weight loss of 10% around 100 °C. This weight loss is associated with the loss of moisture (Vikash Kumar and Sivasankara Raju 2020). Then, a sharp decline (82.5%) was observed at 300–570 °C. The loss of mass after 300 °C in biochar material is attributed to decomposition and degradation of impurities, volatile matter, and also carbon into gaseous products (Shaaban et al. 2013; S. Wang et al. 2015).

Optimization of parameters for fenton-like oxidation of BaP

The evolution of the efficacy of the Fenton-like process begun with testing different variations of

hematite (0–4 mg g⁻¹). Within this step, the concentration of added H₂O₂ was kept constant at 1 M. The resulting data is shown in Fig. 3a. It was apparent that the BaP removal efficiency showed an increasing trend by adding hematite up to a dosage of 2 mg g⁻¹. At 2 mg g⁻¹ and 1 M H₂O₂, 49.2% of degradation was achieved within 48 h of reaction. It is clear that the hematite dosage of less than 2 mg g⁻¹ was not enough for the degradation of BaP. At a higher dosage than 2 mg g⁻¹, the efficiency started the decreasing trend. A similar was reported for the degradation of pyrene by iron nano-oxide (Jorfi et al. 2013). This might be due to the aggregation of hematite particles together, then reducing the active surface area for the occurrence of the reaction. By considering all aspects, the dosage of 2 mg g⁻¹ hematite was selected for further experiments.

The effect of variation of H₂O₂ was studied on the BaP removal efficiency at the optimized hematite dosage. The obtained results are given in Fig. 3b. It can be seen that BaP removal efficiency was increased constantly by the addition of H₂O₂. In the optimized condition, 65% of BaP was removed at the presence of 1.25 M H₂O₂ and 2 mg g⁻¹ hematite. At these conditions, the remaining BaP concentration at the soil reached 35 µg kg⁻¹, which is still higher than the regulatory soil standards in Russia (20 µg kg⁻¹ BaP) (Sushkova,). At a higher concentration of H₂O₂, the declining trend was observed. This could be due to the reason that an excessive amount of H₂O₂ could act as the 'OH quencher Eq. 4 (Yap et al. 2011). In this condition, HO₂· acted as the additional scavenger of 'OH, according to Eq. 5 (Muruganandham and Swaminathan 2004).



Overall, 65% of BaP was removed at the hematite dosage of 2 mg g⁻¹ and H₂O₂ concentration of 1.25 M. In this condition, the H₂O₂ to Fe molar ratio

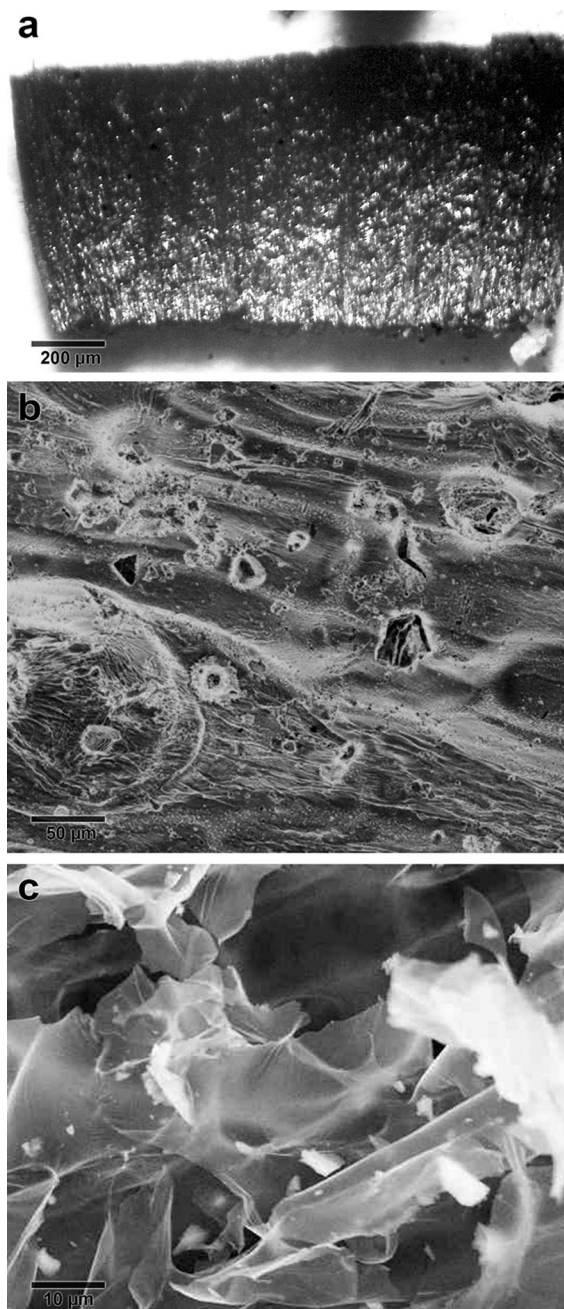


Fig. 1 Light-optical microscopic image **a** and SEM images of biochar at different bar scales **b, c**

