



Carbon dioxide activated biochars as mediators for reductive debromination of 1,2-dibromoethane

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Abstract

The fuel additive and pesticide 1,2-dibromoethane (DBA) is a problematic organic pollutant found in soil and aquifers. Remediation methods face drawbacks because of undesirable by-products and slow rates of removal. Biochars (BCs) are catalysts of reductive dehalogenation in anoxic environments by the layered iron(II)-iron(III) hydroxide green rust (GR). However, so far, such catalytic properties have generally only been observed for BCs produced from animal substrates, while BCs from easily available plant substrates, seem to lack these properties. In this study, the potential of CO₂ activation to enhance the catalytic properties of plant-substrate BCs was tested, specifically for BCs from barley straw (BARST), soybean meal (SOYM), wheat straw (WHST) and eelgrass (*Zostera marina*, ZOST). All BCs were tested for catalyzing reductive debromination of DBA with GR as the reductant. CO₂ activation led to clear increases in the extent of DBA debromination (after 7 days) by a factor of 1.5, 8.8, 3.3, and 2.1 for GR reactions with BARST, SOYM, WHST, and ZOST BCs respectively. Changes in BC properties were observed upon CO₂ activation, and these varied between substrates, making it difficult to define the key properties that led to the observed reactivity increase. However, surface polarity, structural defects and the presence of surface O and N functional groups were identified as key BC properties regulating the extent of DBA sorption and degradation. The findings of this study contribute to the optimization of BC mediators for reduction of halogenated pollutants.

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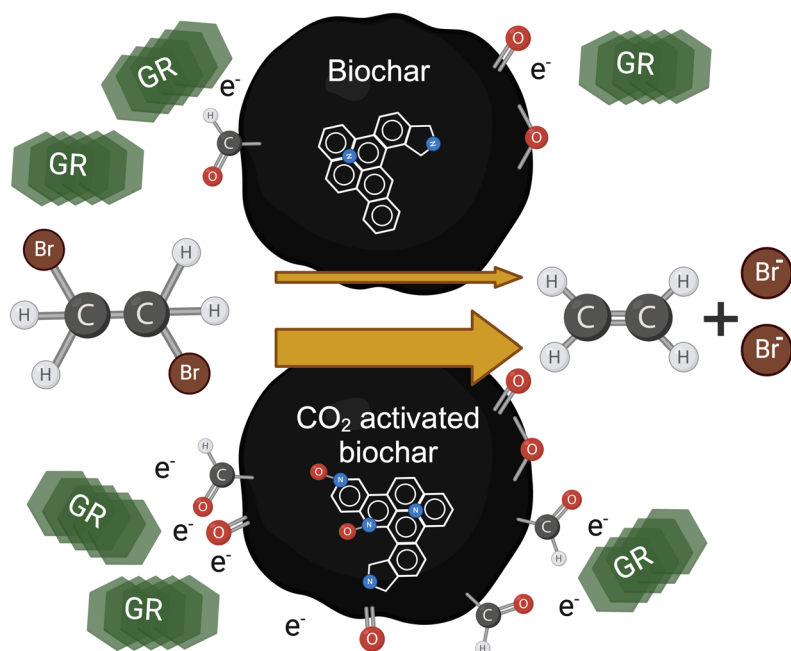
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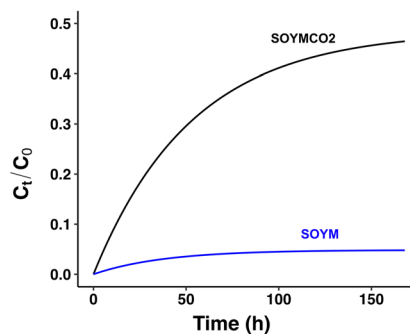
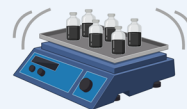
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Graphical abstract



Debromination reactivity



Keywords Environmental pollution · Persistent organic pollutants (POPs) · Green rust · Dehalogenation

Introduction

Halogenated pollutants are ubiquitous, persistent, bio-accumulative and a threat to the environment and human health (Gallistl et al. 2017; Gift et al. 2004; Kuramochi et al. 2004; McGrath et al. 2017; McKeever et al. 2012; Oh et al. 2016). 1,2-dibromoethane (DBA) is one such halogenated pollutant, with origin in leaded fuels, pesticides, and wood fumigants (ATSDR 2018; Falta et al. 2005). Today the extent of DBA pollution is unknown, but it is persistent under anoxic conditions, why its presence in groundwater aquifers and anoxic soils is probable on a global scale and evident on local scale (ATSDR 2018; Wilson et al. 2008). DBA is carcinogenic to animals and considered likely to be carcinogenic to humans (ATSDR 2018; Gift et al. 2004). Established zero valent iron (ZVI) remediation techniques are suited for remediation of brominated ethenes and DBA (Cohen et al. 2009; Rajagopal and Burris 1999), and carbon based catalyst are also efficient when used as electrodes in electrochemical reduction of DBA (Fernández-Verdejo et al. 2020). However, under certain conditions these methods each have critical environmental drawbacks, such as hydrogen production or risk of generating reactive oxygen (Crane and Scott 2012; Qin et al. 2018; Ševců et al. 2011), and corrosion and surface passivation of ZVI (Liu et al. 2024; Phyu Mon et al. 2023). Thus, other methods should be sought for. Green Rust (GR) is a layered iron(II)-iron(III) hydroxide with anionic hydrated

