



Impregnating biochar with Fe and Cu by bioleaching for fabricating catalyst to activate H₂O₂

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Abstract

Biochar is an excellent support material for heterogeneous catalyst in Fenton reaction. However, fabrication of heterogeneous catalyst supported by biochar normally adopts chemical impregnation which is costly and difficult in post-treatment. Here, impregnation by bioleaching driven by *Acidithiobacillus ferrooxidans* was developed. Bioleaching was particularly effective in loading iron to biochar. Iron loading amount was 225.5 mg/g after 10-g biochar was treated in bioleaching containing 40-g FeSO₄·7H₂O for 60 h. When copper was added into bioleaching, simultaneous impregnation with iron and copper could be achieved. Impregnation mechanism for iron was jarosite formation on biochar surface and adsorption for copper. For the high metal content, after pyrolysis, the final composites could activate hydrogen peroxide to decolorize dye effectively. With 15 mg as-synthesized Cu-Fe@biochar containing 254.3 mg/g iron and 33.4 mg/g copper, 50 mg/L reactive red 3BS or methylene blue could be decolorized completely in 20 min in a 100-mL solution by 16-mM H₂O₂ at pH 2.5. Compared with existing impregnation methods, bioleaching was facile, cheap and green, and deserved more concern.

Key points

- High amount of Fe is loaded to biochar uniformly as jarosite by bioleaching.
- Cu is adsorbed onto biochar during bioleaching.
- Synthesized Cu-Fe@biochar is an excellent photo-Fenton catalyst.

Keywords Cu-Fe bimetallic biochar · Bioleaching · *Acidithiobacillus ferrooxidans* · Impregnation · Fenton-like oxidation · Heterogeneous catalyst

Introduction

Biochar is produced in large amounts in thermochemical conversion of biomass. It is known as a carbonaceous, porous, and stable material with high surface area (Wang et al. 2020). These characters make biochar a suitable support material for the heterogeneous catalyst in Fenton or Fenton-like reactions (Kumar et al. 2020; Li et al. 2021).

Biochar as support material for metallic catalyst can favor Fenton or Fenton-like reactions in several ways. It as an electron-rich material can accelerate the reaction greatly (Amen et al. 2020; Zhu et al. 2019). At the same time, biochar can stabilize metal or metal oxide and prevent the catalyst from agglomeration. Meanwhile, biochar itself can activate the decomposition of hydrogen peroxide a little (Bokare and Choi 2014; Kumar et al. 2020; Yan et al. 2017).

Various metallic catalysts supported by biochar have been fabricated to activate hydrogen peroxide for degradation of organic pollutant. Park et al. (2018) constructed an efficient iron oxide catalyst to decompose azo dye Orange G in aqueous solution by H₂O₂ with sugarcane biochar as support material. Mian et al. (2019) produced a series of iron catalysts doped with titanium and nitrogen. Loaded on agar biochar, catalytic capacity of these composites for degradation of methylene blue were improved greatly. After amended on biochar, iron catalytic capacity was enhanced

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in the degradation of acid red 1 (Rubeena et al. 2018). Nanoscale zero-valent iron could also be loaded to biochar and improvements in catalytic capacity were achieved (Deng et al. 2018).

Many methods can be used to fabricate biochar-supported heterogeneous catalyst (Kumar et al. 2020; Zhu et al. 2019). In fact, incorporation of transition metal (mainly iron) with biochar has been studied in many applications such as adsorption, biorefinery, and land amendment for a long time (Kumar et al. 2020; Wang et al. 2020). Fabrication of iron-loaded biochar for Fenton-based reactions is completely the same as those in these applications. Metal-loaded biochar can be synthesized through impregnation-pyrolysis process (Kazemi Shariat Panahi et al. 2020; Li et al. 2018). In this process, catalyst component is pre-loaded to biomass. Then, the impregnated biomass is treated with pyrolysis to produce biochar-supported catalyst. Catalyst can also be loaded to readymade biochar directly in pre-pyrolysis process (Kazemi Shariat Panahi et al. 2020). In both methods, support material should be modified to enhance the adsorption capacity for metal ion. The modification conditions are normally harsh with corrosive chemicals (Gupta et al. 2020; Qian et al. 2019). Sometimes, organic cross-linking agent is also required (Gupta et al. 2020). The spent chemicals would definitely be pollutant at discharge without treatment. The more, to make metal loaded to biochar as much as possible, metal concentration in impregnating solution should be extremely high. Consumption of chemical reagent is also extremely high. Impregnating support material with bimetal is even more complicated. Now, chemical impregnation is normally based on tartrate precursor method (Li et al. 2017b). Multiple steps are required. It would definitely increase the difficulty in operation. Mechanical ball milling can avoid the shortcoming (Zhao et al. 2021). However, ball milling is well-known for the high energy consumption (Li

et al. 2021). At the same time, the suitable feedstock for ball milling is very limited.

All the existing synthesizing methods are based on physicochemical approaches. Disadvantages of these methods (Table 1) make them far from application. Compared to physicochemical method, biological means are normally green and saving. However, according to literature, there is no biological method focusing on constructing biochar-supported catalyst for Fenton or Fenton-like reactions till now. Bioleaching is a widely adopted biological method to extract metal from low grade ore and solid waste by bacteria from *Acidithiobacillus* genus in hydrometallurgical and environmental applications (Gu et al. 2017; Pathak et al. 2009). Bacterium oxidizes reductive iron or sulfur in ore to achieve energy for growth. Meanwhile, metal in ore is released into the water. With bacterial growth, H^+ is produced. In bioleaching, pH can normally be reduced to 1.5–2.0 (Tao and Dongwei 2014). The acidic circumstance is also helpful for the metal extraction.

On the other hand, it is also found that a large amount of various insoluble metal compound (mainly iron compound and metal sulfide) precipitates are formed during bioleaching. The precipitates could cover the ore surface and hinder the dissolution of metal from solid into aqueous phase. This process is called passivation in hydrometallurgy (Tao and Dongwei 2014). Formation of the insoluble metal compound could be quickened greatly by activation of *Acidithiobacillus* bacterium. The more, *Acidithiobacillus* bacterium can produce extracellular polymer substance (EPS) which may introduce the attachment growth of bacterial cell onto a solid surface (Tao and Dongwei 2014). The EPS layer attached to the solid surface can greatly enhance metal accumulation on the solid surface (Yu et al. 2011, 2008). The whole process is definitely a negative factor for metal extraction (Tao and Dongwei 2014). However, conversely, metal concentrated

Table 1 Fabrication of metallic biochar

Synthesis method	Precursors	Products	Disadvantages	Reference
Chemical impregnation-pyrolysis	Cornstalk biochar	Nanoscale zero-valent iron/biochar composite	Toxic chemical reagents and wastewater	Deng et al. (2018)
	Sugarcane residues	Fe-impregnated biochar	Low iron utilization; limited feedstock	Park et al. (2018)
	Resin	Bimetallic nanoparticles embedded mesoporous carbon	Alkaline treatment and wastewater	Wang et al. (2015)
Pyrolysis-chemical impregnation	Rice straws biochar	Nanoscale zero-valent iron	Harsh and complicated operation	Qian et al. (2019)
Gel-pyrolysis	Commercial biochar	Fe_3O_4 /biochar	Bio-toxic byproduct	Li et al. (2021)
	Agar	Metal/biochar	Expensive operation	Mian et al. (2019)
	Sodium gluconate	Cu/Fe_3O_4 @carboxylate-rich carbon	High reagent purity	Le et al. (2020)
	Tartrate	$Fe_3O_4/C/Cu$ composite	High reagent purity	Li et al. (2017b)
Ball milling	Cellulose	$Cu-Fe@C$	High energy consumption	Zhao et al. (2021)

to the solid surface from water solution might be realized in bioleaching. The more, insoluble metal compound precipitates in bioleaching are found to be able to adsorb metal ion (Eftekhari et al. 2020). Potentially, impregnating biochar with one or more metals by bioleaching is feasible. Copper is frequently doped into an iron heterogeneous catalyst for Fenton and Fenton-like reaction because of its ability for catalysis and utilization of visible light (Bokare and Choi 2014; Le et al. 2020; Zhao et al. 2021). At the same time, extraction of iron and copper is also a top focus of research on bioleaching (Gu et al. 2017; Wang et al. 2014; Yu et al. 2013). *Acidithiobacillus* bacterium has high tolerance level for copper. In this experiment, impregnating biochar with iron and copper by bioleaching was investigated. Then, biochar was further treated with pyrolysis. The feasibility of the final composite as a heterogeneous catalyst in visible-light-driven Fenton reaction was examined in detail.

