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Optimization of the electrochemical properties of biochar for the remediation of organic pollutants in soil

Optimización de las propiedades electroquímicas del biochar para la remediación de contaminantes orgánicos en suelo

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Chacón, F.J., Sánchez-Monedero, Cayuela, M.L., 2021. Optimización de las propiedades redox del biochar para favorecer la degradación de contaminantes emergentes. VI Jornadas Doctorales. Universidad de Murcia.

Chacón, F.J., Cayuela, M.L., Cederlund, H., Sánchez-Monedero, M.A., 2022. Enhanced removal of organic contaminants in water-saturated soils using designer biochars with tailored electrochemical properties. 22nd World Congress of Soil Science 2022, Glasgow.

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Abbreviations

ABTS	2,2′-azino- bis(3-ethylbenzthiazoline-6-sulfonicacid) diammonium salt
A_{eq}	Equilibrium adsorption percentage
ANOVA	Analysis of variance
Ar	Argon
BJH	Barrett-Joyner-Halenda analysis
CCME	Canadian Council of Ministers of the Environment
DIET	Direct interspecies electron transfer
DPM	Disintegrations per minute
EAC	Electron accepting capacity
EDC	Electron donating capacity
EEC	Electron exchange capacity
E_h	Redox potential
EPR	Electron paramagnetic resonance spectroscopy
ESI	Electrospray ionization
FcDMAM	Dimethylaminomethyl ferrocene
FTIM	Fourier transform infrared microscopy
FTIR	Fourier transform infrared spectroscopy
HPLC	High-performance liquid chromatography
HTT	High treatment temperature

ICP-MS	Inductively coupled plasma mass spectrometry
k	Degradation rate
K_d	Distribution coefficient
K_f	Freundlich coefficient
k_{max}	Maximum degradation rate
MHM	Modified Hummer's Method
N_2-BET	Nitrogen Brunauer–Emmett–Teller specific surface area
n	Freundlich nonlinearity exponent
NMR	Nuclear magnetic resonance
NR	Neutral red
OCFG	Oxygen-containing functional group
OECD	Organisation for Economic Co-operation and Development
PC	Principal component
PCA	Principal component analysis
PCP	Pentachlorophenol
PCR	Principal component regression
PFR	Persistent free radical
ROS	Reactive oxygen species
UPLC-MS	Ultra-performance liquid chromatography coupled with mass spectroscopy
V_0	Initial volume in the aqueous phase

WHC	Water holding capacity
XPS	X-ray photoemission spectroscopy
XRD	X-ray diffraction

Resumen/Spanish summary

Por parte de la comunidad científica se ha dedicado un gran esfuerzo al desarrollo de materiales funcionales que permitan solucionar problemas medioambientales apremiantes, como la erosión del suelo o la presencia de contaminantes persistentes. Los materiales de carbono, gracias a su bajo impacto medioambiental, su estabilidad y su amplia gama de aplicaciones son excelentes candidatos para esta tarea. Uno de estos materiales es el "biochar", un sólido rico en carbono obtenido de la pirólisis de biomasa en un entorno con oxígeno limitado. La pirólisis de biomasa es un proceso de descomposición termoquímica que transforma sus componentes poliméricos en biochar (residuo sólido), bioaceite (residuo líquido) y gas de síntesis (sintegás). Esta fracción sólida es un material muy heterogéneo, generalmente compuesto por una matriz orgánica con diferentes niveles de oxidación y constituyentes inorgánicos cuya composición variará en función de la materia prima original y la temperatura de pirólisis. Gracias a su estructura aromática, el biochar tiene una considerable estabilidad química y resistencia a la degradación, lo que le permite persistir en el suelo durante décadas o incluso cientos de años.

Además de su composición química, los efectos beneficiosos del biochar se han atribuido a su gran superficie y a su compleja estructura de poros. Estas propiedades dependen del tipo de biomasa de partida y de las condiciones de pirólisis. Los residuos agrícolas y agroindustriales como los residuos de poda o de paja son el tipo de material de partida más común, lo que no es de extrañar teniendo en cuenta las 2×10^{11} toneladas de biomasa lignocelulósica que se producen cada año en el mundo. El biochar suele tener una mayor porosidad y área superficial que el material del que se produce, lo que lo hace especialmente interesante en este caso, ya que es capaz de retener gran parte de la estructura capilar del material lignocelulósico. Junto con su elevado pH y su capacidad de retención de agua, el biochar puede proporcionar hábitats adecuados para las comunidades microbianas y promover el desarrollo de raíces. Además, el gran número de grupos funcionales presentes en la superficie del biochar le proporcionan otras características secundarias beneficiosas, como una mayor capacidad de intercambio catiónico con la que aumentar la capacidad del suelo para retener nutrientes. Debido a estas características, las aplicaciones tradicionales del biochar se centraban principalmente en el secuestro de carbono o en la mejora de las propiedades físicas del suelo y el rendimiento de los cultivos.

Más recientemente, se ha descubierto una nueva gama de propiedades electroquímicas en el biochar, que consisten principalmente en su capacidad redox (su

capacidad para intercambiar electrones a través de reacciones reducción-oxidación) y conductividad (su capacidad para transportar electrones de una parte a otra del material). Estas propiedades se han propuesto como un factor importante en muchos de los procesos medioambientales afectados por el biochar, así como relacionados con otras áreas como las pilas de combustible microbianas y las aplicaciones de almacenamiento de energía. Por tanto, cuando se utiliza como enmienda en suelo, el biochar puede participar en algunos procesos redox del suelo, incluyendo el ciclo de nutrientes, la degradación de contaminantes, la captura de radicales libres, la mediación de electrones con microbios o la transferencia directa de electrones entre especies microbianas, entre otros. En el biochar, se cree que estas propiedades surgen de su estructura grafítica y de la presencia en su superficie de determinados grupos funcionales, radicales y metales con actividad redox. La modulación de estos componentes podría dar lugar a biochars "a la carta" con propiedades electroquímicas adaptadas a aplicaciones medioambientales específicas, siendo este el enfoque de la presente tesis.

El objetivo general es obtener biochar modificados con propiedades electroquímicas mejoradas capaces de promover la remediación de contaminantes en suelo. La hipótesis principal es que el aumento en el número de grupos funcionales, metales con actividad redox y de la aromaticidad del biochar aumentará su capacidad redox y su conductividad, lo que a su vez le permitirá influir en la degradación del contaminante, ya sea de manera directa (reacción redox directa entre el contaminante y el biochar) o indirecta (mediación de electrones).

Para alcanzar el objetivo general de esta tesis, se propusieron los siguientes pasos como objetivos específicos:

1. Una revisión de la literatura para establecer el estado del arte sobre las propiedades electroquímicas del biochar, identificar las lagunas de la investigación y proponer métodos de modificación.

2. La producción de biochars con una amplia gama de propiedades electroquímicas diferentes, obtenidos mediante una variedad de materiales de partida, condiciones de pirólisis y tratamientos.

3. Examinar cómo la modulación de las propiedades electroquímicas del biochar influye en la cinética y el porcentaje de remediación de un contaminante de estructura simple.

4. Determinar la capacidad de los biochar modificados para influir en las vías de degradación de un contaminante emergente con actividad redox.

La tesis se ha estructurado en cuatro capítulos relacionados con los objetivos específicos descritos anteriormente:

-Capítulo 1: En este capítulo se revisan los conocimientos actuales sobre las propiedades electroquímicas del biochar, así como las diferentes técnicas disponibles para medirlas y posibles métodos para su modificación. Las propiedades electroquímicas del biochar más relevantes para la remediación en suelo son su capacidad redox y conductividad. Estas propiedades permiten al biochar actuar como mediador de electrones en el suelo, aceptando (o donando) electrones de ciertos microorganismos o minerales, y transfiriéndolos (o aceptándolos) a otros agentes como microorganismos, minerales o incluso contaminantes. Se ha propuesto la presencia en la superficie del biochar de ciertos grupos funcionales (quinonas y fenoles principalmente), radicales y metales con actividad redox como el origen más probable de su capacidad redox. Por tanto, la mejora de las propiedades redox requeriría principalmente un aumento en el número de estos componentes en la superficie del biochar. La funcionalización de la superficie del biochar es uno de los métodos más sencillos y directos, lo que suele implicar un proceso de oxidación. La oxidación debe ser lo suficientemente fuerte como para introducir nuevas funcionalidades, pero no excesiva para evitar la conversión de los grupos C-OH y C=O (en forma de fenoles y quinonas) al inactivo COOH o incluso su eliminación como CO_2. La adición de metales con actividad redox antes de la pirólisis es otro de los métodos más prometedores. Por ejemplo, minerales como la magnetita (Fe_3O_4), los cuales se ha demostrado que se forman en la superficie del biochar, pueden actuar tanto como donadores como aceptores de electrones gracias a la presencia de hierro en dos estados de oxidación distintos.

La conductividad es una consecuencia de la presencia de estructuras laminares similares a las del grafito y la deslocalización de los electrones π. Cuando la temperatura de pirólisis es suficientemente alta, la condensación del carbono amorfo en el biochar crea láminas grafíticas conductoras capaces de transferir electrones a velocidades muy altas y largas distancias. Si la conductividad es el rasgo deseado, hay que producir un biochar con una estructura más aromática y grafítica, rasgos que aumentan exponencialmente a temperaturas superiores a 700 ºC. Desgraciadamente, combinar una alta capacidad redox y una buena conductividad es difícil de conseguir. El mayor número de grupos funcionales suele encontrarse en los biochar producidos a una temperatura de pirólisis máxima de 400 ºC, que es demasiado baja para que las láminas conductoras se desarrollen y formen una red interconectada. A temperaturas superiores a 600 ºC, en cambio, la degradación térmica elimina la mayor parte de los grupos funcionales responsables de su capacidad redox. Por si fuera poco, los procesos de oxidación que introducen grupos

funcionales en el biochar pueden reducir su conductividad, ya que estos grupos se forman preferentemente en el borde de las láminas grafíticas, impidiendo la transferencia de electrones de una lámina a la siguiente. Por lo tanto, las estrategias de modificación deben seleccionarse cuidadosamente para conseguir las propiedades deseadas, que deben adaptarse a la aplicación prevista.