interlayers, comprising Cl^- , CO_3^{2-} or SO_4^{2-} . GRs have been demonstrated as excellent reducing agents for various inorganic and organic pollutants, incl. nitrate, chromate, selenate, nitro compounds, and carbon tetrachloride (Erbs et al. 1999; Hansen and Bender Koch 1998; Hansen et al. 1994). GR materials have also been shown to reduce brominated and chlorinated pollutants together with a biochar (BC) catalyst (Ai et al. 2019; Lindhardt et al. 2025; Ma et al. 2022). BCs are multifunctional, carbon sequestering materials, produced via pyrolysis of biomass in an O₂ reduced atmosphere (EBC 2012–2022). Post-pyrolysis acid treated BCs made from animal substrates such as bone meal and shrimp shells have been shown to be most effective at catalyzing reductive dehalogenation (Ai et al. 2019; Lindhardt et al. 2022), while BCs produced from plant substrates show relatively low or no catalytic activities (Ai et al. 2021; Lindhardt et al. 2025). In a previous study, it was discovered that CO₂ activation can further increase the catalytic activity of a BC in reaction with GR and a halogenated pollutant (Lindhardt et al. 2022). Specifically, the rate of tribromoethylene debromination was shown to increase tenfold when adding CO₂ activation to the pyrolysis of a shrimp shell BC. Carbon dioxide (CO₂) activation is the physical activation process of adding CO₂ gas to the pyrolysis chamber, either in continuation of the primary pyrolysis, or performed on already charred substrates. CO₂ is a mild oxidant at high temperatures, eliminating carbon from the interior of the particle via



an endothermic reaction resulting in increased porosity and specific surface area, as well as changes in surface functional groups (Rodríguez-Reinoso et al. 1995). CO₂ activation is suggested to promote formation of oxygen functional groups (Phothong et al. 2021), which are of importance in the dehalogenation reactions due to their electron shuttling functions (Ai et al. 2020; Hernandez-Montoya et al. 2012; Klüpfel et al. 2014; Lindhardt et al. 2025; Ma et al. 2022). A simplified stoichiometric reaction of CO₂ activation is presented below (Eq. 1), where C_(s) represent carbon in the carbonaceous material that is transferred into the gas phase as CO (Bergna et al. 2018; Marsh and Rodríguez-Reinoso 2006; Menéndez-Díaz and Martín-Gullón 2006).



The objective of this study was to determine if CO₂ activation could enhance the catalytic reactivity of plant substrate BCs towards reductive debromination of DBA by GR. A further objective was to describe the changes in BC characteristics induced by CO₂ activation and to identify BC characteristics critical for catalyzing DBA debromination with a GR reductant.

Materials and methods

Biochar production

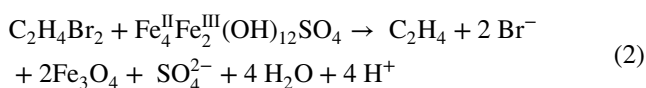
Four plant substrates were collected, dried at 40 °C for 24 h, and ground to a particle size of < 10 mm (SM200 mill, RETSCH, Germany). These were barley straw (BARST), soybean meal (SOYM), wheat straw (WHST), and *Zostera marina* also known as eelgrass (ZOST). Porcelain crucibles of 120 mL volume (LLG Labware, Germany) were filled with ground substrate, dried at 40 °C for 24 h and then weighed before pyrolysis. All BCs were produced in a tube furnace (RSH 120/500/11, Nabertherm, Germany) fitted with modified end gaskets for O₂-reduced atmosphere during pyrolysis. All four substrates were used to produce a standard BC, pyrolyzed under 100 L/h N₂ (99.8%) flow at a heating rate of 300 °C/h and a highest treatment temperature of 850 °C for 2 h. Furthermore, all four substrates were used to produce CO₂ activated BCs under the same initial pyrolysis conditions for two hours, but with an additional hour at 850 °C with 100 L/h pure CO₂ (99.9%) flow and no N₂ flow. Pyrolysis yields and burn-off % are presented in Table S1. The CO₂ activated BCs were labelled with the same abbreviations as the standard BCs plus CO₂ suffix. For both types of BCs, the furnace was left to cool overnight under 100 L/h N₂ flow. The 8 BCs were stored in airtight containers for later characterization or suspended in deoxygenated deionized water (dDW) for reactivity experiments. The dDW was prepared by sparging DW with argon (99.99%) at 20 mL/min for > 1 h under constant stirring.

Green rust synthesis

Green rust was synthesized using a glycine buffered method (Yin et al. 2017). The sulfate form of GR with the formula Fe^{II}₄Fe^{III}₂(OH)₁₂SO₄ · yH₂O, where y is ~8 (Simon et al. 2003) was chosen due to its successful use in previous studies (Lindhardt et al. 2022), and because of its natural occurrence in the pedosphere (Hansen and Bender Koch 1998). 10 mmol Fe(II) and 4 mmol Fe(III) were coprecipitated in 740 mL of dDW containing 4.0 g glycine. NaOH was used to maintain the pH at 8 using a pH-stat setup (719 Titrino, Metrohm, Switzerland). After synthesis, the GR suspension was transferred into an anoxic glovebox (95% N₂, 5% H₂, Coy Laboratories, USA) and left to settle before discarding the supernatant. The settled GR suspension was washed with three cycles of centrifugation at 4200 g for 30 s (EBA 20, Hettich, Germany) and supernatant replacement with dDW. The final pelleted GR was re-suspended in 200 mL dDW, yielding a Fe(II)_{GR} concentration of ~44 mmol/L. The GR stock suspension was kept in the glovebox and used within 48 h.

