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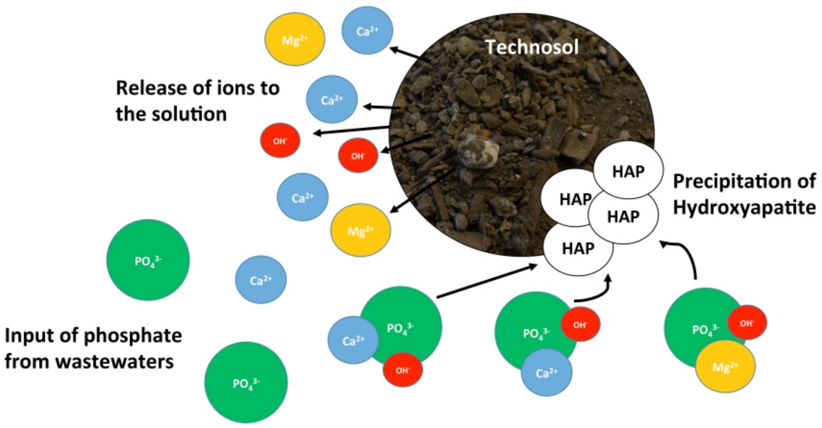
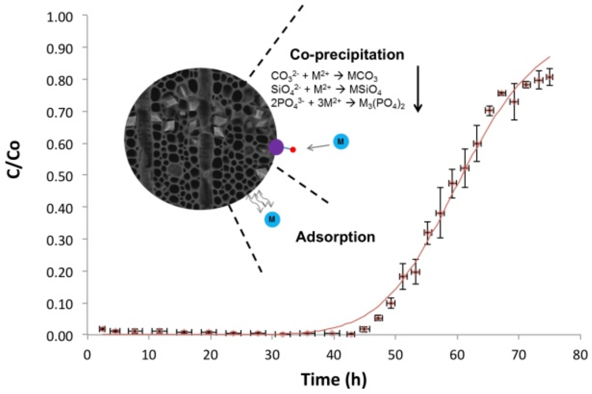
DEPARTAMENTO DE EDAFOLOGIA
Y QUIMICA AGRICOLA

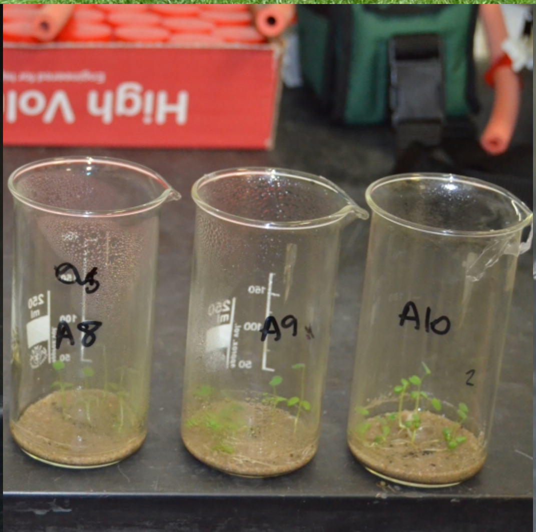
RECUPERACIÓN DE SUELOS CONTAMINADOS CON ANIONES POTENCIALMENTE TÓXICOS Y METALES PESADOS MEDIANTE TECNOSOLES Y BIOCARBONES ADSORBENTES.





DIEGO ARAN FERREIRO

Santiago de Compostela, Septiembre 2017

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Recuperación de suelos contaminados con aniones potencialmente tóxicos y metales pesados mediante Tecnosoles y biocarbones adsorbentes

Recuperación de solos contaminados con anións potencialmente tóxicos e metais pesados mediante Tecnosoles e biocarbóns adsorbentes

Application of Technosols and biochar adsorbents for the recovery of soils contaminated by potentially toxic anions and heavy metals

DIEGO ARAN FERREIRO

Santiago de Compostela, en setembro de 2017

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CERTIFICAN:

Que la presente memoria, titulada "*Recuperación de Suelos Contaminados con Aniones Potencialmente Tóxicos y Metales Pesados Mediante Tecnosoles y Biocarbones Adsorbentes*", realizada por el doctorando Diego Arán Ferreiro para optar al grado de Doctor, reúne todos los requisitos y condiciones necesarias como trabajo de Tesis doctoral.