-Capítulo 2: El objetivo principal es producir biochars con una amplia gama de propiedades electroquímicas que permitan su uso en aplicaciones específicas, con especial atención a la capacidad redox. Para ello se modificó el biochar con varias estrategias, incluyendo la selección de materia prima, la optimización de parámetros de producción y procesamiento, la precarga de biomasa con metales con actividad redox y tratamientos post-pirólisis. Para identificar los componentes responsables de los cambios en las propiedades electroquímicas y entender cómo las diferentes estrategias transformaron el biochar, se midieron las variaciones en su superficie de grupos funcionales, radicales y el contenido en metales redox mediante XPS, EPR e ICP-MS, respectivamente. Para la medición de las capacidades redox mediante voltamperometría, se utilizó un sistema electroquímico de 3 electrodos, con un crisol de carbono vítreo que hace las veces de electrodo de trabajo y recipiente de la disolución. La producción de biochar se realizó a escala de laboratorio en un horno de tubo rotatorio en ausencia de oxígeno mediante la inyección de gas Argón.

Como materiales de partida se utilizaron la poda de olivo, de naranjo, de vid, de algarrobo, de almendro, restos de tomatera, caña y paja de arroz. La medición de las propiedades redox reveló diferencias entre los materiales de partida, destacando la capacidad de donación de electrones de la poda de vid y tomatera (0.302 y 0.335 mmol e$^-$·g^{-1}, respectivamente) y la aceptación de electrones de la poda de naranjo (0.397 mmol e$^-$·g^{-1}). El biochar con mayor capacidad de intercambio de electrones (poda de naranjo, 0.695 mmol e$^-$·g^{-1}) mostró tener el doble que el de menor capacidad (poda de almendro, 0.324 mmol e$^-$·g^{-1}), una diferencia notable que demuestra la variabilidad inherente de estas propiedades debido al material de partida. No se encontró una correlación entre los componentes lignocelulósicos (celulosa, hemicelulosa y lignina) y la capacidad redox, pero sí entre esta y el contenido de ceniza de los materiales de partida. Se ha propuesto que los iones metálicos de las cenizas favorecen las vías de despolimerización durante la degradación térmica de la pirólisis, lo que promueve la generación de grupos funcionales. Se eligió la poda de olivo como el material sobre el que realizar las distintas modificaciones por tener una capacidad de intercambio de electrones intermedia. Entre las condiciones de pirólisis que se modificaron la más importante fue la temperatura (400 ºC, 600 ºC, 800 ºC y 1000 ºC). El biochar con la mayor capacidad redox fue el pirolizado a 400ºC (0.413

mmol e$^-$·g^{-1}), la cual fue disminuyendo conforme se aumentó la temperatura de pirólisis (> 80% de pérdida entre 800 ºC y 1000 ºC) debido a la eliminación de grupos funcionales. El proceso inverso ocurrió con la conductividad, la cual fue insignificante a temperaturas menores de 800 ºC. Por lo tanto, la modificación de los parámetros de producción sólo es capaz de obtener dos tipos de biochar, aquellos con una capacidad redox moderada pero baja conductividad o viceversa.

Para los distintos tratamientos post-pirólisis se utilizaron como oxidantes H_2O_2, HNO_3, $KMnO_4$ (tanto de manera simple en disolución como con el complejo método de Hummers) y $NaClO$, como tratamiento ácido H_3PO_4, KOH como base y radiación UV como método adicional. El tratamiento que más aumentó tanto la donación como la aceptación de electrones respecto al biochar original de 400 ºC fue el método de Hummers, con casi el triple de capacidad redox (1.23 vs 0.413 mmol e$^-$·g^{-1}), seguido por la oxidación directa con $KMnO_4$ (1.11 mmol e$^-$·g^{-1}) y HNO_3 (0.647 mmol e$^-$·g^{-1}). El resto de tratamientos fueron incapaces de aumentar la capacidad redox, especialmente la radiación UV, que la redujo casi un 40%. La capacidad redox de los biochar modificados tuvo una relación directa y lineal con la presencia de grupos C-OH (donación) y C=O (aceptación) en la superficie del biochar.

Por otro lado, la adición de metales con actividad redox (Mn o Fe) antes de la pirólisis fue también un método exitoso a la hora de aumentar la capacidad redox del biochar resultante, aunque menor que los tratamientos oxidativos. Estos biochar se desvían un poco de la linealidad en la relación entre grupos funcionales y capacidad de intercambio de electrones, lo que indica la participación de estos metales en las reacciones redox. En cuanto a la conductividad, como era de esperar los tratamientos provocaron su reducción al alterar la estructura grafítica del biochar. Sin embargo, se consiguió obtener un biochar electroquímicamente "híbrido" con una conductividad y capacidad redox moderadas tratando un biochar pirolizado a una HTT de 800 ºC con $KMnO_4$. Aunque este tratamiento redujo la conductividad en un 64% (1.34 mS·cm^{-1}) respecto al biochar original (3.74 mS·cm^{-1}), ésta era 22 veces mayor que la del biochar pirolizado a una HTT de 400 ºC, con una capacidad redox similar (0.427 mmol e$^-$·g^{-1}). La sinergia entre la conductividad y la capacidad redox de este biochar podría mejorar su capacidad para actuar como mediador de electrones y acelerar la degradación de contaminantes.

-Capítulo 3: En este capítulo se examinó cómo las propiedades electroquímicas de los biochar modificados pueden influir en la remediación de pentaclorofenol (PCP) en suelo. Para ello se contaminó el suelo con una dosis de 10 µg·g^{-1}, tanto en condiciones aerobias como anaerobias. Se almacenaron muestras a los 2, 4, 8, 16, 30 y 50 días, se extrajeron en

un sistema Soxhlet automatizado y se analizaron mediante HPLC. Se utilizó un total de 9 biochar distintos, incluido dos sin modificar pirolizados a una HTT de 400 °C y 1000 °C (B-400 y B-1000). Excepto B-1000-KMnO4 (con B-1000 como biochar original), el resto de biochars fueron producidos a partir de B-400, con el nombre del tratamiento al que fueron sometidos (B-Fe, B-H$_2$O$_2$, B-H$_3$PO$_4$, B-HNO$_3$, B-KMnO$_4$ y B-KOH).

En la incubación aeróbica, todos los biochar fueron capaces de disminuir la concentración de PCP en comparación con el suelo sin biochar. Después de 50 días, el suelo sin enmienda mostró una reducción de apenas el 33,6% en los niveles de PCP, mientras que incluso el biochar menos eficaz (B-H$_3$PO$_4$) fue capaz de eliminar una media del 71,2% de PCP. Los resultados mostraron una mayor degradación del contaminante en aquellos biochar con mayores capacidades redox, además de una cinética de degradación más rápida. B-KMnO$_4$ (el biochar con mayor capacidad redox de los usados, tratado con KMnO$_4$), B-Fe (con metal redox) y B-1000-KMnO$_4$ (híbrido con conductividad y capacidad redox moderadas) fueron los biochar más exitosos, siendo capaces de eliminar prácticamente todo el PCP extraíble del suelo. Esto demuestra que se pueden utilizar diferentes estrategias no sólo para mejorar la capacidad de remediación del propio biochar, sino también para superar las limitaciones propias del suelo. Se cree que la deshalogenación reductiva microbiana es la principal vía de transformación del PCP en suelo. El biochar puede promover este proceso actuando como donante de electrones para las bacterias halógenas que utilizan el PCP como aceptor terminal de electrones. En el suelo aeróbico, las condiciones no son ideales para esta reacción y la contribución de las propiedades electroquímicas del biochar tanto como mediador como en la donación directa de electrones fue probablemente suficiente para mejorar la remediación en todas las enmiendas de biochar. En la incubación anaerobia, sin embargo, el bajo potencial redox del suelo sin enmienda llevó a un nivel elevado de degradación. Gran parte de los biochar, incluyendo los dos sin modificar (B-400 y B-1000, además de B-H$_3$PO$_4$ y B-H$_2$O$_2$), tuvieron un efecto inhibitorio en estas condiciones. La alta adsorción de PCP por parte del biochar podría ser capaz de inmovilizar el contaminante, impidiendo el contacto entre PCP y microorganismos y, por tanto, su reducción. Sin embargo, en nuestro caso tres de los cuatro biochars con mayor adsorción (B-KMnO$_4$, B-HNO$_3$ y B-Fe) se encontraban entre las enmiendas con mayores niveles de remediación. La excepción, B-H$_3$PO$_4$, no tenía conductividad, era el biochar con menor capacidad redox y tenía uno de los porcentajes atómicos más bajos de grupos funcionales C-OH y C=O. Esto apoya la hipótesis de que el PCP puede ser reducido abióticamente en la superficie del biochar, probablemente por su interacción con los grupos funcionales donadores de electrones, radicales y metales redox. El resultado fue la inhibición en la

incubación anaeróbica de los biochar que poseían una alta adsorción de PCP, pero una baja cantidad de funcionalidades o metales redox (como B-400, B-1000, B-H_2O_2 y especialmente B-H_3PO_4). Para aumentar la remediación en estas condiciones, se necesitaría una gran cantidad de grupos con actividad redox. Este fue precisamente el caso de B-$KMnO_4$ y B-Fe, las únicas enmiendas de biochar que aumentaron significativamente la remediación de PCP en suelo anaeróbico. La conductividad podría superar este problema hasta cierto punto mediante la transferencia de electrones de una parte del biochar a otra, lo que explica la mayor remediación y velocidad de la misma del conductor B-1000-$KMnO_4$ en comparación con el no conductor B-400 en suelo aeróbico, aun teniendo capacidades redox similares.