Material and methods

Material

Biochar (0.15 < diameter < 1 mm by sieve) was the by-product of gasification of straw from local agriculture at 1000–1100 °C in a 20-m³ cyclone furnace in Biomass Energy Factory, Tongshan County, Hubei Province, China. Biomass gasification treatment amount was 5 kg at a time for 30-min residence time. Before experiment, biochar was washed with deionized water till no suspended substance and dried at 60 °C in an oven overnight. Except sieving, no more operation was carried out on pristine biochar.

Acidithiobacillus ferrooxidans (ATCC 23,270) was kept in the Environmental Science Research Laboratory, Environmental Engineering School, Wuhan Textile University. A 9 K broth composed of 3-g/L (NH₄)₂SO₄, 0.1-g/L KCl, 0.5-g/L K₂HPO₄, 0.5-g/L MgSO₄·7H₂O, 0.01-g/L Ca(NO₃)₂, 40.0-g/L FeSO₄·7H₂O. PH was adjusted to 4.0 by H₂SO₄.

Reactive red 3BS (RR, C.I. Reactive Red 195, which is an azo dye), methylene blue (MB, C.I. 52,015, which is an anthraquinone dye) and malachite green (MG, C.I. 42,000, which is a triphenylmethane dye) were purchased from Sinopharm Chemical Reagent Co., Ltd., China.

Except biochar, all the chemicals were of analytical grade and used without further purification.

Bioleaching of biochar

A. ferrooxidans was incubated in a 100-mL 9 K broth in a 250-mL flask at 120 rpm, 30 °C at the first. After pH was lower than 2.0 for 12 h (no more than 48 h), *A. ferrooxidans* bacterial broth was used as inoculum for bioleaching of biochar.

Bioleaching of biochar was carried out in a 2.5-L flask containing 1 L of deionized water, 40 g of FeSO₄·7H₂O, 0.5 g/L (NH₄)₂SO₄, and K₂HPO₄ at 30 °C, 120 rpm in a shaker. Solution pH was pre-adjusted to around 2.5 by diluted H₂SO₄. Inoculum was 10 mL. After inoculation for 12 h, CuSO₄·5H₂O powder (the purchased form as chemical reagent) was added into the solution directly. Five concentrations of CuSO₄·5H₂O were investigated: 18.0, 9.0, 7.2, 4.5, and 3.6 g/L. Thus, there were five mole ratios of initial iron to copper in this experiment: 2, 4, 5, 8, and 10. Corresponding treatments and biochar composites were numbered #1–5. At the same time, #0 denoted the investigation with iron barely. After CuSO₄ was dissolved completely, 10 g of biochar was added into the solution. Bioleaching with biochar was carried out for 60 h. Then, floating ash was removed (by dumping). Biochar was separated with filter paper, washed with 1-L deionized water (suction filtration) and dried at 60 °C overnight.

Pyrolysis of biochar

Biochar from bioleaching was pyrolyzed at 1000 °C in corundum tube (2 m in length and 5 cm in diameter) for 10 min (residence time) with biochar loading being 5 g, heating rate being 5 °C/min in carbon dioxide and gas flow being 30 mL/min. Cooled down, the biochar was washed with 1-L deionized water (120 rpm, ambient temperature and 5 min in a shaker) and dried at 60 °C overnight.

Biochar samples after bioleaching and pyrolysis were abbreviated to BBC and PBC, respectively. Pristine biochar was BC. PBC was the Cu-Fe@biochar composite synthesized in this experiment.

Characterization of metal amended biochar composite

Surface functionality of the biochar was analyzed by Fourier transform infrared spectroscopy (FTIR). X-ray photoelectron spectroscopy (XPS) condition was Al K α source, 1486.6 eV passing energy. X-ray diffraction (XRD) was operated at 40 kV and 40 mA. Diffractograms were obtained from 10 to 80° 2 θ using Cu K α radiation at a scan rate of 40 s per 0.05° 2 θ step. The biochar diffractograms were compared to Joint Committee on Powder Diffraction Standards files (pdf file). Surface morphology was observed by scanning electron microscopy (SEM). Surface area was investigated by Brunauer, Emmett, and Teller (BET) method. The electron spin resonance (ESR) analysis was conducted using an A300–10/12 electron paramagnetic resonance spectrometer (Bruker AXS Company, Germany). Biochar was digested with a HCl:HNO₃:HClO₄

(3:1:1) mixture (85 °C). Iron was detected at 510 nm with 721-spectrophotometer by 1,10-phenanthroline monohydrate method. Fe^{3+} was achieved by the difference between Fe^{2+} and total iron. Copper content was investigated by inductively coupled plasma mass spectrometry (ICP).

Degradation of dye

Preliminary decolorization of dye was carried out in aqueous solution at ambient temperature and 120 rpm. In pre-experiment, 50-mg biochar samples were added into a 100-mL dye solution (2000 mg/L). Initial pH was adjusted with 0.1-M HCl to 2.5. The mixture was stirred in the dark for 80 min. Adsorption of biochar for dye was detected. Then, 1 mL of H_2O_2 (30 wt%) (H_2O_2 concentration = 32 mM) was added, and visible light was turned on to stimulate the reaction. The source of visible light was a 14 W domestic fluorescent lamp using a filter to remove ultraviolet light with a wavelength of less than 420 nm. Distance from lamp to solution was 15 ~ 20 cm.

Degradation investigation was carried out with 15 mg PBC#1 and 50 mg/L MB in 100-mL deionized water at 27 °C and 60 rpm. After stirred in the dark for 30 min, 0.5-mL H_2O_2 (30 wt%) was added. Other conditions were the same as those in decolorization investigation. After the reaction, a biochar sample was isolated with magnet and dried at 60 °C overnight for reuse. Initial pH was adjusted with 0.1-M HCl or 0.1-M NaOH to a desired value.

The concentration of dyes was analyzed by a 721-spectrophotometer. The photocatalytic degradation efficiency was determined by calculating the concentration (C / C_0) according to the absorbance (A / A_0) at 540, 664, and 618 nm for RR, MB, and MG respectively, where C_0 and A_0 were the initial concentration and absorbance of dye, respectively; C and A were the concentration and absorbance of dye at time t , respectively. Kinetics investigation was evaluated by first order kinetics: $\ln(C / C_0) = -k_1 t$ and second order kinetics: $1 / C = k_2 t + 1 / C_0$ equations, where k_1 (1/min) and k_2 (L/mg·min) were the constant and t (min) was the reaction time. Total organic carbon (TOC) was also measured to evaluate the mineralization efficiency of MB on a multi N/C 3100 TOC analyzer (Analytic Jena, Germany) using high temperature combustion method. All the investigations were carried out in five repetitions.