Y para que conste, dan el visto bueno para su presentación ante la Comisión de Doctorado del Programa de Doctorado en Medio Ambiente y Recursos Naturales de la Universidad de Santiago de Compostela.

En Santiago de Compostela, a 20 de septiembre de 2017.

Dr. Felipe Macías Vázquez　　　　Dr. Juan Antelo Martínez


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A mi familia


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RESUMEN

Las actividades antrópicas generan numerosos impactos sobre suelos y aguas a través del aporte de contaminantes, tanto inorgánicos como orgánicos, que ocasionan un riesgo para la salud humana y para el medioambiente. Los contaminantes inorgánicos constituyen un gran problema ya que no se pueden degradar, se acumulan en los diferentes compartimentos de los ecosistemas y pueden transferirse y bioacumularse a lo largo de la cadena trófica. Algunos elementos considerados macronutrientes o micronutrientes esenciales para los organismos (Cu, Co, Zn, P,…) a elevadas concentraciones pueden presentar un efecto tóxico, o generar cambios importantes en las dinámicas poblacionales, alteraciones en las funciones y propiedades del suelo, así como modificar los ciclos biogeoquímicos.

Las actividades mineras se encuentran entre aquellas actividades humanas con una mayor importancia económica y social, si bien también generan un mayor impacto al medioambiente. Dentro de este tipo de actividades se encuentran las actividades extractivas de carbón, minerales o rocas. En las últimas décadas se ha desarrollado una mejora en las técnicas de extracción y procesamiento, aunque el impacto generado por este tipo de actividades continúa siendo importante. Los impactos derivados de estas actividades pueden ser directos, como la pérdida del terreno o pérdida de las funciones ecológicas, o indirectos, como la contaminación de los dos compartimentos más sensibles, el aire y el agua, así como una pérdida de la biodiversidad. La magnitud y tipo de impacto es dependiente de numerosos factores entre los que se incluyen el material geológico, la técnica de extracción, los tamaños de partícula, el contenido en materiales reactivos y las condiciones ambientales.

Para mitigar o atenuar estos impactos sobre suelos y aguas existen numerosas técnicas, tanto *ex situ* como *in situ*, siendo estas últimas las más empleadas para la descontaminación de grandes superficies. Dentro de las técnicas de recuperación destacan las que emplean correctivos químicos o enmiendas, como la adición de materia orgánica, materiales alcalinos, biocarbones o materiales pirogénicos, nanopartículas, y Tecnosoles. También se puede destacar la utilización de las fitotecnologías, en especial la fitoestabilización. Todas estas medidas correctoras o tecnologías presentan ciertas ventajas o desventajas, siendo su empleo y modo de aplicación dependientes, entre otros factores, del tipo y concentración de contaminante, o de las condiciones del medio (pH, Eh, conductividad eléctrica,…).

Actualmente, la búsqueda y evaluación de tecnologías de bajo coste, elevada efectividad y que promuevan aspectos de la economía circular, son puntos clave a tener en cuenta en los procesos de recuperación ambiental. Teniendo en cuenta estos aspectos el objetivo principal de esta Tesis Doctoral fue evaluar la eficacia del empleo de Tecnosoles y biocarbones en la recuperación ambiental de suelos y aguas en zonas contaminadas por la presencia de contaminantes inorgánicos. Para llevar a cabo esta evaluación y entender cuál es el comportamiento de estos materiales ante contaminantes inorgánicos (cationes y aniones) se propusieron los siguientes objetivos específicos:

i. Caracterizar el estado ambiental de los suelos y aguas de un sistema minero, determinando las principales afecciones al medio y sus limitaciones de recuperación, lo que permitirá establecer metodologías de recuperación ajustadas a cada problema específico.

ii. Determinar las características físico-químicas y mecanismos que intervienen en la inmovilización de cationes metálicos en biocarbones, tanto en sistemas en discontinuo como en sistemas en continuo típicos para el tratamiento de aguas.

iii. Evaluar la capacidad de Tecnosoles con propiedades ándicas para la eliminación de fosfato en sistemas acuosos bajo diferentes condiciones del medio y operacionales, con el fin de determinar su aplicabilidad en condiciones de campo, a través humedales reactivos o barreras geoquímicas.

iv. Analizar la eficacia de un Tecnosol ándico-eutrófico en la recuperación de las características físicas, químicas y biológicas de los materiales de una escombrera con contaminación polimetálica, así como de la calidad química de los lixiviados generados tras 20 meses de aplicación en condiciones de campo y determinar la disminución del efecto ecotoxicológico.

v. Establecer pautas metodológicas para la gestión y mitigación de los impactos generados por aniones u otros elementos tóxicos en los sistemas superficiales.