was 22:1. Applying Fenton reagent at H_2O_2 and Fe^{2+} molar ratio of 10:1 resulted in the pyrene degradation of 65.4% in loamy sand (Sun and Yan 2008). Ferrarese

et al. (2008) reported a modified Fenton reaction with catechol as a chelating agent to remove more than 96% total PAHs at the molar ratio of 50:1 (Ferrarese et al. 2008). It is suggested the conditions in which the experiment conducted was influential on the results. For example, 85% BaP mineralization without an iron amendment was reported on the slurry mode of silt loam soil using 15 M H_2O_2 (Watts et al. 2002).

Effect of biochar on the fenton-like oxidation of BaP

Figure 4 shows the impact of biochar on the Fenton-like oxidation of BaP. As discussed in the previous section, Fenton-like reaction at the optimized conditions in the absence of biochar resulted in a 65% degradation of BaP. The addition of biochar at different doses could significantly increase degradation. In the presence of 2.5% w/w biochar, the Fenton-like reaction exhibited 75% removal efficiency. By the addition of 5% w/w, the removal efficiency reached 95%. One-way ANOVA calculated by Fisher's least significant test showed the enhancement at a $p \leq 0.001$ level of significance from the control sample without biochar (0.0) for both doses of biochars. One reason for observing the enhancement in biochar-assisted Fenton-like reaction compared to Fenton-like reaction could be due to the excellent ability of biochar for transferring electrons (Faheem et al. 2020; Qin et al. 2017). This could result in the quick reduction of Fe(III) to Fe(II) , as stated in Eqs. 1 and 2. As a result, $\text{Fe(II)/H}_2\text{O}_2$ (Eq. 2) directly produced $\cdot\text{OH}$ to attack BaP in the soil. The same enhancement effect was recently reported for heterogeneous Fenton oxidation of 4-chlorophenol from wastewater using iron-rich biochar (Gan et al. 2020). Another reason for the enhancement could be explained by the Haber–Weiss mechanism as described in Eqs. 6 and 7 (Haber and Weiss 1934; Yan et al. 2017). As expressed in these equations, biochar acted as a direct catalyst for the activation of H_2O_2 to produce $\cdot\text{OH}$ and $\text{HO}_2\cdot$. Similar direct activation of H_2O_2 by biochar was reported during the Fenton-like removal of sulfamethazine (Deng et al. 2018).