Results

Iron in BC was 0.3 mg/g. No detectable copper was found in BC. Also, BC possessed low adsorption capacity for iron and copper. After adsorption in 40-g/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or 18-g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution for 2 h, adsorbed iron and

copper on 10 g/L BC were around 57 mg/g and 4 mg/g at pH 7.0 and 32 mg/g and < 1 mg/g at pH 3.0, respectively. Thus, initial and adsorbed metal was negligible and not taken into account in the following process.

Bioleaching

Bioleaching was efficient in impregnating biochar with iron. According to investigation on bioleaching#0, iron was loaded to the biochar from the beginning of bioleaching (Fig. 1a). The fast loading lasted till 60 h. At this point, the iron loading amount to biochar was 225.5 mg/g (Table 2). Then, variation in the amount was little. After bioleaching for another more 22 h, the amount increased slightly to 227.1 mg/g. To ensure active growth of bacterium, iron concentration in bioleaching was set to be 40-g/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and its influence on impregnation was not investigated.

Copper addition apparently posed impact on iron impregnation. With more copper, iron loading amount decreased more (Table 2). Copper loading also increased with bioleaching time. It could be found in Fig. 1a that copper loading is synchronously with that of iron in bioleaching#1. Metal loading to biochar with copper was a little different from that in bioleaching without copper. The more, after 60 h, there was a little decline in iron loading amount in bioleaching#1. Although copper loading to biochar kept to increase slowly from 60 to 76 h, it decreased to 29.2 mg/g at 82 h finally. Thus, BBC treated in bioleaching for 60 h (Table 2) was used for the following investigation.

According to XRD investigation, the main iron compound on BBC was jarosite (Fig. 2). Patterns of BBC#0 and 1 were the same as each other and fitted to pdf file#71-177 ($\text{KFe}_3[\text{SO}_4]_2(\text{OH})_6$) completely. No copper crystalloid was found on BBC#1. It meant that copper did not involve in crystallization and was mainly adsorbed onto BBC.

Compared with existing impregnating methods, both iron loading amount and iron utilization were definitely much higher. More important, no harsh operation, toxic or refractory organic reagent was adopted. It made the approach ecofriendly. Although copper addition produced negative influence, iron loading was still efficient. Bimetallic biochar could also be produced in this way.

Pyrolysis

To immobilize/fix metal on biochar, pyrolysis was carried out on BBC. After pyrolysis, transformation happened on metal (Fig. 2). On PBC#0, strong characteristic peaks at 44.66° and peak at 65.2° (PDF#87-0721, 0722) denoted the high crystallinity of Fe^0 . Besides iron, peaks at 43.3°, 50.5°, and 74.2° which respectively corresponded to the crystal surface of Cu(111), (200), and (220) (PDF#85-1326) appeared

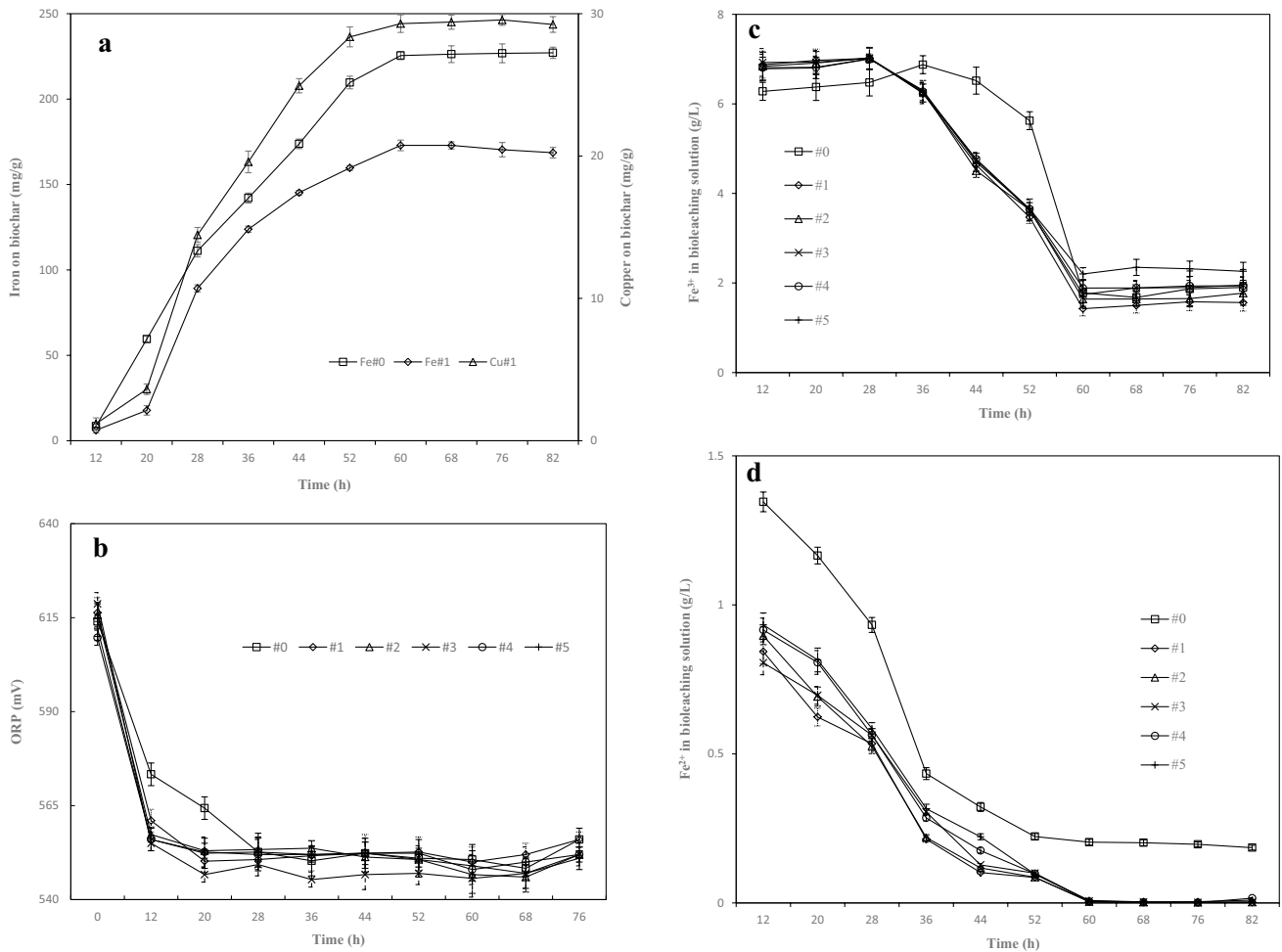


Fig. 1 Bioleaching process with time after biochar addition. **a:** Metal loaded to biochar with bioleaching time; **b:** ORP with bioleaching time; **c:** Fe³⁺ variation during bioleaching; **d:** Fe²⁺ variation during bioleaching