Para cubrir los objetivos propuestos en esta Tesis Doctoral se realizaron una serie de estudios que se resumen a continuación junto con sus principales resultados. En el primer estudio realizado se determinó la calidad ambiental de los suelos y las aguas de la mina Fé, en Saelices el Chico (Salamanca, España), evaluando la situación inicial y las alternativas de recuperación (Capítulo 2). Para ello, se recogieron en el área minera muestras de suelos desarrollados sobre diferentes residuos de mina y rocas encajantes en diferentes proporciones, suelos naturales de la zona adyacente a la mina (usados como control) y las aguas provenientes de las escombreras. Las muestras de suelos fueron analizadas químicamente, determinando su calidad y riesgo, y clasificadas taxonómicamente. Por otra parte se determinaron las características y propiedades clave para la recuperación tanto de los suelos de mina como de los suelos naturales, estableciendo además una comparación entre ambos. Las aguas fueron caracterizadas químicamente para evaluar su calidad y grado de contaminación, así como su comportamiento evolutivo a través del análisis termodinámico. Los resultados del análisis de las muestras de suelo mostraron que los suelos de la mina presentan contenidos de materia orgánica muy bajos, con reacciones predominantemente ácidas y elevadas concentraciones totales de elementos potencialmente tóxicos que pueden generar un elevado riesgo para el ecosistema y la salud humana. Estos suelos fueron clasificados como diferentes Tecnosoles espólicos (sulfúricos, sálicos o háplicos), Tecnosoles úrbicos y ekranicos. Por otro lado, los suelos naturales adyacentes a la mina mostraron una gran influencia antrópica, como consecuencia de la actividad minera cercana u otras actividades de uso intensivo (ganadería y agricultura). Estos suelos se clasificaron como Leptosoles (líticos o háplicos) o Cambisoles (lépticos o háplicos), siendo su horizonte más evolucionado un horizonte B de tipo cámbico, con escaso espesor y bajo grado de evolución químico-mineralógico, en el que predominan las fases sólidas heredadas del material de partida.

Las aguas de mina analizadas son hiperácidas, hiperconductoras e hiperoxidantes. Presentan una composición química variable a lo largo del año, debido a las variaciones hidrológicas estacionales, aunque siempre se caracterizan por sus elevadas concentraciones de sulfatos y distintos elementos potencialmente tóxicos (Al, Cd, Mg, Fe y Mn). Los resultados de la modelización termodinámica, llevados a cabo mediante el programa PHREEQC, indicaron que la mayoría de los metales están formando pares iónicos con el sulfato, siendo este anión el que regula la química de estas aguas. Como resultado de la alteración de los sulfuros se origina una fuerte acidez, además de la presencia de especies iónicas de gran toxicidad Al^{3+}, Mn^{2+}, Zn^{2+}, Ni^{2+} y Cu^{2+}.

Teniendo en cuenta las condiciones limitantes en los suelos y las aguas de la mina y su entorno, es imprescindible actuar sobre estos suelos antrópicos reduciendo la oxidación de los sulfuros y mejorando la fertilidad. El principal objetivo debe ser establecer una cobertura vegetal y estimular los procesos de edafogénesis y biogeoquímicos asociados, como por ejemplo el ciclo de los nutrientes, que consecuentemente permitirán la mejora de la calidad físico-química de las aguas.