Debromination of 1,2-dibromoethane

Debromination experiments with BCs, GR, and DBA were set-up in triplicates inside the anoxic glovebox. Specifically, a 5 mL suspension of ~8.8 mmol/L Fe(II)_{GR}, 0.12 g/L BC and 20 µmol/L DBA was produced inside 10 mL GC vials from magnetically stirred stock suspensions of ~44 mmol/L Fe(II)_{GR}, 2 g/L BC, and 4 mmol/L DBA in methanol. The vials were immediately crimp sealed with PTFE/silicone septa (Mikrolab, Aarhus A/S, Denmark) and then taken outside the anoxic glovebox, and placed at 300 rpm on a shaking table (KS 501, IKA-Werke GmbH, Germany) in darkness at room temperature (~21 °C). GC vials were sacrificially analyzed on gas chromatograph (Trace 1300 GC FID/ECD fitted with a headspace autosampler, Thermo Scientific, USA) to determine DBA and product concentrations regularly over the course of 7 days. A flow rate of 60 mL/min was used in the GC front inlet. The column was a 25 m PoraBOND U and the oven program had a three stage heating cycle with 50 °C for two minutes before heating at a rate of 40 °C/min to 250 °C, where the temperature was kept for two more minutes. Notably, methane was observed in controls and in reaction vials in similar amounts, why it is believed to be present in the glovebox atmosphere. DBA debromination by GR turns out as an elimination reaction where a C=C double bond is formed for every two C–Br as shown in Eq. 2.



First order rate constants and total debromination extent after 7 days (ϵ_{7d}) were calculated based on product, i.e.,



ethylene production. Note that ethylene has negligible adsorption affinity towards GR or BCs. The R package “aomisc” was applied for nonlinear fitting of ethylene production data and pseudo-first order parameter calculations (Eq. 3).

$$C_{t, \text{ethylene}} = C_{0, \text{DBAr}} * [1 - e^{-kt}] \quad (3)$$

where $C_{t, \text{ethylene}}$ is the ethylene concentration at time t , and $C_{0, \text{DBAr}}$ is the experimentally determined reactive concentration of the initial DBA concentration. Adsorption of DBA was quantified as the difference between the initial DBA concentration and the sum of residual DBA and formed product, i.e., ethylene, concentration after 24 h reaction (Eq. 4). The relatively fast initial adsorption processes were assumed to be completed after 24 h.

$$n_{\text{DBA adsorbed}} = n_{\text{DBA}, t0} - (n_{\text{DBA}, t24} + n_{\text{ethylene}, t24}) \quad (4)$$

Here, n is the molar mass of each reactant or product, t is the time from 0, $n_{\text{DBA adsorbed}}$ is the molar mass of DBA removed from solution by adsorption, n_{DBA} is the molar mass of DBA still in solution, and $n_{\text{ethylene}, t24}$ is the molar mass of DBA that has been reduced to ethylene.

Biochar characteristics

BC elemental composition was determined by Inductively Coupled Plasma—Optical Emission Spectrometry (5100, Agilent Technologies, USA, with Si equipment) after the sample was digested using a dry ashing—wet digestion method (Singh et al. 2017). Separately, C and N contents were determined using a Vario Macro Cube elemental analyzer (Elementar, Germany). O and H were estimated from a mass balance principle. BC surface chemistry was probed by X-ray photoelectron spectroscopy (XPS-Nexsa, Thermo Scientific, USA) using an Al- K_{α} X-ray source with photon energy of 1486.7 eV. XPS data were analyzed with CasaXPS version 2.3.24 and the deconvolution of C1s and N1s spectra was based on Gengenbach et al. (2021) and Tang et al. (2017). The BC Brunauer–Emmett–Teller specific surface area (SSA) was determined by N_2 sorption (Gemini VII, 2390, Micromeritics, USA), using a standard Micromeritics Carbon Black reference of 21.07 m^2/g . Samples were degassed under N_2 flow for 5 h at 200 °C before SSA determination. Potential structural differences in BCs were analyzed with Raman (WITec alpha 300R confocal Raman microscope, Oxford Instruments, UK) using a 532 nm Ar laser operated at 100% effect (~69 mW before the objective) and a spectral resolution (UHTS3000 spectrometer VIS) of 3.8/cm. Spectra were obtained as means of 100 scans each with 0.1 s acquisition. Deconvolution of characteristic D (1319/cm) and G (1580/cm) bands was used to estimate the changes in structural defects upon CO_2 activation by determining the intensity ratio of these bands, i.e., the I_D/I_G ratio.

Table 1 Debromination kinetics in reactions with GR and different BCs as mediators

Biochar	ε_{7d} (%)	Rate constant (k/d)	Standard error of k	ε_{7dm} (%)
BARST	1.3	0.18	0.093	1.8
BARSTCO ₂	1.9	0.80	0.37	2.9
SOYM	5.2	0.63	0.23	4.9
SOYMC0 ₂	46	0.45	0.16	50
WHST	1.3	0.054	0.041	3.2
WHSTCO ₂	4.3	0.22	0.066	5.5
ZOST	12	0.21	0.088	16
ZOSTCO ₂	25	0.35	0.048	28

Debromination extent (ε_{7d}) reflects the highest observed percentage of ethylene formed during 7-day reaction, and ε_{7dm} represents the modelled maximum debromination extent

Results and discussion

Debromination kinetics and adsorption

All BCs showed the potential to mediate reductive debromination of DBA, as indicated by the formation of ethylene in all reactions (Fig. S1). However, the extent of debromination (ε_{7d}) and the rate of debromination (k) varied as a function of BC type (Table 1). Specifically, non-activated BCs showed ε_{7d} of 1.3%, 4.4%, 1.3%, and 12.3% for BARST, SOYM, WHST, and ZOST, respectively (example in Fig. 1). With the addition of CO_2 activation, the ε_{7d} substantially increased for all tested substrates, but the magnitude differed. For example, ε_{7d} increased 1.5 and 8.8 times for reactions with BARSTCO₂ and SOYMC0₂ BC, while for WHSTCO₂ and ZOSTCO₂ they increased 3.3 and 2.1 times. Overall, the ε_{7d} and modelled maximum debromination extent (ε_{7dm}) were highest for the SOYMC0₂ BC, followed by the ZOSTCO₂. Note that DBA loss due to evaporation and sampling was insignificant in controls with just DBA and dDW, as shown in a previous study that used the same experimental procedures and DBA analyses (Lindhardt et al. 2025).