Table 2 Biochar composite character

		#0	#1	#2	#3	#4	#5
BBC	Mass increment after bioleaching (%)	21.8 ± 1.4	31.1 ± 1.3	28.1 ± 2.4	27.9 ± 2.7	24.1 ± 3.6	25.0 ± 5.6
	Iron content (mg/g)	225.5 ± 2.4	172.9 ± 3.1	187.2 ± 2.5	192.1 ± 4.6	199.08 ± 5.6	200.5 ± 6.3
	Iron utilization efficiency (%)	34.1	28.1	29.7	30.5	30.7	31.1
	Copper content (mg/g)	-	29.3 ± 0.6	21.1 ± 0.7	14.2 ± 0.7	10.5 ± 0.9	8.5 ± 0.4
	Copper utilization efficiency (%)	-	8.4	11.8	9.9	11.3	11.5
PBC	Mass loss after pyrolysis (%)	29.6 ± 1.4	32.2 ± 1.3	32.3 ± 1.1	31.2 ± 1.2	29.4 ± 1.3	30.1 ± 1.1
	Iron content (mg/g)	332.6 ± 3.4	254.3 ± 3.6	278.6 ± 0.6	288.6 ± 0.1	288.3 ± 0.3	303.3 ± 1.3
	Copper content (mg/g)	-	33.4 ± 0.5	28.9 ± 0.3	20.9 ± 0.7	14.9 ± 0.6	12.4 ± 0.3
	BET surface (m ² /g)	321	326	329	321	331	324
	Adsorption for RR (%)	0.57 ± 0.07	0.52 ± 0.11	0.28 ± 0.03	0.35 ± 0.09	0.45 ± 0.04	0.23 ± 0.01
	Adsorption for MB (%)	0.78 ± 0.09	0.36 ± 0.01	0.42 ± 0.06	0.37 ± 0.04	0.40 ± 0.05	0.36 ± 0.04
	Adsorption for MG (%)	1.31 ± 0.03	0.60 ± 0.02	0.67 ± 0.08	0.68 ± 0.02	0.64 ± 0.02	0.66 ± 0.02

on the pattern of PBC#1. Clearly, metal was reduced after pyrolysis. It could be easily calculated from Table 2 that some biochar loss occurred besides the decomposition of jarosite. Definitely, metal was reduced by the decomposition of biochar.

Decolorization and degradation of dye

Metal-loaded biochar could be used in various applications (Kazemi Shariat Panahi et al. 2020). Because advanced oxidation processes could completely remove organic pollutant (Zhu et al. 2019), PBC was investigated as a heterogeneous catalyst for Fenton-like reactions dealing with dyes.

In preliminary decolorization investigation, considering the inner wastewater in the dyeing industry normally contain extremely high dye (Yaseen and Scholz 2019), concentration of dye in preliminary decolorization investigation was set to be 2000 mg/L. Mere H_2O_2 exhibited low decolorization capacity and achieved only around 5.5% decolorization after an hour for RR. With PBC, decolorization was enhanced greatly. When PBC#0 was used as a catalyst, more than 72% decolorization could be achieved for RR and MB (Fig. 3a and b). Doped with copper, much better performance could be achieved. The best performance was achieved by PBC#1 that RR and MB could be decolorized completely in 20 min. With PBC#2, complete decolorization could be achieved in 30 min. The time for PBC#3 and 4 was 50 min. However, the maximum decolorization value (when increase was lower than 0.1% in following treatment time) for PBC#5 was $84.3 \pm 1.4\%$ after reaction for an hour. Performance increased with the copper content on PBC. Apparently, copper produced synergistic effect with iron in not only decolorization but also decolorization rate.

Although PBC adsorption for MG was the best (Table 2), decolorization after an hour was lower than 13%. However, when concentration of MG was lowered, excellent performance could also be achieved (Fig. 3c). MG solution with concentrations being 500 and 750 mg/L could be decolorized completely in 20 min by PBC#1. At the same time, 500 mg/L MG could be decolorized completely by PBC#0 in 30 min. Definitely, because MG had high chroma, its concentration would influence decomposition of hydrogen peroxide heavily.

Degradation investigation was performed with MB and PBC#1. At pH 8.5 and 10.0, the maximum decolorization values were only 14.7 and 8.9%, respectively. The decolorization could not be described by kinetics equations. PBC worked effectively at acidic and neutral conditions, and the decolorization could be described by first order kinetics equation (Fig. 4a; Table S1). Values of k_1 met with the reaction rate quite well. Activation of hydrogen peroxide by PBC was fast. Mineralization of MB was evaluated by TOC removal efficiency (Fig. 4b). As decolorization, mineralization at pH 2.5 was the best. It could be $83.7 \pm 1.1\%$ at

40 min. At pH 5.5, TOC removal efficiency was highest at 60 min to be $74.3 \pm 1.3\%$. At pH 7.0, highest TOC removal was achieved at 100 min to be $52.0 \pm 7.7\%$.

Although PBC had no magnetism, high content of Fe^0 made it to and could be collected by magnet easily after reaction. Then, PBC was reused. Reused for four times, there was no marked decrease in the decolorization capacity. From sixth reaction (Fig. 4c), time required to achieve the complete decolorization should be prolonged. In the tenth reaction, decolorization decreased to 98.7% after 40 min.

As a conclusion, bioleaching was particularly effective in loading iron to biochar. Iron loading amount at a frequently adopted $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration for bioleaching was far higher than those achieved in former researches. Doped with copper, bioleaching was completely qualified to be an effective impregnating method for fabricating biochar-supported heterogeneous catalyst for Fenton reaction.

Discussion

Pristine biochar

To prepare metal-loaded biochar successfully, the ready-made biochar should possess high metal affinity. Therefore, similar researches were normally based on commercial biochar (Li et al. 2021). Biochar from real production was normally low in affinity or adsorption capacity (Kazemi Shariat Panahi et al. 2020; Li et al. 2021). Although many thermochemical techniques have been performed on biomass, fast pyrolysis and gasification were the most widely applied in practical production because these techniques could be easily performed and produce syngas in a large scale (Perera et al. 2021). Biochar as the byproduct was also produced simultaneously. However, the high temperature would normally weaken the adsorption capacity of biochar. It made the impregnation difficult. The more, for energy crisis, more and more biomass was used as energy resource. With different biomass feedstock, biochar characteristic would vary greatly (Tursi 2019). Different thermochemical techniques would also subsequently produce biochar with different characters (Perera et al. 2021). A feasible impregnation method which could load metal to biochar efficiently regardless of the character of biochar was definitely valuable in application.

Biochar produced from energy utilization normally possessed rare chemical group for the high pyrolysis temperature (Li et al. 2017a). Initial BC was low in both category and amount of chemical groups (Fig. 5). Chemical groups on BC was $-\text{OH}$ at 3426 cm^{-1} , aromatic $\text{C}=\text{O}$ group at around 1616 cm^{-1} , and $\text{C}=\text{C}$ group at around 1437 cm^{-1} and a weak peak at around 872 cm^{-1} . The weak stretching vibration indicated that chemical groups, especially the oxygen-containing ones, on BC were low. At the same time, BC was

covered by a thick layer of tar-like material (Fig. 6) which would produce heavily negative effect on the performance of biochar (Lam et al. 2019). As a consequence, although BC had 198 m²/g BET specific surface area, it was low in adsorption capacity for iron and copper. To enhance metal loading, modification was necessary in chemical impregnation. Modification was normally carried out under harsh conditions with strong acid, alkali or oxidant (Kazemi Shariat Panahi et al. 2020; Li et al. 2021). It would heavily increase the cost and make post-treatment difficult. The more, huge amount of reagent and operation would be consumed in chemical impregnation.