Hubo una correlación lineal significativa entre la capacidad redox y la velocidad máxima de remediación para todos los biochars con baja conductividad, excepto B-Fe. Sin embargo, los biochars conductores tuvieron tasas de remediación mucho más altas de lo que cabría esperar a partir de su capacidad redox por sí sola. La concentración de PCP después de 50 días para B-1000 fue mayor que en otras enmiendas de biochar (en ambas incubaciones) y B-1000-$KMnO_4$ no fue capaz de mejorar la remediación en suelo anaeróbico (especialmente en comparación con los biochars con mayor capacidad redox, que sí mejoraron la remediación). Esto sugiere que la principal contribución de la conductividad está en la tasa de remediación, mientras que la capacidad redox tiene un papel tanto en la tasa de remediación de PCP como en el alcance de la misma.

-Capítulo 4: En este capítulo se estudió el efecto de biochar con distintas propiedades electroquímicas en las vías de degradación de paracetamol (ACT) en suelo mediante la cuantificación de metabolitos intermedios. Para ello se añadió 1 µg·g^{-1} de ACT al suelo, de nuevo tanto en condiciones aerobias como anaerobias. Muestras a los 2, 4, 8, 16, 32 y 60 días se extrajeron mediante un sistema Soxhlet automatizado y se analizaron con UPLC-MS. Se utilizaron los biochar modificados más exitosos del capítulo 3, además de los biochar originales (B-400, B-Fe, B-KMnO4, B-1000 y B-1000-$KMnO_4$).

La capacidad del suelo sin enmienda para degradar ACT fue alta, especialmente en condiciones aerobias, donde tardó sólo 32 días para la degradación completa (60 días en suelo anaerobio). La enmienda con biochar sin modificar no sólo no fue capaz de promover la degradación del contaminante, sino que tuvo un efecto inhibitorio, probablemente debido a la alta adsorción del contaminante y su inmovilización. B-400 (↓conductividad, ~capacidad redox) inhibió la degradación del contaminante en los dos tipos de incubación, mientras que B-1000 (↑conductividad, ↓capacidad redox) sólo lo hizo de forma significativa en la incubación aerobia y en menor medida que B-400. La red

conductora de B-1000 podría resolver en cierta medida la baja biodisponibilidad al transferir electrones de una parte del material a la otra, haciendo que su inhibición sea mucho menor. Esto derivó en una cinética de degradación similar entre el suelo no enmendado y el que contine B-1000, especialmente en condiciones anaeróbicas. Así, la ausencia de conductividad en los biochars pirolizados a temperaturas relativamente bajas podría suponer un mayor riesgo potencial para el medio ambiente durante las primeras semanas tras la contaminación. La modificación del biochar aumentó en gran medida la tasa de transformación del ACT, con la excepción de la enmienda con B-Fe en suelos anaeróbicos. La enmienda con B-1000-KMnO$_4$ resultó en una remediación más rápida y completa, gracias al sinergismo entre conductividad y propiedades redox. A pesar de los posibles problemas de biodisponibilidad, como en el caso del PCP, dos de los biochars con mayor adsorción de ACT (B-KMnO$_4$ y B-1000-KMnO$_4$) mostraron una mayor degradación en comparación con los de menor adsorción (B-Fe y B-400). La hipótesis de que el ACT puede transformarse directamente en la superficie del biochar fue confirmada con un análisis electroquímico, que reveló la existencia de una transferencia de electrones del ACT al biochar en disolución.

Además de ACT, 11 metabolitos adicionales fueron detectados en las incubaciones de suelo. Aunque investigaciones anteriores han propuesto la unión permanente al suelo como el destino mayoritario de ACT, en las incubaciones con biochar modificado la transformación del contaminante fue el mecanismo de remediación principal. Los metabolitos catecol y fenol presentaron las mayores concentraciones de entre ellos (en condiciones aerobias y anaerobias, respectivamente), acumulándose como productos de transformación antes de la apertura de sus anillos. En base a los metabolitos identificados, se propusieron 4 vías de degradación principales, incluyendo la oxidación del hidroxilo, desacetilación, hidroxilación y metilación. Las tres primeras rutas son favorecidas por la presencia de oxígeno, lo que llevó a una remediación mayor en estas condiciones. La metilación, en cambio, fue la vía principal en la incubación anaerobia. La oxidación del hidroxilo llevó a la formación de dímeros de ACT y NAPQI, éste último con una toxicidad mayor que el compuesto de origen. Aunque en el suelo sin enmienda NAPQI sólo apareció en condiciones aerobias, en suelos con biochar modificado la producción de NAPQI apareció en ambas incubaciones y a concentraciones mucho mayores. Esto fue probablemente debido a la oxidación de ACT mediante reacciones redox en la superficie del biochar, que abrió una nueva vía de degradación en condiciones anaerobias, permitiendo a los biochar modificados promover la transformación de ACT.

Los resultados obtenidos en esta tesis se pueden resumir de manera general en las siguientes conclusiones:

1. Se demostró la posibilidad de controlar las propiedades redox del biochar modificando la naturaleza y el número de grupos funcionales y metales con actividad redox en su superficie. La capacidad redox muestra una relación lineal con el número de grupos funcionales de C-OH y C=O.

2. La modulación de la conductividad del biochar implica el ajuste de la temperatura de pirólisis. Conseguir una mayor conductividad requiere temperaturas de pirólisis superiores a 600ºC, lo que desgraciadamente disminuye la capacidad redox del biochar. Se puede encontrar un punto intermedio entre ambas propiedades tratando un biochar altamente conductivo pirolizado a una HTT de 1000 ºC con $KMnO_4$.

3. La modificación de las propiedades electroquímicas del biochar es una estrategia adecuada para mejorar la remediación de diferentes contaminantes tanto en suelos aeróbicos como anaeróbicos. Esta estrategia no sólo es capaz de superar las limitaciones del biochar sin modificar, sino también las del propio suelo. Además, se reducen los problemas derivados de la variabilidad en las propiedades electroquímicas de biochars obtenidos a partir de diferentes materiales de partida, ya que estas propiedades se pueden ajustar y optimizar al nivel requerido en función del contaminante y de las condiciones del suelo.

4. Para los suelos limitados en su capacidad de degradar un contaminante debido al potencial redox del suelo, los biochar con una capacidad redox aumentada son la mejor opción para la enmienda, ya que pueden promover una remediación más rápida y completa. Para los suelos que no están limitados, son más adecuados los biochar híbridos que posean a la vez una capacidad redox y conductividad moderadas, ya que consiguen una cinética de remediación superior.

5. Aunque la precarga de la biomasa con metales es una estrategia exitosa para mejorar la capacidad redox del biochar, en ciertas condiciones pueden tener un impacto negativo en la remediación. Dependiendo del comportamiento redox del contaminante, la presencia de oxígeno o un alto potencial redox del suelo puede transformar el metal a un estado de oxidación que inhiba la degradación. El resto de biochar modificados tuvieron comportamientos similares tanto en condiciones aerobias como anaerobias.

6. Diferentes contaminantes como el pentaclorofenol y el paracetamol pueden reducirse abióticamente en la superficie del biochar por su interacción con los componentes redox.

En este caso, una adsorción elevada aumentaría la remediación para aquellos biochar modificados con una alta capacidad redox, mientras que sería perjudicial para aquellos con capacidades redox bajas o moderadas.

7. En ausencia de modificación, la falta de conductividad de los biochar pirolizados a temperaturas relativamente bajas ($< 700^o$C) podría dar lugar a un mayor riesgo ambiental durante las primeras semanas después de la contaminación. Esto se debe a la reducida biodisponibilidad del contaminante causada por la alta adsorción del biochar, que puede inmovilizarlo e impedir su contacto con microorganismos y otras partes del biochar.

8. La enmienda con biochar es capaz de añadir nuevas vías de transformación durante la degradación de contaminantes con actividad redox en el suelo, teniendo sus propiedades electroquímicas un papel directo en este resultado.

Introduction, objectives and thesis structure

Context

A significant amount of research has been devoted to the development of functional materials that could ameliorate pressing environmental issues such as soil erosion and pollution. Carbon materials, due to their environmentally friendly nature, stability and wide range of applications are excellent candidates for this task (Lithoxoos et al. 2010; Mauter and Elimelech 2008). One of these materials is biochar, a carbon-rich solid produced by the pyrolysis of biomass in an oxygen-limited environment. The pyrolysis of biomass is a thermochemical decomposition process that transforms its polymeric components into carbon-rich biochar (solid residue), bio-oil (liquid residue), and syngas (Kan et al. 2016). The solid fraction is a very heterogeneous material, generally comprised of an organic aromatic matrix with different levels of oxidation and inorganic constituents whose composition will vary depending on the original feedstock and temperature of pyrolysis (Zhao et al., 2013). Thanks to its aromatic structure, biochar has a considerable chemical stability and resistance to degradation, allowing it to persist in soil for decades or even hundreds of years (Lehmann et al., 2015).