En el **Capítulo 3** se evalúa la idoneidad de diferentes biocarbones para la eliminación de contaminantes catiónicos de efluentes acuosos. El metal considerado para este estudio fue el cobre. Para ello se realizaron ensayos en *batch* (sistemas en discontinuo) con seis biocarbones derivados de diferentes residuos: gallinaza, acacia, eucalipto, maíz, residuo de oliva y cascara de arroz. Estos biocarbones, obtenidos por pirolisis a 300-400 ºC, fueron caracterizados físico-químicamente para determinar los parámetros que influyen en la retención del cobre, así como los principales mecanismos de reacción. Los resultados mostraron que los diferentes biocarbones estudiados presentan una buena retención de cobre y que esta capacidad está condicionada principalmente por mecanismos de adsorción, precipitación o co-precipitación. La capacidad de retención de los biocarbones está directamente relacionada con la relación O/C, el contenido de P y el contenido de cenizas que presentan estos materiales. La secuencia de retención de cobre para los diferentes biocarbones fue la siguiente: biocarbón de cascara de arroz > biocarbón de gallinaza > biocarbón de residuo de oliva > biocarbón de acacia > biocarbón de eucalipto > biocarbón de maíz. Además, la distribución de este contaminante en las diferentes fases (Cu-Biocarbón, Cu-C orgánico disuelto y Cu^{2+}) es también dependiente de la naturaleza del biocarbón, siendo este un criterio de selección importante a tener en cuenta para el empleo de estos materiales para la descontaminación de aguas. También se evaluó el efecto del pH del medio sobre la retención de cobre, determinándose que la capacidad de retención aumenta con el aumento de pH, independientemente del material de partida empleado para la elaboración del biocarbón.

La evaluación de la eficacia de los biocarbones en sistemas en continuo (Capítulo 4), para simular su empleo en barreras reactivas o columnas de lecho fijo, se llevó a cabo con biocarbones derivados de diferentes materias primas: gallinaza, eucalipto, maíz, residuo de oliva y serrín de pino. En primer lugar se analizó el efecto que tiene el flujo de entrada del influente (2.5, 5.0, 7.0 y 13 mL min^{-1}) sobre la capacidad de retención de cobre en el biocarbón de maíz. Este parámetro presenta una fuerte influencia, ya que se observa una disminución en la retención de cobre, desde 5.51 hasta 3.48 mg Cu g^{-1}, cuando el flujo decrece de 13 a 2.5 mL min^{-1}, respectivamente. Se evaluó, a flujo constante (7 mL min^{-1}), la capacidad de retención de los diferentes biocarbones, utilizando para ello el modelo empírico modificado de Bohart-Adams. Se obtuvo así un rango en la capacidad de retención de cobre entre ~1.3 y 26 mg Cu g^{-1}, siguiendo la secuencia: biocarbón de gallinaza > biocarbón de residuo de oliva >> biocarbón de maíz > biocarbón de serrín de pino. Además, se determinó que las características físico-químicas de los biocarbones determinaban su capacidad de retención de cobre y los mecanismos de inmovilización del mismo. Los biocarbones que presentan elevados contenidos en cenizas son aquellos que presentan una mayor capacidad de retención del cobre, pudiendo de esta forma ser los más adecuados para su empleo en sistemas de tratamiento de aguas para la eliminación de cationes metálicos. Por último, se relacionaron los parámetros de sorción obtenidos aquí con los parámetros obtenidos previamente para sistemas en discontinuo (Capítulo 3), existiendo una buena correlación entre ambos. Esta buena correlación entre parámetros nos permitiría predecir el comportamiento de distintos biocarbones y optimizar las condiciones operacionales con un número mínimo de ensayos de sorción.

En el Capítulo 5 se determinó la eficacia del empleo de Tecnosoles con propiedades ándicas para la eliminación de fosfato en aguas. Para ello se realizaron en primer lugar ensayos en discontinuo o *batch*, de tal forma que se puedan simular situaciones con mayores tiempos de contacto entre el efluente acuoso y el Tecnosol. Este tipo de situaciones serán similares a las encontradas en humedales y en sistemas que emplean barreras geoquímicas reactivas. En los ensayos en *batch* se determinó la cinética de retención, el efecto del pH (de