Bioleaching process

Bioleaching was efficient in impregnating biochar with iron. Thus, its process was followed. In bioleaching, metal precipitate, especially iron compound, formation on the surface of

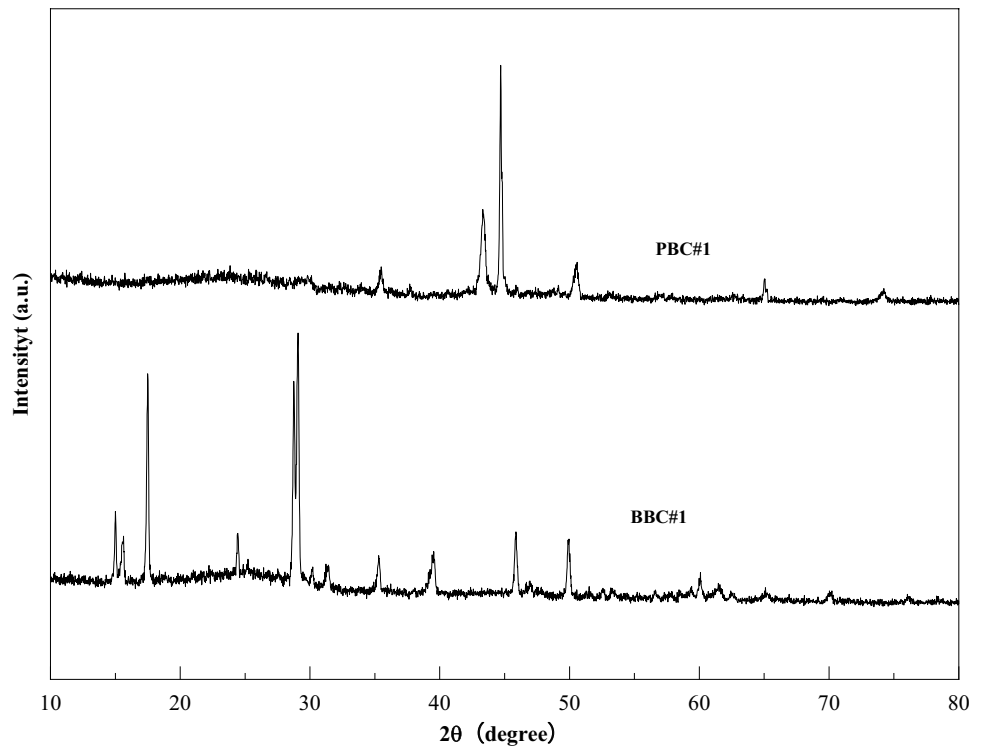
ore would impact metal leaching efficiency (Tao and Dongwei 2014). It was the basis of this research. Normally, component of precipitation was substantially influenced by pH (Eftekhari et al. 2020). In this experiment, to lower Fe(OH)₃ formation (Eftekhari et al. 2020; Yu et al. 2011) and shorten the bioleaching process (Pathak et al. 2009), the initial pH of the bioleaching of biochar was acidified to 2.5. Influence by pH was thereby eliminated. After inoculation for 12 h, pH could drop to a final value. Final pH value varied according to different feedstocks (Pathak et al. 2009; Tao and Dongwei 2014). In this experiment, the final pH value varied a little in the range from 1.83 to 1.97. When pH was lower than 2.0, bioleaching was thought to reach the final value and copper, and biochar was added into a bioleaching solution. In the following bioleaching process, pH varied little and was not presented in detail.

Oxidation reduction potential (ORP) was an important parameter indicating the activity of bacterium and would

Table 3 Abbreviations and nomenclatures

Abbreviation		Nomenclature	
BBC	Biochar samples after bioleaching	BET	Brunauer, Emmett, and Teller method
BC	Pristine biochar	ESR	Electron spin resonance
EPS	Extracellular polymer substance	FTIR	Fourier transform infrared spectroscopy
MB	Methylene blue	SEM	Scanning electron microscopy
MG	Malachite green	TOC	Total organic carbon
PBC	Synthesized Cu-Fe@biochar	XPS	X-ray photoelectron spectroscopy
RR	Reactive Red 3BS	XRD	X-ray diffraction

Fig. 2 XRD pattern. On PBC#1, characteristic peaks for both Fe⁰ (on PBC#0) and Cu⁰ could be observed



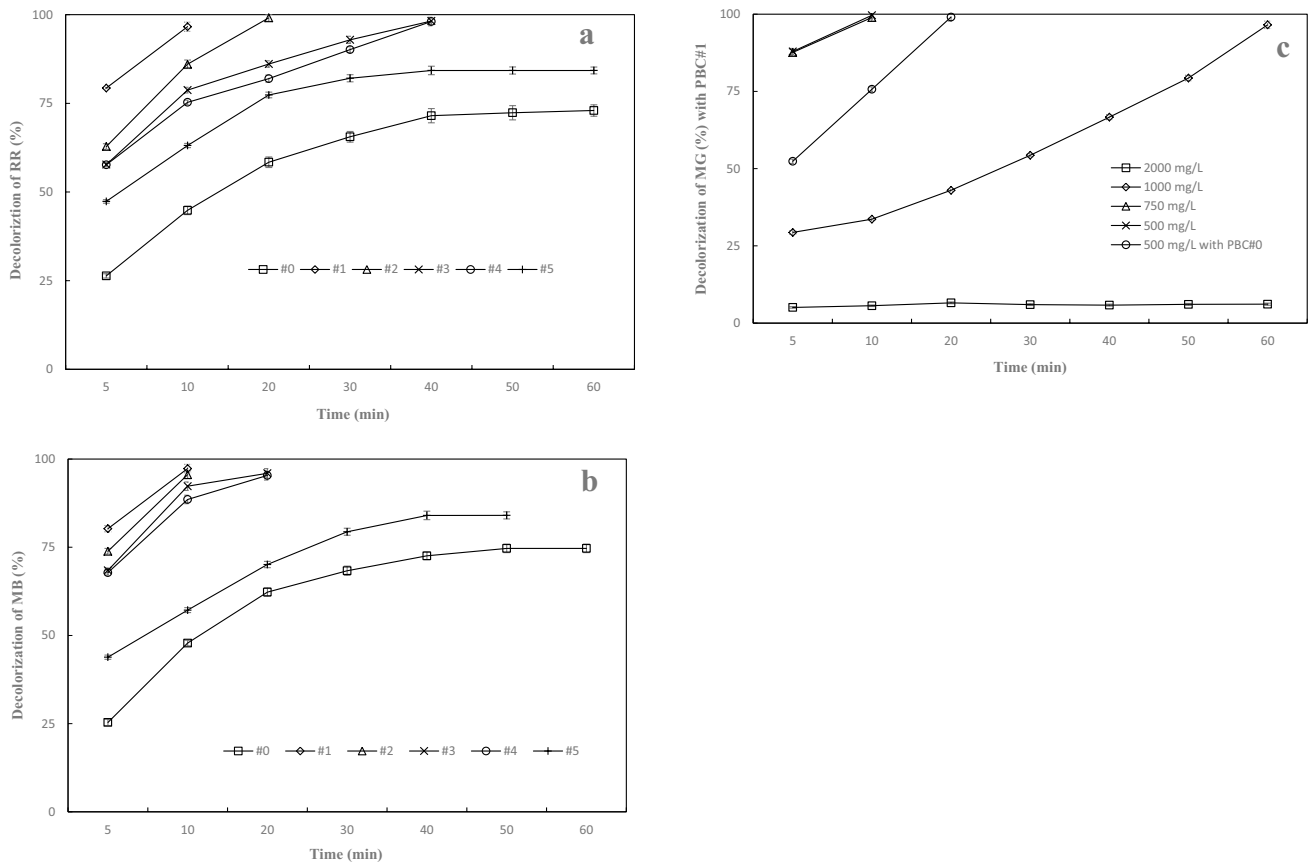


Fig. 3 Decolorization of dyes. **a:** Decolorization of RR; **b:** Decolorization of MB; **c:** Decolorization of MG

greatly influence accumulation of metal on a solid surface (Yu et al. 2011, 2008). *A. ferrooxidans* oxidized ferrous ion to ferric ion, consequently led to an increase in ORP (Pathak et al. 2009). Initial ORP of the bioleaching solution was 64 mV. After inoculation for 12 h, it increased to around 620 mV. With copper and biochar addition, ORP varied a little. Then, ORP began to decrease. The decrease in bioleaching with copper was much faster than that in bioleaching#0 (Fig. 1b). After 20 h, ORP in bioleaching with copper varied little. The time for bioleaching#0 was 28 h. Considering copper valence state, definitely, copper posed influence on bacterial activity.