In addition to its chemical composition, the beneficial effects of biochar have been generally attributed to its large surface area and complex pore structure. These properties depend on the type of feedstock biomass and the pyrolysis conditions. Agricultural and agro-industrial waste such as pruning or straw residues are its most common feedstock material (Zabanitou et al., 2017), which is reasonable considering the enormous output of lignocellulosic biomass that are produced every year (Saini et al., 2015). Biochars generally have higher porosity and surface area than the feedstocks from which they are produced, which is especially interesting in this case, as it can retain much of the capillary structure of the lignocellulosic material. Along with its high pH and water retention capacity, biochar can provide suitable habitats for microbial communities and promote root development (Joseph et al., 2021). Additionally, the large number of functional groups present on the surface of biochar provides it with other beneficial characteristics, such as a high cation exchange capacity that increases the ability of soil to retain nutrients (Igalavithana et al., 2015). Given these characteristics, traditional applications of biochar were mainly focused on carbon sequestration or improving soil physical properties and crop yields (Melorose et al., 2015; Montanarella and Lugato, 2013).

More recently, a new range of electrochemical properties have been discovered in biochar, consisting of its redox capacity (its ability to exchange electrons through reduction-oxidation reactions) and conductivity (its capacity to transport electrons from one part of the material to another) (Klüpfel et al., 2014; Sun et al., 2017). These properties

have been proposed as an important factor in many environmental processes affected by biochar (Xu et al., 2019; Yuan et al., 2017), as well as others related to areas such as microbial fuel cells and energy storage applications (Cheng et al., 2017; Yuan et al., 2013). Thus, when used as a soil amendment, biochar can be involved in some soil redox-mediated processes including nutrient cycling, contaminant degradation, free radical scavenging, microbial electron shuttling and direct interspecies electron transfer, among others (Chen et al., 2014; Fang et al., 2014; Joseph et al., 2015; Yu et al., 2015). In biochar, these properties arise from its graphitic structure and the presence on its surface of certain functional groups, radicals and redox-active metals (Klüpfel et al., 2014). The modulation of these components could result in biochars with tailored electrochemical properties suited for specific environmental applications, which will be the focus of the present thesis.

Objectives

The general objective is to obtain engineered biochars with enhanced electrochemical properties able to promote contaminant degradation in soil. The main hypothesis is that increasing the abundance of functional groups, redox-active metals and the aromaticity of biochar will boost its redox capacity and conductivity, which will in turn allow biochar to enhance contaminant degradation either directly (direct redox reaction between the contaminant and biochar) or indirectly (microbial electron shuttling).

In order to reach the aim of this thesis, the following steps were proposed as specific objectives:

- A literature review to establish a state-of-the-art understanding on the electrochemical properties of biochar, identify research gaps and propose biochar modification methods.

- The production of biochars with a broad range of electrochemical properties through different feedstocks, pyrolysis conditions and treatments.

- To examine how modulating the electrochemical properties of biochar can influence the kinetics and remediation extent of a contaminant of simple structure in soil.

- To determine the capacity of the engineered biochars to modify the degradation pathways of an emerging contaminant with redox activity.

Structure of the thesis

The thesis has been structured in four chapters related to the specific objectives described previously:

-**Chapter 1**: In this chapter, the current knowledge on the electrochemical properties of biochar is reviewed, as well as the different techniques available to measure them. Different modification methods and production parameters (feedstocks, additives, pyrolysis conditions) are discussed, focused on developing biochars with enhanced electrochemical properties.

-**Chapter 2**: The objective was to produce biochars with a broad range of electrochemical properties to allow their use in specific applications, with the redox capacity as the main target. For this purpose, we altered biochar with various strategies, including optimizing production and processing parameters, feedstock selection, preloading biomass with redox-active metals and post-pyrolysis treatments. To identify the components responsible for the changes in the electrochemical properties and understand how the different strategies altered biochar, we measured the variations in surface functional groups, radicals and redox-active metal content of the modified biochars. Since other biochar properties like surface area and pH can also influence its effect on various applications, our secondary goal was to characterize them and when appropriate, establish their relationship with the electrochemical properties.

-**Chapter 3**: In this chapter, we examined how modulating the electrochemical properties of biochar can influence pentachlorophenol (PCP) remediation in soil. Soil contaminated with PCP was incubated in both aerobic and anaerobic conditions, with raw and designer biochars produced in the previous chapter as amendments. The extent of PCP remediation as well as the kinetics of the process were closely examined over a 50-day incubation. This revealed the potential role that the redox capacity and conductivity of the biochars had in the remediation, which allowed us to propose the best biochar modification strategies for this purpose. The influence of biochar on PCP transformation pathways was discussed, with a focus on the possible mechanisms of electron transfer among microorganisms, biochar, and PCP, as well as the effect of biochar modification on these mechanisms. Besides the changes caused to the electrochemical properties, biochar modification altered other properties like pH, surface area or the adsorption of the contaminant, which we also characterized and determined their impact on PCP remediation.

-**Chapter 4**: Here, we evaluated the influence of biochar amendment on the degradation pathways of paracetamol (ACT) in soil. In order to do this, we identified its main transformation metabolites and proposed a general degradation pathway. Raw and tailored biochars with enhanced electrochemical properties were also tested to optimize and promote ACT remediation. Biochar altered some of the mechanisms of ACT degradation in soil, allowing us to understand what properties are necessary for an enhanced degradation and their role in this process.

References

Cheng, B.-H., Zeng, R.J., Jiang, H., 2017. Recent developments of post-modification of biochar for electrochemical energy storage. Bioresource Technology 246, 224–233. https://doi.org/10.1016/j.biortech.2017.07.060

Chen, S., Rotaru, A.-E., Shrestha, P.M., Malvankar, N.S., Liu, F., Fan, W., Nevin, K.P., Lovley, D.R., 2014. Promoting interspecies electron transfer with biochar. Scientific Reports 4. https://doi.org/10.1038/srep05019

Fang, G., Gao, J., Liu, C., Dionysiou, D.D., Wang, Y., Zhou, D., 2014. Key role of persistent free radicals in hydrogen peroxide activation by biochar: Implications to organic contaminant degradation. Environmental Science & Technology 48, 1902–1910. https://doi.org/10.1021/es4048126

Joseph, S., Cowie, A.L., Van Zwieten, L., Bolan, N., Budai, A., Buss, W., Cayuela, M.L., Graber, E.R., Ippolito, J.A., Kuzyakov, Y., Luo, Y., Ok, Y.S., Palansooriya, K.N., Shepherd, J., Stephens, S., Weng, Z. (Han), Lehmann, J., 2021. How biochar works, and when it doesn't: A review of mechanisms controlling soil and plant responses to biochar. GCB Bioenergy 13, 1731–1764. https://doi.org/10.1111/gcbb.12885

Joseph, S., Husson, O., Graber, E., van Zwieten, L., Taherymoosavi, S., Thomas, T., Nielsen, S., Ye, J., Pan, G., Chia, C., Munroe, P., Allen, J., Lin, Y., Fan, X., Donne, S., 2015. The Electrochemical Properties of Biochars and How They Affect Soil Redox Properties and Processes. Agronomy 5, 322–340.

Kan, T., Strezov, V., Evans, T.J., 2016. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. Renewable and Sustainable Energy Reviews 57, 1126–1140. https://doi.org/10.1016/j.rser.2015.12.185

Klüpfel, L., Keiluweit, M., Kleber, M., Sander, M., 2014. Redox properties of plant biomass-derived black carbon (biochar). Environmental Science & Technology 48, 5601–5611. https://doi.org/10.1021/es500906d

Lehmann, J., Abiven, S., Kleber, M., Genxing, P., Singh, B., Sohi, S., Zimmerman, A.R., 2015. "Persistence of biochar in soil", in Biochar for Environmental Management, eds J. Lehmann and S. Joseph. Routledge.

Lithoxoos, G.P., Labropoulos, A., Peristeras, L.D., Kanellopoulos, N., Samios, J., Economou, I.G., 2010. Adsorption of N_2, CH_4, CO and CO_2 gases in single walled carbon nanotubes: A combined experimental and Monte Carlo molecular simulation study. The Journal of Supercritical Fluids 55, 510–523. https://doi.org/10.1016/j.supflu.2010.09.017

Mauter, M.S., Elimelech, M., 2008. Environmental applications of carbon-based nanomaterials. Environmental Science & Technology 42, 5843–5859. https://doi.org/10.1021/es8006904

Saini, J.K., Saini, R., Tewari, L., 2015. Lignocellulosic agriculture wastes as biomass feedstocks for second-generation bioethanol production: concepts and recent developments. 3 Biotech, 5(4), 337–353. https://doi.org/10.1007/s13205-014-0246-5

Sun, T., Levin, B.D.A., Guzman, J.J.L., Enders, A., Muller, D.A., Angenent, L.T., Lehmann, J., 2017. Rapid electron transfer by the carbon matrix in natural pyrogenic carbon. Nature Communications 8. https://doi.org/10.1038/ncomms14873

Xu, Y., Yan, Y., Obadamudalige, N.L., Ok, Y.S., Bolan, N., Li, Q., 2019. "Redox-mediated biochar-contaminant interactions in soil", in: Biochar from Biomass and Waste. Elsevier.

Yuan, Y., Bolan, N., Prévoteau, A., Vithanage, M., Biswas, J.K., Ok, Y.S., Wang, H., 2017. Applications of biochar in redox-mediated reactions. Bioresource Technology 246, 271–281. https://doi.org/10.1016/j.biortech.2017.06.154

Yuan, Y., Yuan, T., Wang, D., Tang, J., Zhou, S., 2013. Sewage sludge biochar as an efficient catalyst for oxygen reduction reaction in a microbial fuel cell. Bioresource Technology 144, 115–120. https://doi.org/10.1016/j.biortech.2013.06.075

Yu, L., Yuan, Y., Tang, J., Wang, Y., Zhou, S., 2015. Biochar as an electron shuttle for reductive dechlorination of pentachlorophenol by *Geobacter sulfurreducens*. Scientific Reports 5. https://doi.org/10.1038/srep16221

Zabaniotou, A., Rovas, D., Delivand, M.K., Francavilla, M., Libutti, A., Cammerino, A.R., Monteleone, M., 2017. Conceptual vision of bioenergy sector development in Mediterranean regions based on decentralized thermochemical systems. Sustainable Energy Technologies and Assessments 23, 33–47.