4 a 9) y el efecto de la presencia de diferentes aniones (bicarbonato, sulfato, cloruro, cromato y molibdato) sobre la retención de fosfato. Los resultados de estos ensayos indicaron que los mayores porcentajes de retención de fosfato se encuentran a valores de pH elevados. El mecanismo principal de eliminación del fosfato a valores de pH por encima de 7 es la precipitación (como fases sólidas de Ca-P), lo cual fue corroborado mediante cálculos termodinámicos utilizando el PHREEQC. Para ello se obtuvieron los índices de saturación para las distintas fases sólidas de Ca-P: hidroxiapatita, $Ca_3(PO_4)_2$ (beta), $Ca_4H(PO_4)_3 \cdot 3H_2O$, $CaHPO_4$ y $CaHPO_4 \cdot 2H_2O$. Por otro lado, a valores de pH entre 4 y 6 el mecanismo principal de retención de fosfato sobre el Tecnosol es la adsorción superficial, si bien no se puede descartar la precipitación superficial. La capacidad de retención del fosfato varió en relación al anión presente en el medio y a las condiciones de pH del mismo. A pH 4, la presencia de bicarbonato, sulfato o cloruro no modificó la capacidad de retención del Tecnosol. Sin embargo, la presencia de cromato provocó un incremento de la retención de fosfato en más de un 50 %, mientras que la adición de molibdato produjo una fuerte reducción en la capacidad de retención de fosfato al competir ambos iones por la superficie del Tecnosol. Por otro lado, a pH 9 se observó que la presencia del sulfato, cloruro y cromato no afecta a la retención de fosfato, mientras que la presencia de molibdato (> 0.1 M) produce la reducción del fosfato, aunque en menor medida que a pH ácido. La presencia del bicarbonato conlleva una importante reducción de la capacidad de retención del fosfato debido a la competencia bicarbonato-fosfato.

En este **Capítulo 5** también se llevaron a cabo ensayos en continuo mediante columnas de lecho fijo, evaluando el efecto de diferentes variables: flujo de influente, tamaño de la capa reactiva, pH de la disolución del influente y reutilización del material. La concentración de fosfato inmovilizado en el Tecnosol se calculó utilizando el modelo empírico modificado de Bohart-Adams. El incremento del flujo produjo una reducción en los tiempos de ruptura y de saturación, así como en las cantidades de fosfato retenidas por el Tecnosol, pasando de 6.19 mg PO_4 g^{-1} a un flujo de 1.5 mL min^{-1} a 2.37 mg PO_4 g^{-1} a un flujo de 5 mL min^{-1}. Tiempos de contacto mayores favorecen los procesos de sorción (adsorción superficial, precipitación o precipitación superficial) y consecuentemente mayores capacidades de retención del Tecnosol. Una reducción de la cantidad de Tecnosol a la mitad (de 11.20 g a 5.60 g), manteniendo las demás variables constantes (pH, flujo), conlleva una reducción del 65 % en el tiempo de ruptura y una reducción del 14 % en la cantidad de fosfato retenido.

Por otra parte, la capacidad de retención del Tecnosol se vio incrementada de 2.37 a 6.21 mg PO_4 g^{-1} cuando el pH del influente disminuyo de 5.5 a 3.0, A pH < 6.0 el mecanismo principal de retención es la adsorción superficial, siendo este proceso favorable a valores de pH ácidos. Por último se evaluó la posible reutilización del Tecnosol a través de varios ciclos de sorción-desorción. Tras el primer ciclo, el Tecnosol pierde una efectividad de un 40 % en la retención de fosfato, sin embargo posteriores ciclos no producen un efecto adicional y la capacidad de retención se mantiene constante. Esto permite concluir que el Tecnosol puede ser reutilizado después en sistemas de tratamiento de aguas después de un ciclo de lavado y con los lixiviados del lavado se podría generar un fertilizante líquidos, además cuando se sature el Tecnosol, éste se podría reciclar como una enmienda rica en fosfato.