Adsorption occurred immediately after DBA was spiked to the BC and GR mixture, with obvious DBA removal without ethylene being produced in reactions with the BARST and WHST BCs in non-activated and CO_2 -activated treatments. DBA removal was particularly fast in reactions with BARSTCO₂ and the WHSTCO₂, which also exhibited the highest specific surface areas (SSA). The total adsorbed DBA after 7 days was, however, comparable across the non-activated and CO_2 activated BARST and WHST BCs (Fig. 1). DBA removal via adsorption also dominated in reactions with non-activated SOYM and ZOST BCs. However, this was not the case for reactions with SOYMC0₂ and the ZOSTCO₂, which yielded higher ε_{7d} compared to DBA adsorption extents. This was surprising as SOYMC0₂ and the ZOSTCO₂ had a 33-fold and twofold higher SSA



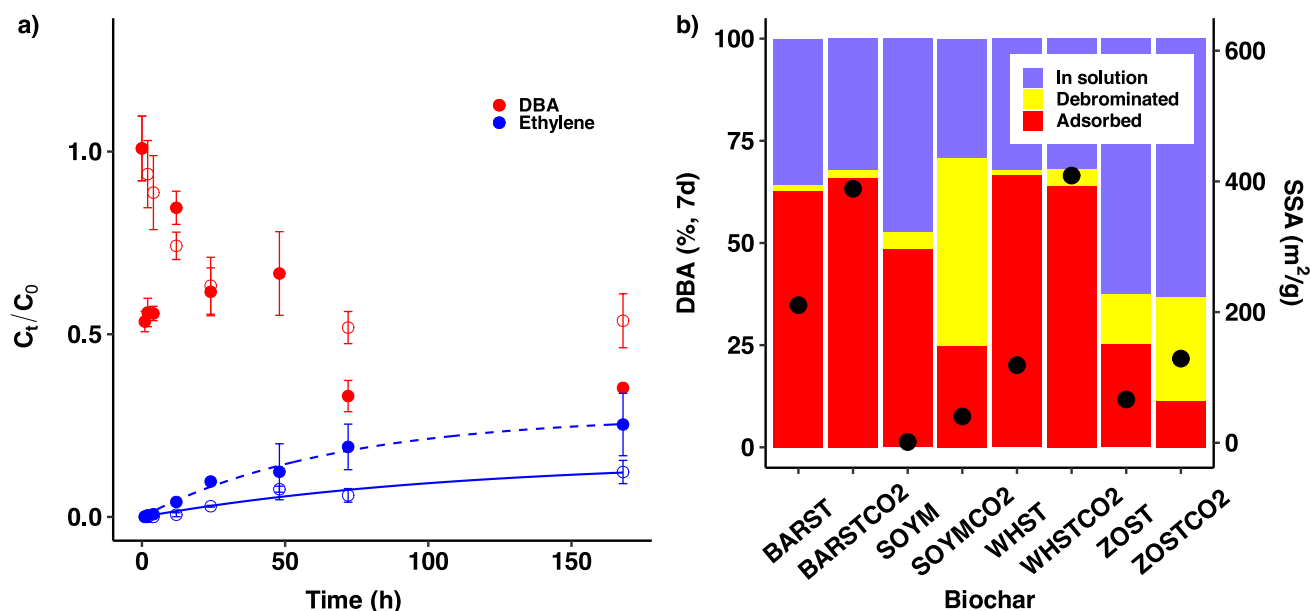


Fig. 1 **a** Time trends of DBA (red symbols) and products/ethylene (blue symbols) during reactions of GR with ZOST (empty circles) and ZOSTCO₂ (filled circles) BCs (8.8 mmol/L Fe(II)_{GR}, 0.12 g/L BC, 20 μ mol/L DBA). Error bars represent standard deviation of triplicates, and the lines represent the fit to pseudo-first order kinetics. **b** Left axis: Relative amounts of dissolved, adsorbed (after 24-h reaction) and debrominated (i.e. produced ethylene) DBA after 7-day reaction. Right axis: black points represent the specific surface area of each BC

compared to non-activated SOYM and ZOST, but a twofold and 2.3-fold decrease in the adsorbed DBA fraction, respectively. The fact that all reactions still exhibited significant amounts of DBA in solution after the 7-day reaction, with very little further DBA degradation expected based on the fitted kinetics, i.e., ε_{7dm} (Table 1), indicates that BC surface sites for DBA degradation and adsorption became quickly blocked.

Biochar characteristics

The elemental composition of BCs mostly differed as a result of the substrate, but the relative abundance of some elements was changed upon CO₂ activation (Table S2-S3). Carbon is by far the most abundant element in the BCs, although the C content of ZOST BCs was significantly smaller compared to the other BCs, due to its high Si content. On average BCs lost 10% C during the activation step and thereby increased the relative abundance of other non-C elements. The nitrogen content of BCs is considered an important parameter in terms of BC catalytic activity, as N functional groups can act as electron donating moieties (Leng et al. 2020). Comparison amongst the BCs showed that SOYM BCs had considerably higher N contents compared to the other BCs.