Zhao, L., Cao, X., Mašek, O., Zimmerman, A., 2013. Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. Journal of Hazardous Materials 256-257, 1–9. https://doi.org/10.1016/j.jhazmat.2013.04.015

Chapter 1

Understanding, measuring and tuning the electrochemical properties of biochar
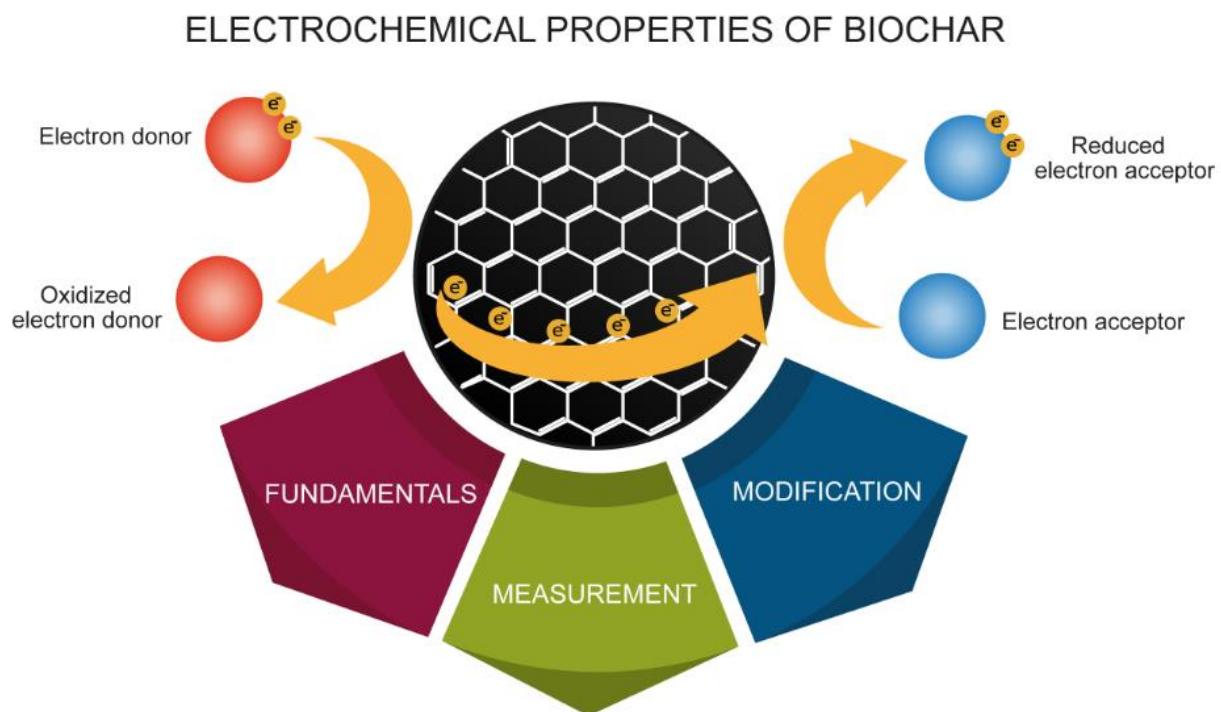
Understanding, measuring and tuning the electrochemical properties of biochar for environmental applications

Francisco J. Chacón · María L. Cayuela · Asunción Roig · Miguel A. Sánchez-Monedero

Abstract Biochar, the solid carbon product from the pyrolysis of biomass, has been gaining attention due to its many possible applications such as soil amendment and water or air purification. Several effects have been observed when biochar is applied to soil, including reduced greenhouse gas emissions, contaminant degradation and increased microbial activity. Recently, it has been demonstrated that some of these effects are a direct consequence of its electrochemical properties. Understanding the mechanisms that allow biochar to store and transfer electrons is essential to obtain a complete view on its role in biogeochemical redox reactions. This paper reviews the current knowledge on the electrochemical properties of biochar as well as the different techniques available to measure and modify these properties. Specific conditions (different feedstocks, additives, pyrolysis conditions) and treatments that influence biochar's electrochemical properties are also discussed, with the aim of developing biochars with enhanced electrochemical properties for specific environmental applications.

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Chapter 2

Enhancing biochar redox properties through feedstock selection, metal preloading and post-pyrolysis treatments
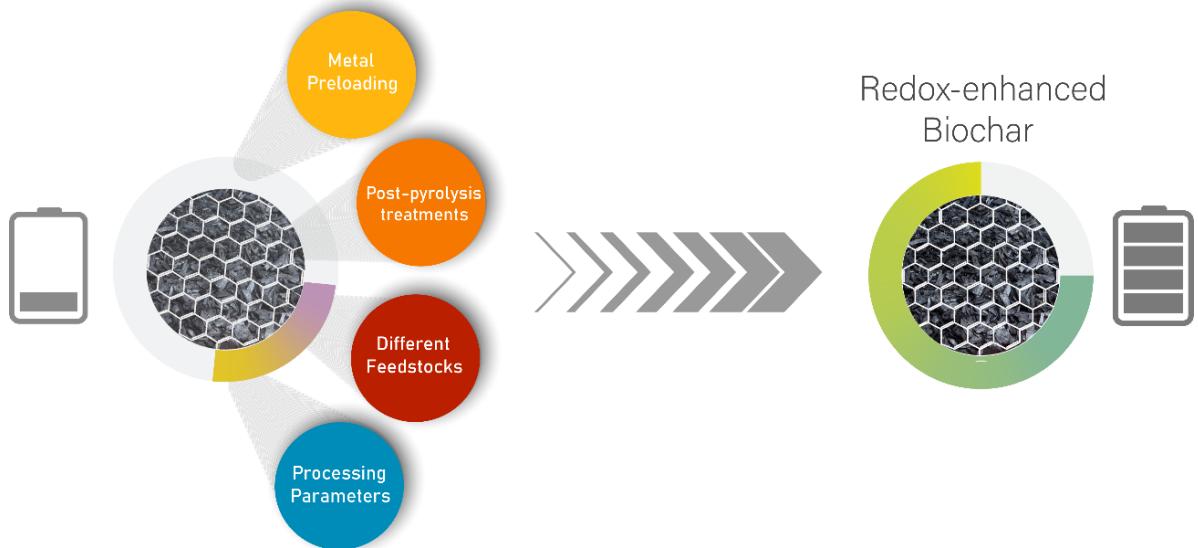
Enhancing biochar redox properties through feedstock selection, metal preloading and post-pyrolysis treatments

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HIGHLIGHTS

- A variety of approaches were tested to enhance the redox properties of biochar.
- Post-pyrolysis modification was able to triplicate the EEC of the original biochar.
- Surface area, pH and conductivity can also be tuned by selecting the right method.
- Biochar with an acceptable conductivity and EEC was produced for electron shuttling.
- Tailored designer biochars can be produced to target specific applications.

GRAPHICAL ABSTRACT
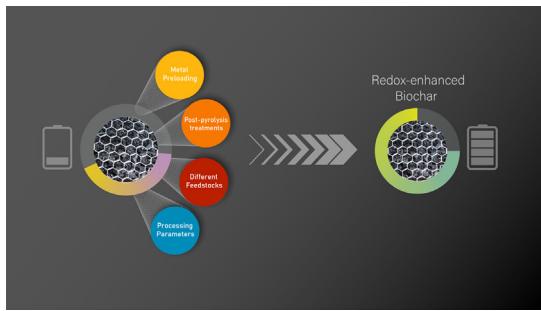
ABSTRACT

There is growing evidence on the importance of the redox properties of biochar for many environmental applications. However, its variability and the difficulty in controlling its redox properties could be delaying the use of biochar in those areas that involve the exchange of electrons, like microbial fuel cells or contaminant degradation related to microbial electron shuttling. To help with these issues, we produced a wide range of biochars showing different redox capacities through a variety of strategies. These include optimizing production and processing parameters, feedstock selection, preloading biomass with redox-active metals and post-pyrolysis treatments. A modified Hummer's method was the most efficient treatment, increasing the electron donating capacity from 0.244 mmol e^-/$g_{biochar}$ to 0.590 mmol e^-/$g_{biochar}$ and the electron accepting capacity from 0.169 mmol e^-/$g_{biochar}$ to 0.645 mmol e^-/$g_{biochar}$. The characterization of the phases responsible for the redox properties, mainly surface functional groups, radicals and redox-active metals, allowed us to better understand the changes caused to biochar by the different strategies. It revealed that the most important approach to enhance redox properties is to increase the number of C–OH and C=O groups in biochar, while the methods that use redox-active metals showed higher than predicted electron donating capacities. We also measured other attributes such as surface area, pH and conductivity, with a focus on their relationship with the redox properties. By selecting the appropriate production and modification methods, we were able to produce a balanced biochar with acceptable conductivity (1.34 mS/cm) and electron exchange capacity (0.418 mmol e^-/$g_{biochar}$), even though these properties usually have an inverse relationship. This work opens the possibility for the production of designer biochars with tailored properties optimized for specific applications.