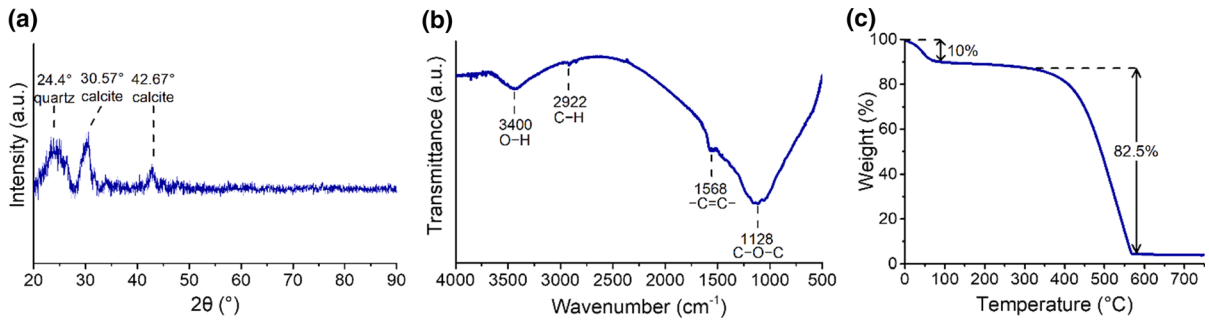


Fig. 2 XRD **a**, FTIR **b**, and TGA **c** spectra of biochar

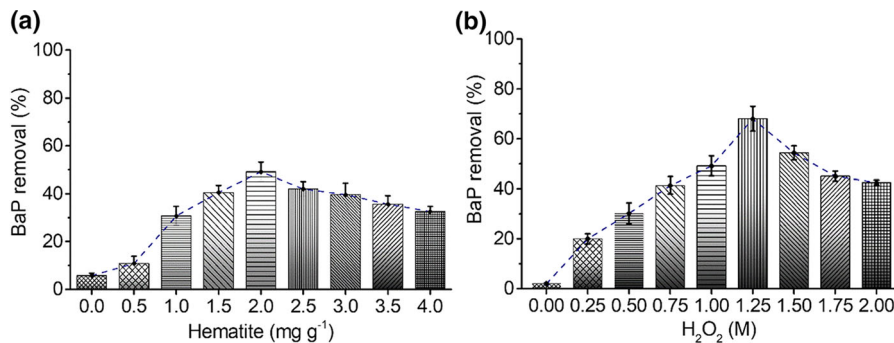


Fig. 3 BaP removal efficiency (%) as a function of hematite at fixed amount of 1 M H₂O₂ **a** and H₂O₂ concentration at fixed amount of 2 mg g⁻¹ hematite **b** [Other experimental

conditions: 50 g Haplic Chernozem; initial BaP concentration 100 µg kg⁻¹; pH 7.8 without adjustment; 48 h reaction time; and soil: water = 1:0.5]

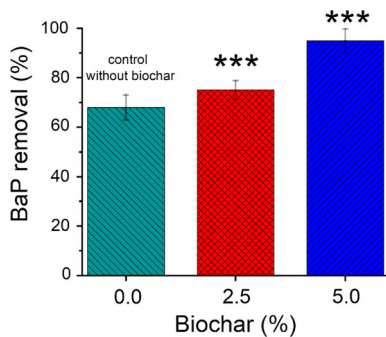
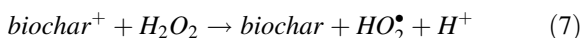
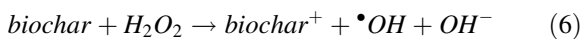


Fig. 4 Effect of biochar addition in the enhancement of BaP degradation on the optimized conditions. *, **, and *** show a significant difference from control sample without biochar (0.0) at $p \leq 0.05$, $p \leq 0.01$, and $p \leq 0.001$, respectively



The proposed mechanism for the generation of radicals during biochar-assisted Fenton-like reaction is presented in Fig. 5. As shown, the highly oxidative

species, including $\cdot\text{OH}$ and $\text{HO}_2\cdot$, were produced. These oxidizing agents could degrade BaP into mineralization products.

Effect of fenton-like reaction and biochar-assisted fenton-like reaction on the soil properties

The addition of a high amount of chemical oxidants for initiating the Fenton-like reaction might impact other

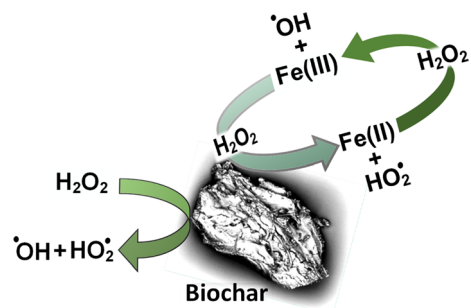


Fig. 5 Reaction pathways for the generation of radicals during biochar-assisted Fenton-like reaction

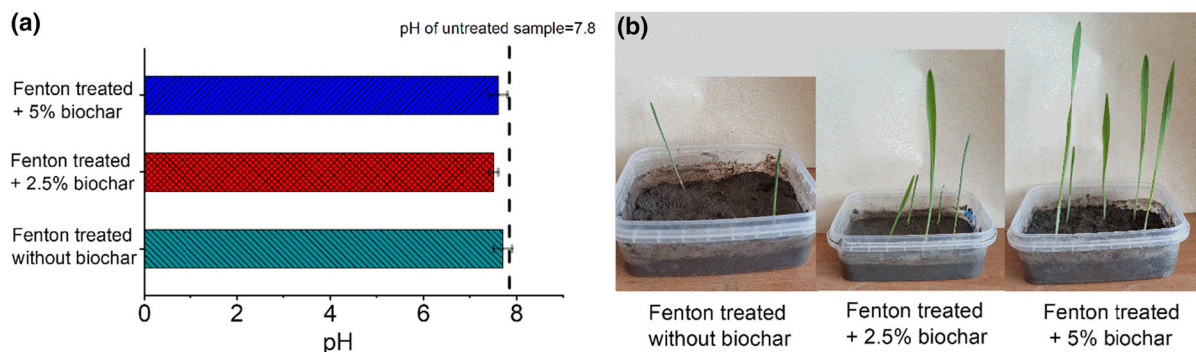


Fig. 6 Effect of Fenton-like reaction on the pH of the soil **a** and growth of spring barley (*Hordeum sativum distichum*) **b**