ORP was mainly determined by the concentration of oxidation ion to that of a reductive one. In bioleaching, valence state of iron was definitely the key factor. On ore or sewage sludge (Pathak et al. 2009; Yu et al. 2008), ORP would always increase for the continuous leaching and oxidation of metal. Because iron and copper precipitate generated with bioleaching time (Wang and Zhou 2012; Yu et al. 2011, 2008), metal accumulated on the solid surface also increased with time. However, because there was no endogenous metal supply in this experiment, ORP decreased from the beginning. At the same time, it could

be found that variation in iron ion was inconsistent with ORP (Fig. 1c). The fast decrease in ferric ion in bioleaching with copper happened after 28 h. In bioleaching#0, variation in ferric ion was also later than ORP. Ferrous ion also decreased fast after biochar addition (Fig. 1d). With copper, residual ferrous ion would decrease more. Apparently, parameters in bioleaching with biochar were different from that on ore (Yu et al. 2013, 2011, 2008). Relationship between ORP and aquatic ferric ion was also not close here. At the same time, variation in ORP was also different from the accumulation on metal on biochar. The accumulation kept to increase till 60 h which was not consistent with ORP. The more, accumulation of metal on biochar reached the maximum value in 60 h which was much shorter than that on ore (Yu et al. 2013). All these differences should be caused by the different iron sources.

Another important factor influencing the accumulation of metal on solid surface was EPS. During attachment growth of bacterial cell, it could produce EPS which would cover the solid surface (Tao and Dongwei 2014). EPS could not only favor the growth of bacterium and subsequently accelerate formation of ferric precipitation, but also accumulate some metal in itself (Zeng et al. 2010). In Fig. 6, it could be clearly

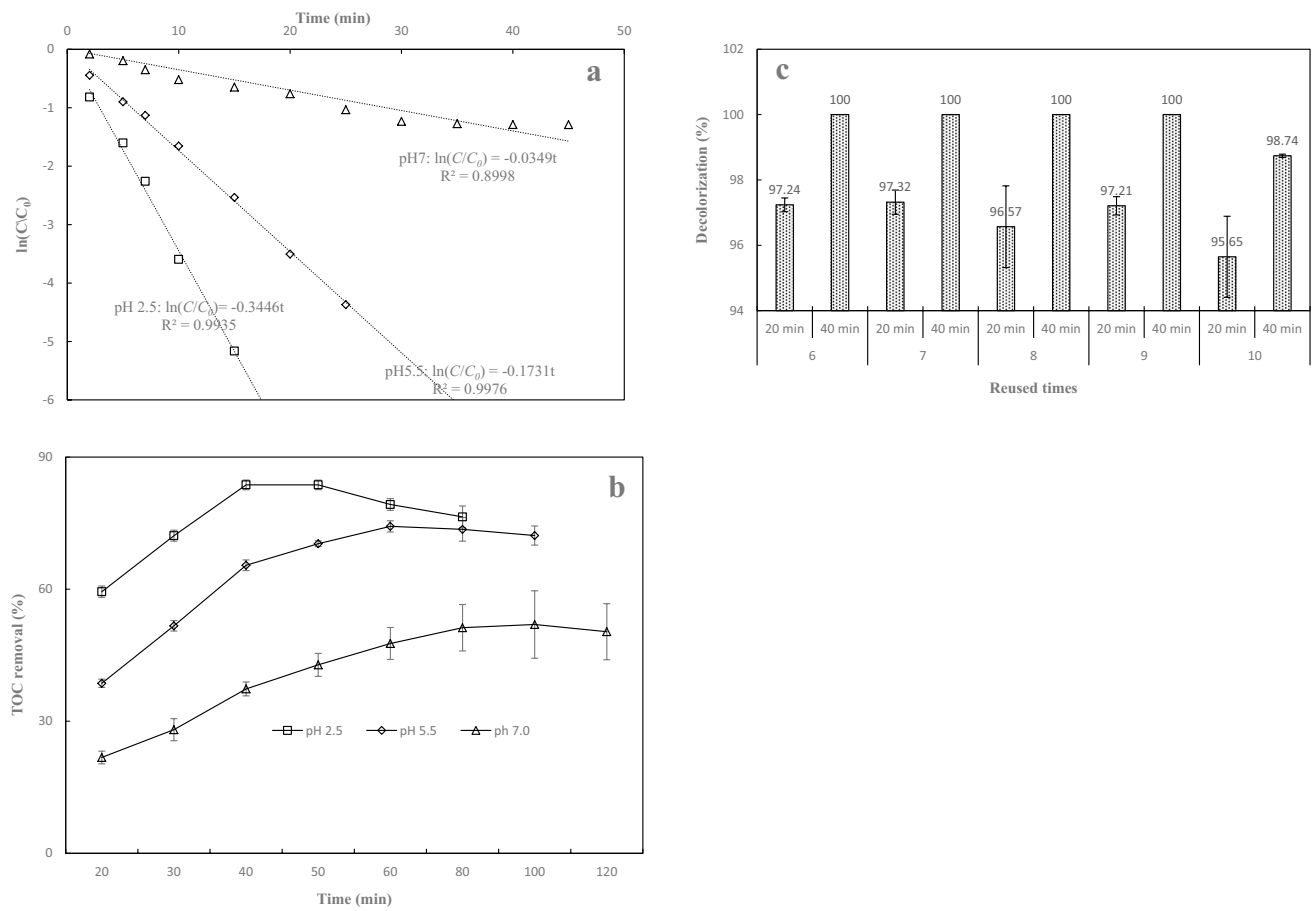


Fig. 4 Degradation of methylene blue. **a**: Kinetics investigation; **b**: TOC removal; **c**: Reusing PBC#1

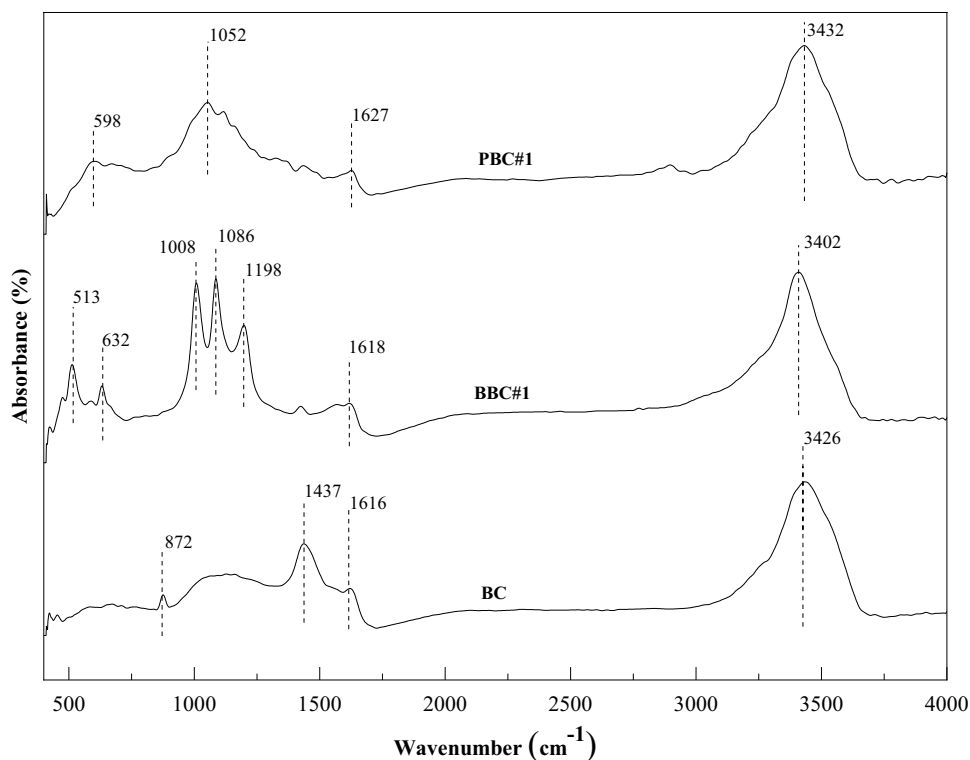
observed that BBC#1 is covered by a layer of mixture of EPS and iron precipitate. EPS would definitely be helpful in stabilizing iron precipitate on biochar. After bioleaching, abundant chemical groups could be observed on BBC (Yu et al. 2013; Zhang et al. 2020) which could be another evidence for EPS (Fig. 5). Another benefit from EPS was also evident. It made jarosite on BBC distribute uniformly. However, compared with a former research (Wang et al. 2013), adsorbed copper was lower owing to the more complicated conditions.