Chapter 3

Overcoming biochar limitations to remediate pentachlorophenol in soil by modifying its electrochemical properties
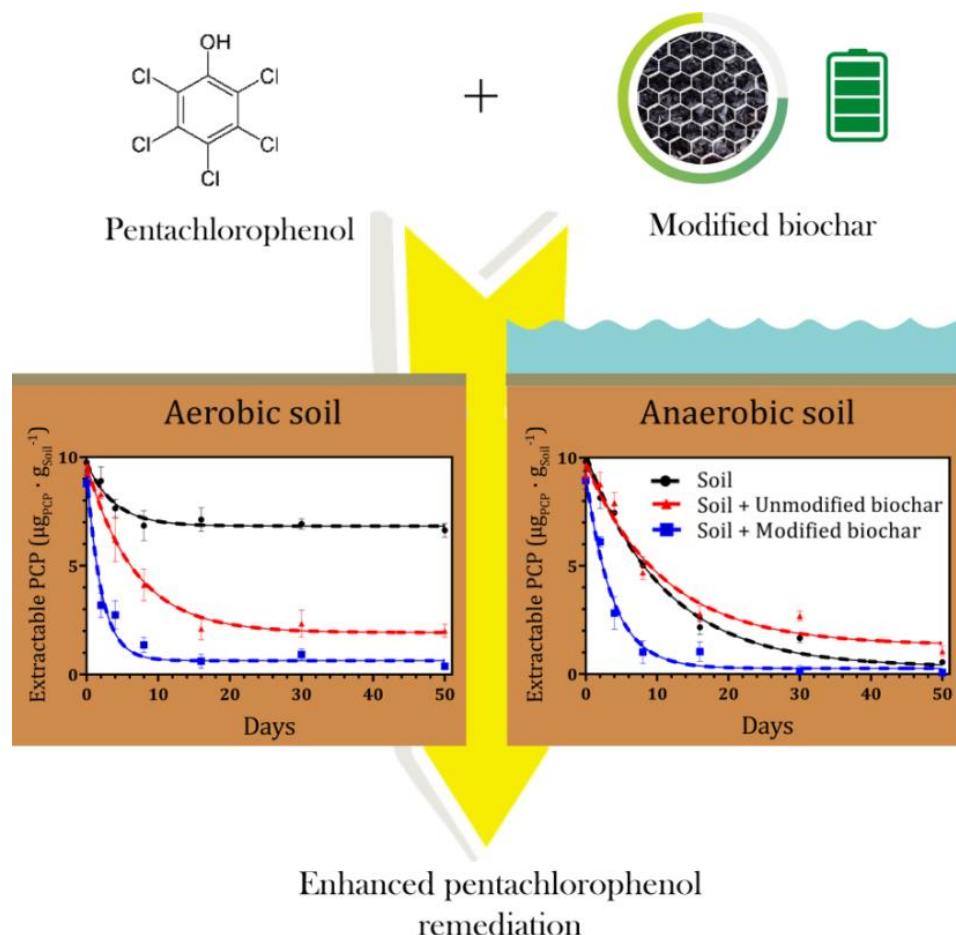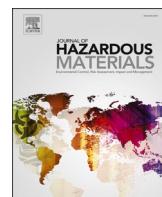
Overcoming biochar limitations to remediate pentachlorophenol in soil by modifying its electrochemical properties

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HIGHLIGHTS

- Raw biochar inhibited PCP remediation in anaerobic soil.
- Biochar modification enhanced PCP remediation in both aerobic and anaerobic soil.
- Biochar redox capacity determines both the rate and extent of PCP remediation.
- Biochar conductivity mainly influences the rate of PCP remediation

GRAPHICAL ABSTRACT
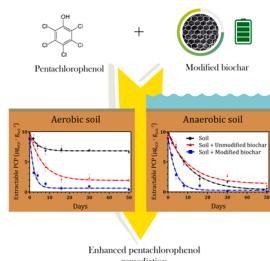
ABSTRACT

In this study, we produced modified biochars with enhanced electrochemical properties to increase PCP remediation in soil. Although all biochars enhanced PCP remediation in aerobic conditions, only a few did in anaerobic soil. The most successful modifications were (i) the preloading of biomass with 10% w/w $FeCl_3$, to obtain a biochar rich in redox-active metals (B-Fe); (ii) the oxidation of a conductive biochar pyrolyzed at 1000 ℃ with 0.025 M $KMnO_4$, to produce a biochar with both moderate conductivity and redox capacity (B-1000-$KMnO_4$); and (iii) $KMnO_4$ oxidation of an amorphous biochar pyrolyzed at 400 ℃ to obtain a biochar with very high redox capacity (B-$KMnO_4$). B-Fe reduced extractable PCP to almost zero after 50 days in both incubations, but showed slow kinetics of remediation in aerobic soil. B-1000-$KMnO_4$ had the highest rate of remediation under aerobic conditions, but no significant effect under anaerobic conditions. B-$KMnO_4$, however, presented high rates of remediation and high removal of extractable PCP under both conditions, which made it the recommended modification strategy for increased PCP remediation. We found that the degree of remediation primarily depends on the redox capacity, while the rate of remediation was determined by both the conductivity and redox capacity of biochar.

1. Introduction

There is a continuous stream of new chemical and pharmaceutical compounds being produced every year that end up being released into the environment. Some of them are recalcitrant to degradation, which causes their accumulation and the resulting pollution of soil and water bodies. Among the many novel technologies developed for the remediation of emerging contaminants, biochar is receiving increasing

Chapter 4

Paracetamol degradation pathways in soil after biochar addition
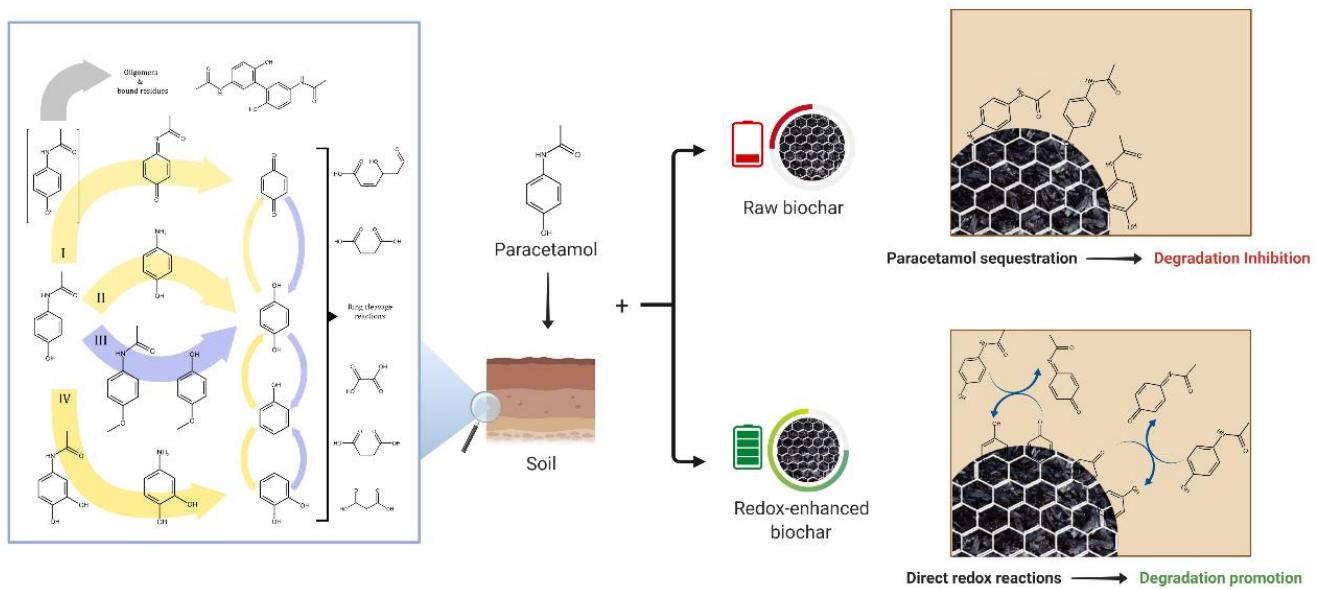
Chacón, F.J., Cayuela, M.L., Sánchez-Monedero, M.A., 2022. Paracetamol degradation pathways in soil after biochar addition. Environmental Pollution 307, 119546. https://doi.org/10.1016/j.envpol.2022.119546

Paracetamol degradation pathways in soil after biochar addition☆

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ABSTRACT

Little is known about the effect of biochar on the degradation of paracetamol in soil, considering the ubiquity of this pollutant in the environment. Given the importance of the electrochemical properties of biochar for contaminant remediation, we investigated the influence of raw and designer redox-active biochars on paracetamol degradation in soil. Metabolite quantification indicated that a minimum of 53% of the spiked paracetamol was transformed in biochar-amended soil, resulting in the accumulation of different degradation products. The identification of these products allowed us to chart paracetamol degradation pathways in soil with and without biochar amendment. Some of the major degradation routes were observed to proceed via catechol and phenol, despite being previously described as having only a minor role in paracetamol metabolism. Additionally, a new transformation route from paracetamol to NAPQI was discovered in anaerobic soil originating from direct redox reactions on the surface of the designer biochars. These results may contribute to change our understanding of the environmental fate of paracetamol in soil and the role of biochar in its biodegradation.