The distribution of C and N surface species as determined by XPS analysis (Fig. 2a) showed clear differences between substrates, while changes induced by CO₂ activation were generally less clear. Overall, XPS wide scans showed that BARST and WHST BCs had higher C and lower O and N

contents. surface abundances (atomic %) compared to SOYM and ZOST BCs, while CO₂ activation had little influence on these abundances. An exception was an almost sevenfold increase in surface N content in the SOYMCO₂ BC, compared to the non-activated SOYM BC. Looking specifically at the distribution of C functional groups, the C1s spectra for the SOYM BCs showed higher relative contributions from O functional groups than the BARST, WHST, and ZOST, especially the relative content of carboxylic acid groups increased with CO₂ activation (Fig. 2b, Fig. S2). The relative contribution of O functional groups did not increase with CO₂ activation for the BARST, SOYM, and ZOST BCs. In terms of N functional groups, N contents were generally low in BARST, WHST, and ZOST BCs and the relative distribution of N functional groups varied little as a result of CO₂ activation. The biggest change was observed for the SOYM BC, which had considerably higher N contents, and where CO₂ activation induced the formation of pyridinic N oxides (Fig. S3). Raman spectra showed characteristic D (1319/cm) and G (1580/cm) bands, which indicate the presence of defects and graphitized structures in BCs (Fig. S4). CO₂ activated SOYM, WHST, and ZOST BCs exhibited considerably higher I_D/I_G ratios (by 25%, 22%, and 9%, respectively) than the corresponding, non-activated BCs ($p < 0.05$) (Fig. 2c), suggesting that CO₂ activation introduced structural defects in these BCs (Jelavic et al. 2022). In contrast, BARSTCO₂ exhibited an I_D/I_G ratio 11% lower compared to the BARST BC (Fig. 2c). Defects have previously been suggested as a critical characteristic for the catalytic abilities



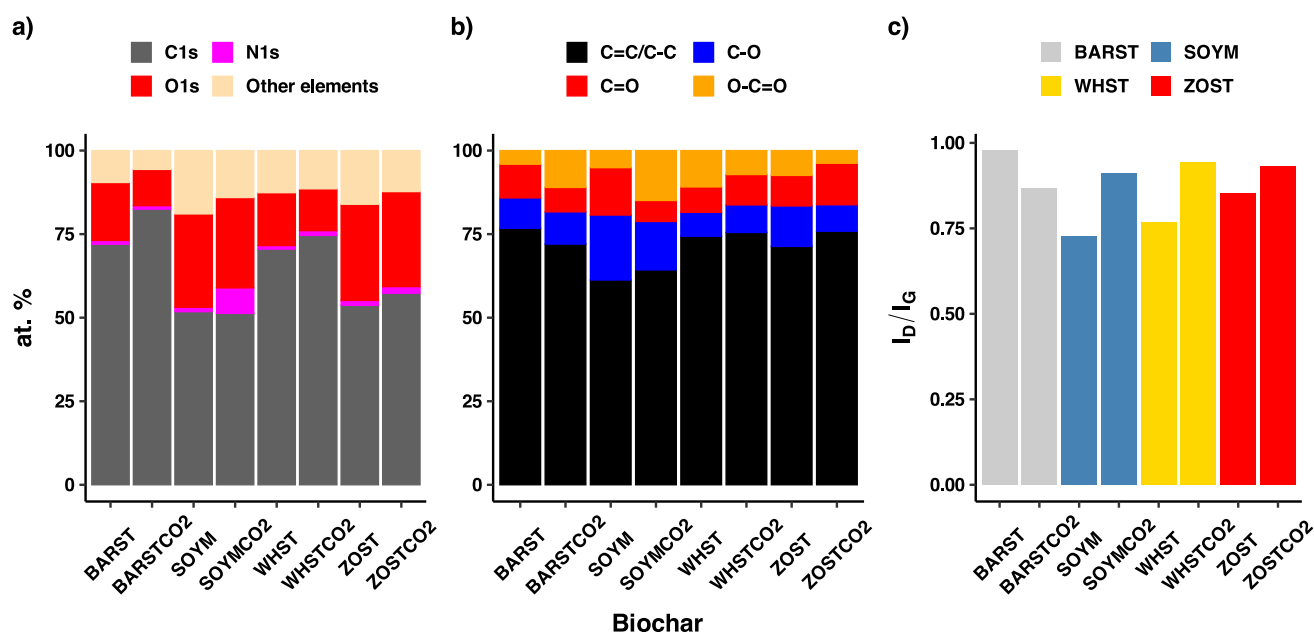


Fig. 2 **a** Surface elemental distribution as determined by XPS wide scans (atomic %), and **b** distribution of C functional groups based on high resolution XPS C1s scan shown in Fig. S2. **c** I_D/I_G ratios determined from raman spectra of non-activated and CO₂ activated biochars (Fig. S4)

of BCs, because defects create surface reactive sites, where electrons may be exchanged (Gabhi et al. 2020; Ma et al. 2022, 2025).

Reactivity and biochar characteristics

In reactions with GR and DBA, BARST and WHST BCs with and without CO₂ activation showed the lowest debromination reactivity compared to SOYM and ZOST BCs. The BARST and WHST BCs were distinctively different from the SOYM and ZOST BCs in terms of their higher abundance of surface C species, and especially C=C/C-groups; lower elemental contents of N and Fe, higher SSA values, and higher DBA adsorption extents.