soil characteristics more than BaP concentration in the soil ecosystem. The leftover or excess amount of used oxidants could remain in the soils and affect the soil revegetation capacities. Hence, it is vital to evaluate the impact of the Fenton reaction on soil physical properties (Riding et al. 2013). The pH of the soil was chosen as a preliminary indicator. The results are presented in Fig. 6a. After performing the Fenton-like process, the pH of the soil was not shown any significant change from the untreated one (7.8). Moreover, the presence of biochar did not exert any change in the pH of soil after the treatment. The unchanged pH could be due to the fact that a high amount of carbonate in the soil made it difficult for any pH change. Fenton treatment driven by low and high concentrations of oxidants also demonstrated no pH change over the reaction (Laurent et al. 2012). In another study, the same trend for the pH was reported during the Fenton-like oxidation of phenanthrene (Jung et al. 2009).

Spring barley (*Hordeum sativum distichum*) growth was selected to show the Fenton-like impact on the soil revegetation. As shown in Fig. 6b, *Hordeum sativum distichum* faced difficulty with being grown in the untreated soil. Without biochar, the Fenton-like reaction destroyed BaP and other organic matters that were necessary for plant growth. This observation was in line with the previous study, where the germination of lettuce seeds was completely hindered in the soil treated by Fenton reagent (Luo et al. 2018). A similar observation was reported for lettuce seedlings in the phenanthrene-contaminated soil treated by Fenton reagent (J. Wang et al. 2019). On the other hand, the biochar addition promoted the conditions for the plant growth, as can be seen in Fig. 6b. At both biochar

treatments, the quantity of *Hordeum sativum distichum* was higher than other treatments in the absence of biochar. According to the previous studies, the beneficial changes of soil property were often observed by the biochar amendment. In this regard, the application of biochar suggested to have several advantages as follows: 1) increasing the immobilization and supplementation of nutrients in the soil (Kończak and Oleszczuk 2018; Y. Li et al. 2019), 2) improving bacterial and fungal community compositions (W. Wang et al. 2020), 3) enhancing the soil physicochemical properties including specific surface areas, bulk density, water retention, cation exchange capacities (Laird et al. 2010). According to these potential benefits of biochar as a soil amendment, biochar application might be considered a practice to mitigate the Fenton process for sustainable soil farming.

Conclusions

In this study, the biochar was applied for the modification of a Fenton-like reaction catalyzed by hematite in BaP-polluted soil. The sunflower husks were successfully pyrolyzed to biochar as confirmed by elemental analysis, SEM, XRD, FTIR. By employing the Fenton-like process in the absence of biochar, 65% BaP was degraded with hematite dosage 2 mg g^{-1} and H_2O_2 concentration 1.25 M without pH adjustment. At similar conditions, the addition of 2.5 and 5% w/w biochar led to 75 and 95% degradation, respectively. This enhancement was suggested to result from biochar to activate H_2O_2 directly and mediate electron transfer between Fe(III) to Fe(II).

The results obtained from the pH monitoring showed that there was no significant fluctuation could be observed. The biochar amendment promoted the soil revegetation ability to grow *Hordeum sativum* distichum as compared to soil treated only by Fenton-like reaction. Given these advantages, the proposed Fenton-like reaction combined with biochar could offer future practical directions to remediate PAH-contaminated soils.

Author contributions Mahmoud Mazarji: Data curation, Formal analysis, Methodology, Investigation, Conceptualization, Supervision, Visualization, Writing—original draft preparation—review and editing. Tatiana Minkina: Conceptualization, Supervision, Writing—review and editing. Svetlana Sushkova: Conceptualization, Supervision, Writing—review and editing. Saglara Mandzhieva: Data curation, Methodology, Visualization, Conceptualization, Supervision, Writing—review and editing. Aleksei Fedorenko: Formal analysis, Methodology, Writing—review and editing. Tatiana Bauer: Data curation, Methodology, Visualization, Conceptualization. Alexander Soldatov: Conceptualization, Supervision. Anatoly Barakhov: Investigation, Data curation, Formal analysis, Methodology. Tamara Dudnikova: Investigation, Data curation, Formal analysis, Writing—review and editing, Methodology.

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Data availability The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

Compliance with ethical standards

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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