1. Introduction

The increasing abundance and variety of emerging contaminants represents an environmental threat. Paracetamol, also known as acetaminophen (ACT), is one of the most consumed medications around the world (Hider-Mlynarz et al., 2018; Lalic et al., 2018). It is also present in combination with other pharmaceuticals in more than 600 different prescription medicines and commonly used in veterinary practices (FDA, 2020; Livingston, 2010). Despite the toughening environmental and waste management regulations in the pharmaceutical and agro-food industry, ACT is frequently detected in water, sediments, sewage sludge and soil (Wu et al., 2012). Water concentrations are highly variable, with reported values ranging from a few micrograms up to 461 $\mu g\ L^{-1}$ (Kleywegt et al., 2019; Masoner et al., 2014; Phong Vo et al., 2019). Data on the presence of ACT in contaminated soil is scarce (Pérez Solsona, S., Montemurro, N., Chiron, S., Barceló, 2021), although the typical concentrations found are lower than 100 $\mu g\ kg^{-1}$ (Ashfaq et al., 2017; Ek Henning et al., 2020). However, the initial concentration of ACT at the moment of contamination is probably much higher, given its relatively fast binding to soil and degradation (Li et al., 2014). Furthermore, ACT can accumulate in soils irrigated with wastewater (Kinney et al., 2006a). A common agricultural practice in many areas, especially arid and semi-arid agroecosystems (Singh, 2021). The application of biosolids

and manure to soil is another common source of ACT pollution (Ek Henning et al., 2020). ACT has been found in biosolid samples in concentrations up to 1400 $\mu g\ kg^{-1}$ (Kinney et al., 2006b), while contaminated animal manure derived from veterinary practices in animal farms is also frequently detected (Ek Henning et al., 2020).

Although studies about ACT toxicity to soil organisms and microbiota are severely lacking, ACT uptake and toxicity has been extensively researched for plants and aquatic organisms. ACT is known to cause oxidative stress to plants at concentrations as low as 1000 $\mu g\ kg^{-1}$ (Bartha et al., 2010; Kummerová et al., 2016; Türkoğlu et al., 2017), while reproductive disruption, DNA damage and oxidative stress are some of the most notable effects found in aquatic organisms (Guiloski et al., 2017; Oliveira et al., 2015; Solé et al., 2009). Furthermore, some ACT metabolites present a higher toxicity than the parent compound (Macherey and Dansette, 2008), making its remediation a priority. Despite the high removal efficiencies of many municipal wastewater and biosolid treatment plants (Żur et al., 2018), the continuous presence of ACT in the environment proves them insufficient, supporting the need for in-site remediation strategies (Yang et al., 2021b).

Biochar, the product of the pyrolysis of biomass, is increasingly being considered as a promising material for soil and water remediation (Qiu et al., 2022; Yang et al., 2021a; Zama et al., 2018). It has been successfully applied for both organic and inorganic contaminant removal

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General Discussion

Among the broad range of environmental applications where biochar characteristics are able to contribute, soil remediation is one of the most promising fields. Biochar amendment has been proven beneficial in soil contaminated with organic pollutants, where it can increase adsorption and promote their transformation (Hu et al., 2020). The ability of biochar to transfer and store electrons seems to play a key role in this last process (Yuan et al., 2017). Unfortunately, biochars obtained from different feedstocks and pyrolysis conditions vary significantly in their physical and chemical properties, which makes it difficult to obtain consistent results (Guo et al., 2020). The lack of research on enhancing and controlling these properties could be delaying the use of biochar in many areas. To fill this knowledge gap, the main objective of the thesis was to obtain biochars with tailored electrochemical properties able to promote contaminant remediation in soil. The first chapter reviewed the current knowledge on how these properties originate and proposed several methods to optimize them, which were experimentally tested in chapter 2 to obtain a range of biochars with different electrochemical properties. These biochars were then applied to soil in chapter 3 in order to examine their effect on contaminant remediation, identify which combination of properties are more suitable for the transformation of pollutants and understand their role in this process.

Production of designer biochars with enhanced electrochemical properties

The literature review revealed that the redox capacity and conductivity of biochar are the electrochemical properties more relevant to soil remediation. Accordingly, optimization efforts must focus on the modification of these two properties. The redox capacity is assumed to originate mainly from quinoid/phenolic groups on the surface of biochar, followed by redox-active metals and radicals as minor contributors. Common biochar functionalization methods like the use of oxidizing agents or its doping with heteroatoms are among the most promising strategies to increase its redox-active functional groups. Additionally, pre-loading the feedstock with redox-active metals can influence the thermochemical conversion of biomass, favoring the creation of radicals and functional groups, which further benefits the redox capacity of biochar. In the case of conductivity, biochar needs to develop an interconnected aromatic network in order to be able to transfer electrons from one part of the material to another, with pyrolysis temperature and residence time playing a central role in this process.

The use of these and other strategies in chapter 2 created a collection of biochars with diverse electrochemical properties. Pyrolysis temperature was the most important production parameter, as it determined the initial number of functional groups and

graphitization of the biochar. 400 °C was the pyrolysis temperature with the higher redox capacity and redox-active functional groups, while the biochar pyrolyzed at 1000 °C had the highest conductivity. Unfortunately, a biochar with a high redox capacity and conductivity was not possible. A temperature of 400 °C was too low to develop a conductive network (with a conductivity 135 times lower than the biochar pyrolyzed at 1000 °C), while higher temperatures removed functional groups from biochar, reducing its redox capacity to a fraction of that obtained at lower temperatures. Although usually overlooked, storing conditions also had a significant effect on the redox capacity, as it determined the changes induced by aging. While no changes were seen after 20 months in a biochar stored in an inert atmosphere, the presence of oxygen increased the redox capacity of biochar with time.

When comparing biochars obtained from different lignocellulosic materials, the biochar with the highest redox capacity (orange tree pruning) was shown to have twice as much as the one with the lowest capacity (almond tree pruning). This supports the hypothesis that some of the inconsistent results of biochar application found in the literature are the consequence of the intrinsic variability in the electrochemical properties between biochars produced from different feedstocks. Although previous research suggested that the amount of cellulose, hemicellulose and lignin determined to some extent the type and concentration of functional groups, we found no significant relationship between the redox capacity and the lignocellulosic fractions. Instead, ash content was the characteristic correlated with the redox capacity. During pyrolysis, the presence of metal ions can promote certain depolymerization pathways that favor the generation of functional groups, which was probably the case here.

The use of oxidizing agents was the most effective strategy to increase the redox capacity of biochar. Modified Hummer's Method (MHM) and a simple oxidative treatment with $KMnO_4$ were the most successful among them, multiplying the initial redox capacity by three. Functionalization methods reduced conductivity by preventing the transfer of electrons between conductive sheets. Although it was not possible to create a biochar with both a high redox capacity and conductivity, a balanced biochar with a moderate amount of both properties was produced by treating a highly conductive biochar with $KMnO_4$. The synergy between these properties is expected to increase its electron shuttling ability, which can give it and advantage in soil processes related to contaminant degradation such as microbial electron shuttling.

The addition of redox-active metals (Mn and Fe) prior to pyrolysis was also a successful method in increasing the redox capacity of the resulting biochar, although less than the oxidative treatments. In all cases (raw and modified biochars), the redox capacity

of biochar had a clear linear relationship with the presence of C-OH (electron donation) and C=O (electron acceptance) groups on the surface of biochar. Biochars with pre-loaded metals, however, showed a higher electron donating capacity then was to be expected according to their atomic percentages of functional groups. This supports the existence of redox-active forms of the metal on the surface of biochar, which was confirmed by XRD.

The specific redox capacity and conductivity of the designer biochars will still depend to some extent on the type of feedstock used, but the treatments and the pyrolysis conditions proposed here will allow to create biochars with the desired characteristics and able to surpass their initial limitations.

Promoting contaminant remediation in soil

Once the production of designer biochars with a wide range of electrochemical properties was achieved, the next step was to examine their effect on contaminant remediation in soil. In chapter 3, soil was amended with nine different biochars and contaminated with pentachlorophenol (PCP), both in aerobic and anaerobic conditions. PCP is a persistent pesticide with a simple structure and a straightforward transformation mechanism (reductive dechlorination, where chlorines are removed one by one). Furthermore, electron shuttling plays a key role in this transformation (Yu et al., 2015), which makes it the perfect model pollutant to study for our purposes. Treatments were performed on a biochar pyrolyzed at 400 ºC (B-400) and named after their respective treatment (B-Fe, B-H$_2$O$_2$, B-H$_3$PO$_4$, B-HNO$_3$, B-KMnO$_4$ and B-KOH), except B-1000-KMnO$_4$, a balanced biochar with both moderate redox capacity and conductivity obtained by treating a biochar pyrolyzed at 1000 ºC (B-1000) with KMnO$_4$.

In aerobic conditions, all biochars (both raw and modified) were able to greatly increase PCP remediation compared to unamended soil. The high redox potential of aerobic soil is not appropriate for microbial reductive dechlorination, the main pathway of PCP degradation. Biochar could promote this process by acting as an electron donor for the halogenic bacteria that use PCP as a terminal electron acceptor. In these conditions, even the biochars with moderate redox capacities were enough to enhance remediation. The most successful were B-KMnO$_4$ (the biochar with the highest redox capacity), B-Fe (pre-loaded with Fe) and B-1000-KMnO$_4$ (balanced biochar), which were able to virtually eliminate all of the extractable pollutant from soil. Conversely, in the anaerobic soil many of the biochars inhibited remediation, including both unmodified biochars (B-400, B-1000, B-H$_2$O$_2$ and B-H$_3$PO$_4$). In these conditions, the low reduction potential led to a high level of degradation even in the unamended soil.

The high PCP adsorption shown by most biochars might be able to sequester the contaminant, preventing the contact between PCP and microorganisms and inhibiting its reduction. However, in our case three of the four biochars with the highest adsorption (B-$KMnO_4$, B-HNO_3 and B-Fe) were among the amendments with the highest remediation levels. The exception, B-H_3PO_4, had no conductivity, was the modified biochar with the lowest redox capacity, and had one of the lowest atomic percentages of C-OH and C=O functional groups. This supports the hypothesis that PCP can be abiotically reduced on the surface of biochar, probably by its interaction with electron-donating functional groups, radicals and redox-active metals. The result was the inhibition in the anaerobic incubation of those biochars possessing high PCP adsorption, but low number of redox-active functionalities or metals (such as B-400, B-1000, B-H_2O_2 and especially B-H_3PO_4). To increase remediation under these conditions, a large number of redox-active groups would be needed. This was precisely the case for B-$KMnO_4$ and B-Fe, the only biochar amendments that significantly increased PCP remediation in anaerobic soil. Conductivity could overcome this problem to some extent by transferring electrons from one part of the biochar to another, which explains the faster and more complete remediation of the conductive B-1000-$KMnO_4$ compared to the non-conductive B-400 in aerobic soil, even though they have similar redox capacities.