Overall, this suggests that BARST and WHST BCs surfaces are less polar, i.e., more hydrophobic than SOYM and ZOST BCs, thus enabling higher extents of DBA adsorption. This could be problematic, as GR requires polar sites for effective GR-BC interactions, i.e., electron shuttling across the BC. Moreover, there could be steric and electrostatic hindrance for GR to access redox-active sites if BC surface sites are largely covered by adsorbed DBA. Overall, this may explain the low DBA reduction extents, ε_{7d} , measured in reactions with BARST and WHST BCs. In contrast, the higher reactivity for non-activated SOYM and ZOST BCs may be related to their higher relative contribution of O functional groups and other elements, which may give rise to enhanced GR-BC interactions, less DBA adsorption and hence more DBA available redox active sites on the BC. In terms of the increase in DBA reactivity observed with CO₂ activation, and particularly so for the SOYM where ε_{7d} increased more than 8-fold, it is more

challenging to conclude on the key BC characteristics and/or changes thereof, enabling increased reactivity. While SSA values clearly increased for all BCs with the applied CO₂ activation, it does not correlate well with the measured reactivity increase, which has also been observed in other BC catalyzed dehalogenation studies by GR (Lindhardt et al. 2025; Ma et al. 2022). In previous studies, increases in defect density and/or N functional groups (such as pyridinic N oxide groups) have been inferred as key factors for increased BC catalytic activities (Ai et al. 2021; Ma et al. 2022; Ouyang et al. 2023). This may explain the particularly large reactivity increase for SOYMCO₂ compared to SOYM, as CO₂ treatment led to a considerable increase in both defect density and pyridinic N oxide groups.

Overall, this study shows that there is much potential in the application of CO₂ activation to enhance the reactivity of plant-substrate BCs towards DBA reduction with GR. The major advantage of CO₂ activation is that it can be done directly in the pyrolysis unit and that it does not involve corrosive and hazardous production steps such as acid treatment (Sun et al. 2022; Zhang et al. 2019, 2004). However, more extensive studies are needed to pinpoint the key changes in BC characteristics that enable the higher reactivity. For example, it will be important to assess how variation in CO₂ flow rate and treatment time, performed also at different pyrolysis temperatures, affect BC properties and catalytic reactivity. With such understanding, we can then move towards tailoring BCs with specific mediation properties for reduction of DBA and other simple halogenated pollutants. Compared to other studies on reductive debromination catalyzed by carbonaceous materials, the current study found a maximum total extent of DBA debromination at 46%, whereas Fernández-Verdejo



et al. (2020) found complete DBA debromination and a 5-fold higher kinetic rate constant using a constant flow electron source and a carbon fiber brush electrode at a cathode potential of -0.8 V vs SHE. However, the carbon fiber brush electrode is stationary and cannot be dispersed in a DBA contaminated plume, why it has different in situ application possibilities than the GR-BC method. Furthermore, a study applying ZVI for the degradation of DBA, showed complete DBA removal within a few hours. However, the applied ZVI mass loading was 100-fold higher compared to the amount of GR used here (Rajagopal and Burris 1999). ZVI is a more powerful reductant than GR, but it also comes with drawbacks like corrosion and surface passivation and hydrogen formation. These challenges are mitigated by the method used in the current study. Hence, GR with an activated plant-substrate BC mediator is a promising material for environmentally secure remediation of DBA polluted soil and water.

Conclusion

The reactivity towards catalyzing reductive debromination of DBA by GR and CO_2 activated plant substrate BCs was assessed and the key changes in physicochemical properties were determined. CO_2 activation increases the debromination extent of BC mediators for reductive debromination of 1,2-dibromoethane. The highest comparative increase in debromination extent was 8.8 times, using a CO_2 activated biochar made from a soymeal substrate. Activation by CO_2 increased the SSA and changed the elemental composition of BCs by gasifying C and therefore increasing the relative contribution of other elements. It was indicated that CO_2 activation of the soymeal biochar led to an increase in the relative contribution of N containing surface structures, and especially pyridinic N oxide surface functional groups. A higher degree of defects in the graphite-like structures on the biochar surface was also observed.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s13762-025-06576-1>.

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Declarations

Conflict of interest The authors declare no competing financial or non-financial interest.