Jarosite was an insoluble ferric oxyhydroxy sulfate produced mainly at low pH (Anderson et al. 2017). Co-precipitation with jarosite could lead to the accumulation of copper on the solid surface. However, it was not supported by the investigation. Copper accumulation on biochar should be caused by the adsorption by jarosite (Anderson et al. 2017; Eftekhari et al. 2020) for the loaded copper increased with the increase in loaded iron (Fig. 1a). Copper loading to BBC might also be partly attributed to adsorption to EPS (Wang et al. 2013). Copper accumulation on biochar increased with initial copper (Table 2). Considering copper tolerance, initial copper did not increase more. Compared with metal removal from acidic solution by jarosite (Anderson et al. 2017),

copper utilization here was lower. More research should be carried out on bioleaching in the future. The amount of iron loaded to biochar decreased with the increase in copper (Table 2). Iron precipitation on the solid surface was reported to be determined by several factors (Eftekhari et al. 2020; Tao and Dongwei 2014). Because other conditions were similar, copper was definitely the main factor influencing the accumulation of iron on biochar.

As a conclusion, jarosite formation on biochar surface was the main mechanism for iron loading to biochar. EPS might participate in the process of jarosite formation and copper loading. ORP could not be the indicator for amount of metal accumulation on solid surface anymore. However, it could be found in Fig. 1 that the amount of metal loaded to biochar reaches the maximum value when ferric ion in solution drops to the lowest value. It might be useful in application. With easy operation, a large amount of iron was loaded to biochar in bioleaching. However, it could be noticed that copper produced a negative effect on the loading of iron. In application, bacterium could still be active under high copper concentration. It meant that improvement might be achieved with more research.

Fig. 5 FTIR investigation. EPS produced great amount of C–O groups on BBC (from 1000 to 1500 cm^{-1}). Peaks at 513 and 632 cm^{-1} could be assigned to Fe–O group. There were chemical groups on PBC#1 including C–O at 1052 cm^{-1} and –OH at 3432 cm^{-1} aromatic C=O at 1627 cm^{-1} . As BC, PBC was poor in oxygen-containing chemical groups



The more, as a well-built microbiological process, bioleaching produced a little error in procedure (Fig. 1) and impregnation efficiency (Table 2). In this experiment, feedstock was uniform. At the same time, pre-acidification and fast decrease in pH could inhibit growth of competitor. Thus, main influencing factors (Pathak et al. 2009) were eliminated. It illustrated that bioleaching would be a robust and reliable impregnation method in application.

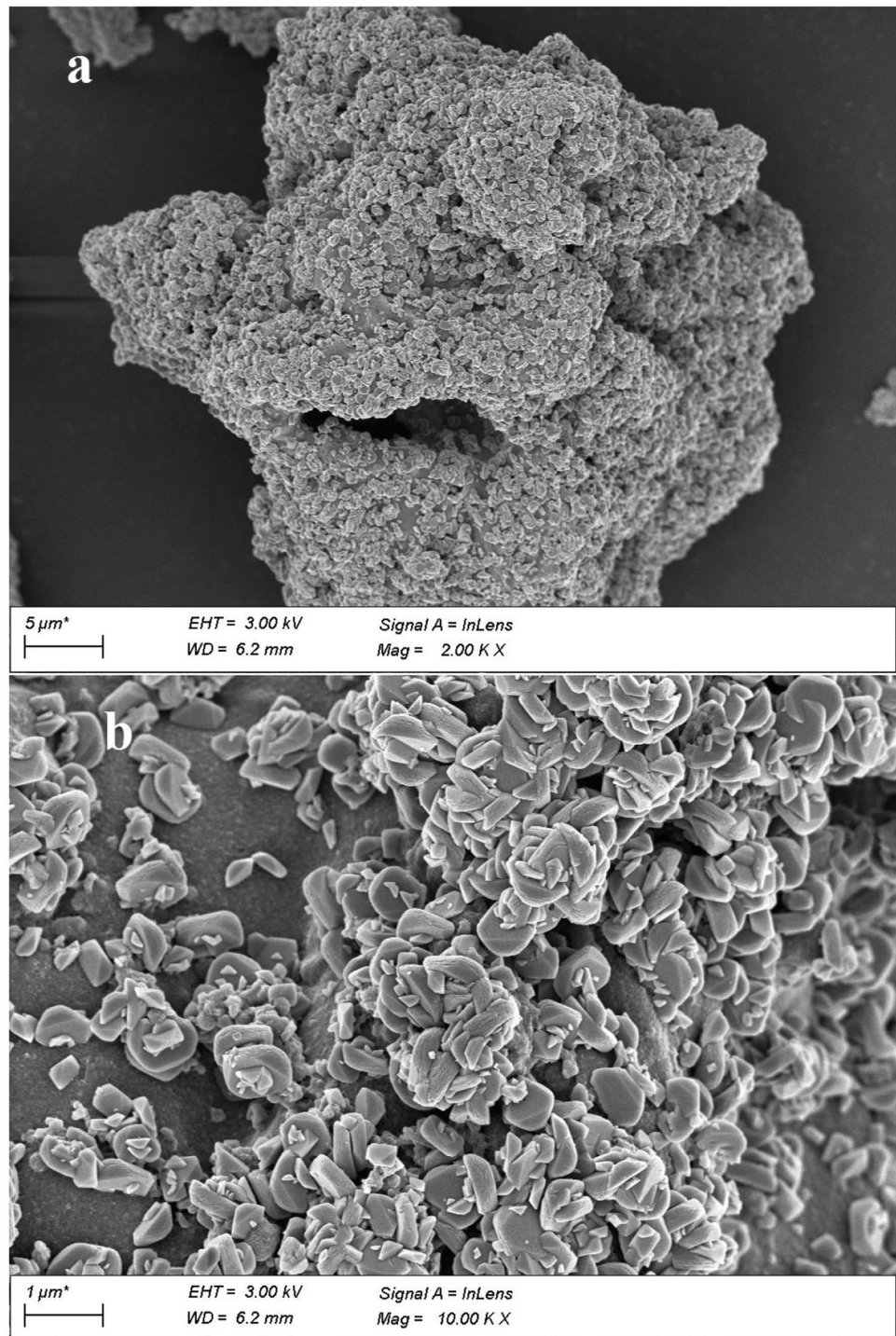
Cu-Fe@biochar character and degradation of dye

PBC composites exhibited excellent performance to degradation of dye. PBC#1 had the best decolorization performance in this experiment. Thus, its character was investigated. PBC was a biochar with high BET specific surface area and high loaded metal (Table 2). SEM photo revealed that PBC surface was uniformly covered by congested fine metal particles (Fig. 6a and b) in petal-shape with a diameter in the range from 200 to 500 nm. These characters would definitely partly contribute to the fast decolorization (Li et al. 2017b; Wang et al. 2015; Zhao et al. 2021). Another important factor was the metal composition. Main species of metal on PBC were identified to be Fe^0 and Cu^0 . Fe^0 was fixed on biochar with high crystallinity (Fig. 2) (Qian et al. 2019). Metal particle was covered by their oxides (Fig. S1). Copper could contribute to the synergistic effect and enhance the performance under visible light (Zhao et al. 2021). PBC also had some chemical groups (Fig. 5) such

as aromatic C=C group (Wang et al. 2013), C–O and –OH group (Le et al. 2020; Wang et al. 2013). These chemical groups could also activate peroxides to degrade organic pollutants and work together with metal (Yan et al. 2017; Zhang et al. 2020). Fe–O also could be found on the surface of PBC (Le et al. 2020). According to the composition, iron, copper, and biochar could work together during the reaction (Zhu et al. 2019). Consequently, PBC was verified to be an excellent catalyst for activation of hydrogen peroxide.