Biochars with higher redox capacities showed a faster and more complete remediation than other biochars. There was a significant linear correlation between redox capacity and the maximum rate of remediation for non-conductive biochars (except B-Fe). Conductive biochars (B-1000 and B-1000-$KMnO_4$), on the other hand, presented rates of remediation much higher than those predicted from their redox capacity. However, their levels of PCP remediation were lower than biochars with higher redox capacities. Although PCP reduction can be facilitated by the fast long-range electron transfer through the conductive network, the amount of transformed PCP would still depend in the end on the electron donating capacity of biochar. Another special case was B-Fe, whose rate of remediation was particularly slow in aerobic conditions probably due to the conversion of Fe(II) to Fe(III) by oxygen.

Previous research on this pollutant showed inconsistent effects after biochar addition, from degradation promotion to inhibition (Tong et al., 2014; Xu et al., 2020; Zhu et al., 2020). The results of this chapter demonstrated that biochar modification in order to enhance its electrochemical properties is an adequate strategy to overcome not only the inherent variability of these properties, but also the limitations of the biochar and the soil itself. In chapter 4, the role of the designer biochars in the degradation of organic pollutants was examined on a deeper level, mapping the transformation pathways of an

emerging contaminant to evaluate how their electrochemical properties can affect these routes. Paracetamol (ACT) was chosen as a pollutant, due to its redox-active nature and ubiquity in the environment, being one of the most consumed pharmaceuticals in the world. Considering the previous experience with PCP, besides the raw biochars (B-400 and B-1000) only the most promising modification methods were tested, including B-Fe, B-1000-KMnO$_4$ and B-KMnO$_4$.

Unlike the case with PCP, soil without biochar was able to completely degrade ACT in both incubations, but was still faster in aerobic conditions (32 vs 60 days). The amendment with raw biochars resulted in an inhibitory effect, which was much more pronounced for B-400 than B-1000. The high adsorption of the biochars was the most likely cause, which immobilized the pollutant and prevented its transformation. The conductive network of B-1000 could solve this bioavailability problem to some extent by transferring electrons from one part of the material to another, which explains its lower inhibition. Thus, the absence of conductivity of biochars pyrolyzed at relatively low temperatures could pose a potential risk to the environment during the first weeks after contamination, at least for those not modified. Biochar modification greatly increased the rate of ACT transformation, especially in the case of B-1000-KMnO$_4$, thanks to the synergism between conductivity and redox capacity. Although B-Fe had one of the highest kinetics of degradation in aerobic conditions, it presented an inhibitory effect similar to B-400 in the anaerobic incubation, probably due to the transformation of Fe(III) to Fe(II) caused by low soil redox potential. As was the case with PCP, two of the biochars with the higher adsorption (B-KMnO$_4$ and B-1000-KMnO$_4$) showed higher degradation compared to those with a lower adsorption (B-Fe and B-400). The hypothesis that ACT can be directly transformed on the surface of biochar was confirmed by electrochemical analysis, which revealed the existence of electron transfer from ACT to biochar in solution.

A total of 11 different metabolites (plus ACT) were detected in soil after extraction. Although previous research had proposed permanent binding to soil as the primary fate of ACT, its transformation to other metabolites was the main remediation mechanism in soil amended with designer biochars. ACT degradation through *p*-aminophenol and hydroquinone is the dominant pathway described in most of the literature. Although also present here, catechol and phenol were the main degradation products under aerobic and anaerobic conditions, respectively, accumulating prior to their ring opening reactions. This shows the intrinsic variability of microbial communities between different soils. As expected from their faster kinetics of remediation, the appearance of transformation metabolites and their peaks occur several

days earlier in soils amended with designer biochars than the rest.

Based on the identified metabolites, 4 main degradation pathways were proposed, including hydroxyl oxidation, deacetylation, hydroxylation and methylation. The first three pathways were favored by the presence of oxygen, which was what led to a faster transformation in these conditions. Methylation, on the other hand, was the main pathway in the anaerobic incubation. Hydroxyl oxidation led to the formation of NAPQI, with a much higher toxicity than the parent compound. Although in the unamended soil NAPQI appeared only under aerobic conditions, in soils amended with designer biochars NAPQI production appeared in both incubations and with much higher concentrations. This was probably due to the direct oxidation of ACT on the surface of biochar, which opened a new degradation pathway under anaerobic conditions, allowing the enhanced biochars to promote ACT transformation.

References

Guo, M., Song, W., Tian, J., 2020. Biochar-facilitated soil remediation: Mechanisms and efficacy variations. Frontiers in Environmental Science 8. https://doi.org/10.3389/fenvs.2020.521512

Hu, B., Ai, Y., Jin, J., Hayat, T., Alsaedi, A., Zhuang, L., Wang, X., 2020. Efficient elimination of organic and inorganic pollutants by biochar and biochar-based materials. Biochar 2, 47–64. https://doi.org/10.1007/s42773-020-00044-4

Igalavithana, A.D., Ok, Y.S., Usman, A.R.A., Al-Wabel, M.I., Oleszczuk, P., Lee, S.S., 2015. The effects of biochar amendment on soil fertility. SSSA Special Publications 123–144. https://doi.org/10.2136/sssaspecpub63.2014.0040

Tong, H., Hu, M., Li, F.B., Liu, C.S., Chen, M.J., 2014. Biochar enhances the microbial and chemical transformation of pentachlorophenol in paddy soil. Soil Biology and Biochemistry 70, 142–150. https://doi.org/10.1016/j.soilbio.2013.12.012

Xu, Y., Liu, J., Cai, W., Feng, J., Lu, Z., Wang, H., Franks, A.E., Tang, C., He, Y., Xu, J., 2020. Dynamic processes in conjunction with microbial response to disclose the biochar effect on pentachlorophenol degradation under both aerobic and anaerobic conditions. Journal of Hazardous Materials 384, 121503. https://doi.org/10.1016/j.jhazmat.2019.121503

Yu, L., Yuan, Y., Tang, J., Wang, Y., Zhou, S., 2015. Biochar as an electron shuttle for reductive dechlorination of pentachlorophenol by *Geobacter sulfurreducens*. Scientific Reports 5. https://doi.org/10.1038/srep16221

Yuan, Y., Bolan, N., Prévoteau, A., Vithanage, M., Biswas, J.K., Ok, Y.S., Wang, H., 2017. Applications of biochar in redox-mediated reactions. Bioresource Technology 246, 271–281. https://doi.org/10.1016/j.biortech.2017.06.154

Zhu, M., Lv, X., Franks, A.E., Brookes, P.C., Xu, J., He, Y., 2020. Maize straw biochar addition inhibited pentachlorophenol dechlorination by strengthening the predominant soil reduction processes in flooded soil. Journal of Hazardous Materials 386, 122002. https://doi.org/10.1016/j.jhazmat.2019.122002

Conclusions

The main results obtained in this thesis can be summarized in the following general conclusions:

1. It was demonstrated the possibility of controlling the redox properties of biochar by modifying the nature and number of functional groups and redox-active metals on its surface. The redox capacity shows a lineal relationship with the number of C-OH and C=O functional groups.

2. Modulating the conductivity of biochar involves adjusting pyrolysis temperature. Achieving an increased conductivity requires pyrolysis temperatures higher than 600ºC, which unfortunately decreases the redox capacity of biochar. A middle ground between the two properties can be found by treating a highly conductive biochar pyrolyzed at a HTT of 1000 ºC with $KMnO_4$.

3. Modifying the electrochemical properties of biochar is a suitable strategy to enhance the remediation of different contaminants in both aerobic and anaerobic soil. This strategy can not only overcome the limitations of the raw biochar, but also of the soil itself. Furthermore, problems arising from the variability in the electrochemical properties of biochars obtained from different feedstocks are reduced, as these properties can be adjusted and optimized to the required level depending on the pollutant and soil conditions.

4. For soils limited in their ability to degrade a contaminant due to the redox potential of the soil, redox-enhanced biochars are the best option for amendment, as they can promote a faster and more complete remediation. For those not limited, hybrid biochars with both a moderate redox capacity and conductivity are more suitable, achieving superior kinetics of remediation.

5. Although preloading biomass with redox-active metals is a successful strategy to enhance the redox capacity of biochar, in certain conditions they can have a negative impact on contaminant degradation. Depending on the redox behavior of the contaminant, the presence of oxygen or a high soil redox potential can transform the metal to an oxidation state that inhibits its remediation. The rest of designer biochars had similar behaviors in both aerobic and anaerobic conditions.

6. Different contaminants such as pentachlorophenol and paracetamol can be abiotically transformed on the surface of biochar by their interaction with the redox-active components of biochar. In this case, a high adsorption would increase remediation for those modified biochars with a high redox capacity and/or redox metals, while it would

be detrimental to those with low or moderate redox capacities.

7. In the absence of modification, the lack of conductivity of biochars pyrolyzed at relatively low temperatures (< 700ºC) could result in a higher potential environmental risk during the first weeks after contamination. This is due to the reduced bioavailability of the contaminant caused by the high adsorption of biochar, which can immobilize it and prevent its contact with microorganisms and other parts of the biochar.

8. Biochar amendment can modify and add new transformation pathways during the degradation of redox-active contaminants in soil, with its electrochemical properties having a direct role in this outcome.