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References

- Ai J, Yin WZ, Hansen HCB (2019) Fast dechlorination of chlorinated ethylenes by green rust in the presence of bone char. *Environ Sci Tech Lett* 6:191–196. <https://doi.org/10.1021/acs.estlett.9b00053>
- Ai J, Ma H, Tobler DJ, Mangayayam MC, Lu C, van den Berg FWJ, Yin W, Bruun Hansen HC (2020) Bone char mediated dechlorination of trichloroethylene by green rust. *Environ Sci Technol* 54:3643–3652. <https://doi.org/10.1021/acs.est.9b07069>
- Ai J, Lu C, van den Berg FWJ, Yin W, Strobel BW, Hansen HCB (2021) Biochar catalyzed dechlorination—Which biochar properties matter? *J Hazard Mater* 406:124724. <https://doi.org/10.1016/j.jhazmat.2020.124724>
- ATSDR (2018) Toxicological profile for 1,2-dibromoethane. agency for toxic substances and disease registry, Atlanta, U.S.A. <https://www.atsdr.cdc.gov/ToxProfiles/tp37.pdf>
- Bergna D, Varila T, Romar H, Lassi U (2018) Comparison of the properties of activated carbons produced in one-stage and two-stage processes. *C J Carbon Res* 4:4–41. <https://doi.org/10.3390/c4030041>
- Cohen EL, Patterson BM, McKinley AJ, Prommer H (2009) Zero valent iron remediation of a mixed brominated ethene contaminated groundwater. *J Contam Hydrol* 103:109–118. <https://doi.org/10.1016/j.jconhyd.2008.09.010>
- Crane RA, Scott TB (2012) Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. *J Hazard Mater* 211–212:112–125. <https://doi.org/10.1016/j.jhazmat.2011.11.073>
- EBC (2012–2022) European biochar certificate—guidelines for a sustainable production of biochar. European Biochar Foundation, Arbaz, Switzerland
- Erbs M, Hansen HCB, Olsen CE (1999) Reductive dechlorination of carbon tetrachloride using iron(II) iron(III) hydroxide sulfate (green rust). *Environ Sci Technol* 33:307–311. <https://doi.org/10.1021/es980221t>
- Falta RW, Bulsara N, Henderson JK, Mayer RA (2005) Leaded-gasoline additives still contaminate groundwater. *Environ Sci Technol* 39:379A–384A. <https://doi.org/10.1021/es053352k>
- Fernández-Verdejo D, Sulonen MLK, Pérez-Trujillo M, Marco-Urrea E, Guisasola A, Blázquez P (2020) Electrochemical dehalogenation of dibromomethane and 1,2-dibromoethane to non-toxic products using a carbon fiber brush electrode. *J Chem Technol Biotechnol* 96:335–340. <https://doi.org/10.1002/jctb.6542>
- Gabhi R, Basile L, Kirk DW, Giorcelli M, Tagliaferro A, Jia CQ (2020) Electrical conductivity of wood biochar monoliths and its dependence on pyrolysis temperature. *Biochar* 2:369–378. <https://doi.org/10.1007/s42773-020-00056-0>
- Gallistl C, Lok B, Schlienz A, Vetter W (2017) Polyhalogenated compounds (chlorinated paraffins, novel and classic flame retardants, POPs) in dishcloths after their regular use in households. *Sci Total Environ* 595:303–314. <https://doi.org/10.1016/j.scitotenv.2017.03.217>
- Gengenbach TR, Major GH, Linford MR, Easton CD (2021) Practical guides for x-ray photoelectron spectroscopy (XPS): interpreting the carbon 1s spectrum. *J Vac Sci Technol, a: Vac, Surf Films* 39:013204. <https://doi.org/10.1116/6.0000682>