Iron, copper, and oxygen weights on PBC surface decreased respectively from 15.9, 1.8 and 35.1 to 14.1, 1.4, and 30.7% after reaction for ten times according to the EDS investigation. It confirmed that iron and copper oxidizes were the main catalytic component. ESR was performed to examine $\bullet\text{OH}$ produced in the heterogeneous Fenton reaction. ESR spectra exhibited characteristic peaks of $\bullet\text{OH}$ adducts with an intensity ratio of 1:2:2:1. It indicated that H_2O_2 was activated to generate $\bullet\text{OH}$. Based on the character investigation, catalytic mechanism could be deduced to be similar to former researches (Le et al. 2020; Li et al. 2017b; Yan et al. 2017; Zhang et al. 2020; Zhao et al. 2021). Catalytic mechanism had been researched thoroughly before (Kumar et al. 2020; Zhu et al. 2019). The main obstacle hindering metallic biochar application was the difficulty in fabrication. In this experiment, impregnation was definitely facile and cheap. The route for fabricating metallic biochar developed here should be feasible in application. Compared with some summarized results (Wang et al. 2019; Zhang et al. 2020), the synthesized

Fig. 6 SEM photo. **a** and **b**: PBC#1; **c**: BC; **d**: BBC#1

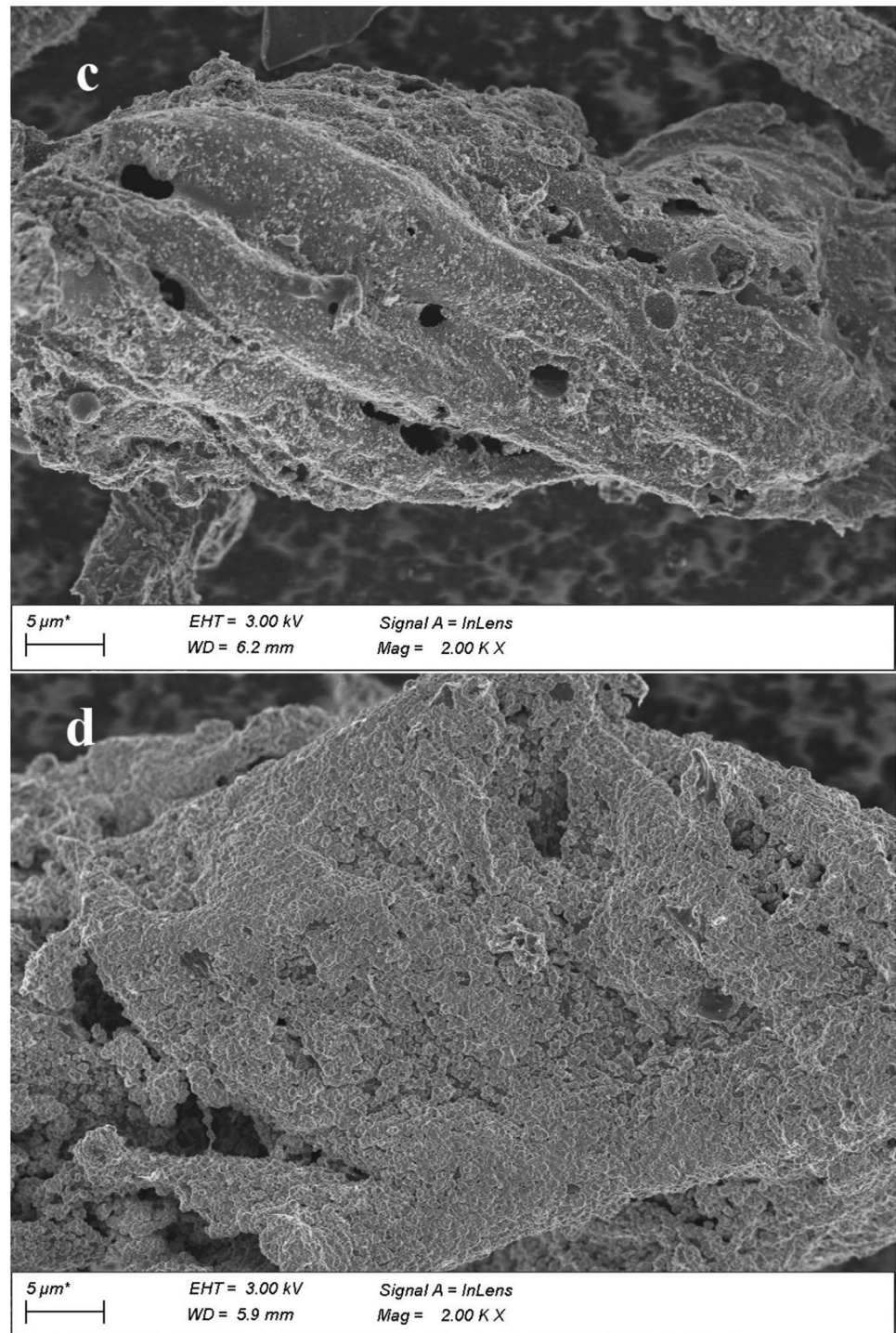


Cu-Fe@biochar exhibited higher performance. It should be partly attributed to the exceedingly high iron content. Besides existing strategies, this experiment strongly implied that increasing iron loading amount was also an effective method to enhance the catalytic ability of metallic biochar.

As a conclusion, bioleaching had some advantages over existing impregnating methods. It was cheap, facile and green, and operated under mild conditions. It could

impregnate biochar with a high amount of iron, at the same time, guarantee the uniform distribution of iron. With copper, it could realize bimetallic impregnation. In this experiment, bioleaching was verified to be a feasible impregnating method for fabrication of heterogeneous catalyst. Definitely, these advantages could also make bioleaching a potentially impregnating method for other metal-loaded biochar applications.

Fig. 6 (continued)



Some points requiring more research

Here, a microbiological impregnating method was developed. This impregnation could make use of the existing techniques of bioleaching and thermochemical conversion. Biochar as support material for catalyst would meet the requirement of sustainable development (Aghbashlo et al. 2021). At the same time, impregnating biochar could make

utilization of bioleaching more diversified. However, some researches should be carried out in the future.

In this experiment, pyrolysis was used to fix metal on biochar. Theoretically, it would make biochar more stable in environment. However, sustainability assessment should be further carried out on the resultant composite (Aghbashlo et al. 2021; Rosen 2018). The more, gas for pyrolysis was CO_2 . It could produce some merits for the

catalysis (Yek et al. 2020). If other factors of pyrolysis could be taken into account, other frequent gas such as steam and nitrogen might also be used (Xia et al. 2021).

Abbreviations and nomenclatures in this article were presented in Table 3.

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Author contribution XL, XW, and QP conducted the experiments. WY contributed reagents and material. FY wrote the manuscript. BW conceived and designed the research and wrote the manuscript. All the authors read and approved the manuscript.

Data availability All the data generated or analyzed during this study are included in this published article (and its supplementary information files).

Declarations

Ethical statement This article does not contain any studies with human participants performed by any of the authors.

Conflict of interest The authors declare no competing interests.

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