- Gift J, Greenberg M, Hogan K, Cummings A, Liccione JJ, Spinnato JA, and Gaylor D (2004) Toxicological Review of 1,2-Dibromoethane. Washington DC Retrieved from www.epa.gov/iris
- Hansen HCB, Bender Koch C (1998) Reduction of nitrate to ammonium by sulphate green rust: activation energy and reaction mechanism. *Clay Miner* 33:87–101. <https://doi.org/10.1180/claymin.1998.033.1.09>
- Hansen HCB, Borggaard OK, Sørensen J (1994) Evaluation of the free-energy of formation of Fe(II)-Fe(III) hydroxide-sulfate (green rust) and its reduction of nitrite. *Geochim Cosmochim Acta* 58:2599–2608. [https://doi.org/10.1016/0016-7037\(94\)90131-7](https://doi.org/10.1016/0016-7037(94)90131-7)
- Hernández-Montoya V, García-Servín J, Ivn J (2012) Thermal treatments and activation procedures used in the preparation of activated carbons. In: Montoya Virginia Hernández (ed) Lignocellulosic precursors used in the synthesis of activated carbon—characterization techniques and applications in the wastewater treatment. InTech. <https://doi.org/10.5772/39365>
- Jelavić S, Thygesen LG, Magnin V, Findling N, Müller S, Meklesh V, Sand KK (2022) Soot and charcoal as reservoirs of extracellular DNA. *Peer Commun J*. <https://doi.org/10.24072/pcjournal.207>
- Klöpffel L, Keiluweit M, Kleber M, Sander M (2014) Redox properties of plant biomass-derived black carbon (biochar). *Environ Sci Technol* 48:5601–5611. <https://doi.org/10.1021/es500906d>
- Kuramochi H, Maeda K, Kawamoto K (2004) Water solubility and partitioning behavior of brominated phenols. *Environ Toxicol Chem* 23:1386–1393. <https://doi.org/10.1897/03-279>
- Leng L, Xu S, Liu R, Yu T, Zhuo X, Leng S, Xiong Q, Huang H (2020) Nitrogen containing functional groups of biochar: an overview. *Bioresour Technol* 298:122286. <https://doi.org/10.1016/j.biortech.2019.122286>
- Lindhardt JH, Lu CY, Holm PE, Hansen HCB (2022) Reductive debromination of bromo-substituted C₂ aliphatics using a biochar-iron(II) composite. *J Chem Technol Biot* 97:2243–2252. <https://doi.org/10.1002/jctb.7102>
- Lindhardt JH, Holm PE, Zhu Y-G, Lu C, Hansen HCB (2025) Plant-substrate biochar properties critical for mediating reductive debromination of 1,2-dibromoethane. *J Environ Sci* 147:1–10. <https://doi.org/10.1016/j.jes.2023.09.018>
- Liu M, Chen G, Xu L, He Z, Ye Y (2024) Environmental remediation approaches by nanoscale zero valent iron (nZVI) based on its reductivity: a review. *RSC Adv* 14:21118–21138. <https://doi.org/10.1039/d4ra02789b>
- Ma H, Ai J, Lu C, Hansen HCB (2022) Element doping of biochars enhances catalysis of trichloroethylene dechlorination. *Chem Eng J* 428:132496–132496. <https://doi.org/10.1016/j.cej.2021.132496>
- Ma H, Hansen HCB, Pu S, Ouyang Q, Thygesen LG, Tobler DJ (2025) Nitrogen doping turns carbonaceous materials into fast-reacting catalysts for reductive dechlorination. *Environ Pollut* 368:125578. <https://doi.org/10.1016/j.envpol.2024.125578>
- Marsh H, Rodríguez-Reinoso F (2006) Activated carbon. Elsevier, Amsterdam. <https://doi.org/10.1016/B978-0-08-044463-5.X5013-4>
- McGrath TJ, Ball AS, Clarke BO (2017) Critical review of soil contamination by polybrominated diphenyl ethers (PBDEs) and novel brominated flame retardants (NBFRs); concentrations, sources and congener profiles. *Environ Pollut* 230:741–757. <https://doi.org/10.1016/j.envpol.2017.07.009>
- McKeever R, Sheppard D, Nusslein K, Baek KH, Rieber K, Ergas SJ, Forbes R, Hilyard M, Park C (2012) Biodegradation of ethylene dibromide (1,2-dibromoethane [EDB]) in microcosms simulating in situ and biostimulated conditions. *J Hazard Mater* 209–210:92–98. <https://doi.org/10.1016/j.jhazmat.2011.12.067>
- Menéndez-Díaz JA, Martín-Gullón I (2006) Chapter 1 Types of carbon adsorbents and their production. Activated carbon surfaces in environmental remediation. Elsevier, pp 1–47. [https://doi.org/10.1016/S1573-4285\(06\)80010-4](https://doi.org/10.1016/S1573-4285(06)80010-4)
- Oh SY, Seo YD, Ryu KS (2016) Reductive removal of 2,4-dinitrotoluene and 2,4-dichlorophenol with zero-valent iron-included biochar. *Bioresour Technol* 216:1014–1021. <https://doi.org/10.1016/j.biortech.2016.06.061>
- Ouyang Q, Hansen HCB, Thygesen LG, Tobler DJ (2023) Nitrogen amended graphene catalyses fast reduction of vinyl chloride by nano zerovalent iron. *Water Res* 244:120535. <https://doi.org/10.1016/j.watres.2023.120535>
- Phothong K, Tangsathitkulchai C, Lawtae P (2021) The analysis of pore development and formation of surface functional groups in bamboo-based activated carbon during CO₂ activation. *Molecules* 26:5641. <https://doi.org/10.3390/molecules26185641>
- Phyu Mon P, Phyu Cho P, Chanadana L, Ashok Kumar KV, Dobhal S, Shashidhar T, Madras G, Subrahmanyam C (2023) Bio-waste assisted phase transformation of Fe₃O₄/carbon to nZVI/graphene composites and its application in reductive elimination of Cr(VI) removal from aquifer. *Sep Purif Technol*. <https://doi.org/10.1016/j.seppur.2022.122632>
- Qin H, Guan X, Bandstra JZ, Johnson RL, Tratnyek PG (2018) Modeling the kinetics of hydrogen formation by zerovalent iron: effects of sulfidation on micro- and nano-scale particles. *Environ Sci Technol* 52:13887–13896. <https://doi.org/10.1021/acs.est.8b04436>
- Rajagopal VK, Burris DR (1999) Reduction of 1,2-dibromoethane in the presence of zero-valent iron. *Environ Toxicol Chem* 18:1779–1782. <https://doi.org/10.1002/etc.5620180825>
- Rodríguez-Reinoso F, Molina-Sabio M, González MT (1995) The use of steam and CO₂ as activating agents in the preparation of activated carbons. *Carbon* 33:15–23. [https://doi.org/10.1016/0008-6223\(94\)00100-e](https://doi.org/10.1016/0008-6223(94)00100-e)
- Ševců A, El-Temsah YS, Joner EJ, Černík M (2011) Oxidative stress induced in microorganisms by zero-valent iron nanoparticles. *Microbes Environ* 26:271–281. <https://doi.org/10.1264/jsme2.me11126>
- Simon L, François M, Refait P, Renaudin G, Lelaurain M, Génin JMR (2003) Structure of the Fe(II-III) layered double hydroxysulphate green rust two from Rietveld analysis. *Solid State Sci* 5:327–334. [https://doi.org/10.1016/S1293-2558\(02\)00019-5](https://doi.org/10.1016/S1293-2558(02)00019-5)
- Singh B, Arbertain MC, Lehmann J (2017) Biochar—a guide to analytical methods. CRC Press/Taylor and Francis Group, LLC
- Sun Y, Dong B, Wang L, Li H, Thorin E (2022) Technology selection for capturing CO₂ from wood pyrolysis. *Energy Convers Manag*. <https://doi.org/10.1016/j.enconman.2022.115835>
- Tang ZJ, Fang P, Huang JH, Zhong PY (2017) Parameter setting for peak fitting method in XPS analysis of nitrogen in sewage sludge. *IOP Conf Ser Earth Environ Sci* 100:012207. <https://doi.org/10.1088/1755-1315/100/1/012207>
- Wilson JT, Banks K, Earle RC, He Y, Kuder T, and Adair C (2008) Natural attenuation of the lead scavengers 1,2-dibromoethane (EDB) and 1,2-dichloroethane (1,2-DCA) at motor fuel release sites and implications for risk management
- Yin W, Huang L, Pedersen EB, Frandsen C, Hansen HCB (2017) Glycine buffered synthesis of layered iron(II)-iron(III) hydroxides (green rusts). *J Colloid Interface Sci* 497:429–438. <https://doi.org/10.1016/j.jcis.2016.11.076>
- Zhang TY, Walawender WP, Fan LT, Fan M, Daugaard D, Brown RC (2004) Preparation of activated carbon from forest and agricultural residues through CO₂ activation. *Chem Eng J* 105:53–59. <https://doi.org/10.1016/j.cej.2004.06.011>
- Zhang S, Shi X, Wróbel R, Chen X, Mijowska E (2019) Low-cost nitrogen-doped activated carbon prepared by polyethylenimine (PEI) with a convenient method for supercapacitor application. *Electrochim Acta* 294:183–191. <https://doi.org/10.1016/j.electacta.2018.10.111>

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