En el **Capítulo 6**, se presenta un estudio en el que se evalúa, a nivel físico-químico, biológico y ecotoxicológico, la eficiencia de un Tecnosol con propiedades ándicas y eutróficas para la rehabilitación de escombreras compuestas por una mezcla de materiales ricos en sulfuros y rocas encajantes. Para ello, en la mina Fé (Saelices el Chico, Salamanca) se estableció un ensayo piloto en el que se aplicó sobre una escombrera una capa de 20 cm de Tecnosol (en un área de 625 m^2). Transcurridos 20 meses de la aplicación se recogieron muestras del Tecnosol, de la escombrera recuperada (situada bajo la capa de Tecnosol), y de la escombrera sin recuperar. Las muestras fueron analizadas, determinando los elementos en la fracción total (agua regia), la fracción disponible (soluble + intercambiable) y los lixiviados simulados. A nivel biológico se determinó la actividad de cuatro enzimas (deshidrogenasa, β-glucosidasa, fosfatasa ácida y ureasa), las cuales indican el estado de la comunidad microbiana y su vez están involucradas en los ciclos de C, P y N. Además, la calidad y capacidad metabólica de las distintas comunidades microbianas se determinó mediante cambios en las concentraciones de CO_2 y CH_4, llevando a cabo para ello un análisis de la respirometría del suelo en continuo durante 450 horas. Por último, a nivel ecotoxicológico se evaluaron los distintos materiales y sus correspondientes lixiviados empleando dos plantas basadas en las recomendaciones ISO que se emplean habitualmente en las mezclas de semillas para revegetación, *Lollium perenne* L. y *Trifolium pratense* L. Para ello, se realizaron tres bioensayos: test de papel de filtro, test hidropónico y test de suelo, en condiciones de cámara de germinación (25 ± 1 ºC; 16 horas luz + 8 horas oscuridad), así como ensayos de microcosmos en condiciones de invernadero. Para la evaluación en los bioensayos se determinaron aspectos visuales, tasa de germinación, elongación de la parte aérea y radicular, y biomasa seca, de semillas y de plántulas expuestas a los materiales y sus lixiviados. En el ensayo de microcosmos se evaluaron aspectos visuales, porcentaje de cobertura y biomasa seca de la parte aérea.

La caracterización de los materiales y de sus lixiviados mostró que la escombrera sin tratar presenta un riesgo ambiental considerable, debido a su pH (moderadamente ácido), carencia de estructura y altas concentraciones de diversos elementos potencialmente tóxicos, observándose diferencias significativas con la escombrera recuperada y con el Tecnosol. El efecto ecotoxicológico evaluado en la escombrera mediante los distintos bioensayos y para ambas especies no fue concluyente, mientras que el ensayo de microcosmos presentó diferencias, al inhibir la germinación del *Trifolium pratense* y limitar intensamente la germinación y desarrollo del *Lollium perenne*. La aplicación del Tecnosol mejoró significativamente las características físicas, químicas y biológicas de los materiales de escombrera (escombrera recuperada). Se observó una disminución en la concentración total de elementos potencialmente tóxicos (Co, Mg, Mn, Ni y Pb), entre un 17 y un 55 % dependiendo del elemento químico, y un incremento de la concentración de nutrientes, Ca y P. El contenido de materia orgánica y la concentración de nutrientes en los lixiviados y en la fracción disponible también aumento, lo que conlleva una mayor estimulación de las actividades microbianas y un buen desarrollo de ambas especies en los bioensayos y en el ensayo de microcosmos. El Tecnosol, tras 20 meses de aplicación sobre la escombrera, presentó características adecuadas para la rehabilitación de la escombrera, así como para asegurar las funciones ecológicas del medio y de cobertura vegetal. Por otra parte, el Tecnosol no presentó efectos ecotoxicológicos y el ensayo de microcosmos evidenció que el Tecnosol presenta potencial para la revegetación con pastos, si bien es necesario un análisis de los mismos para evaluar que no existe un riesgo para el consumo por los animales.

Como conclusiones generales de la tesis (Capítulo 7) se indica que el empleo de los Tecnosoles, tanto en laboratorio como en campo, constituye una solución tecnológica adecuada para la recuperación de suelos o escombreras contaminadas, revalorizando los mismos y contribuyendo con un aprovechamiento económico tras la recuperación. En aguas contaminadas, la utilización de Tecnosoles puede contribuir en la recuperación en sistemas estáticos, como los humedales, y en sistemas dinámicos, empleándolos como barreras geoquímicas reactivas. El empleo de biocarbones, como un material para el tratamiento de aguas contaminadas presentó una elevada eficiencia, tanto en sistemas en discontinuo como

en continuo. Su utilización representa una alternativa sostenible que puede emplearse en barreras geoquímicas y columnas de adsorción, o puede ser un constituyente reactivo de los Tecnosoles.

SUMMARY

Anthropogenic activities produce numerous impacts on soils and water system through the presence of inorganic and organic contaminants, which pose a risk to human health and the environment. Inorganic contaminants are a major problem since these compounds are non-degradable. They can be easily accumulated in the different compartments of the ecosystems and then transferred and bioaccumulated in the trophic chain. Some elements considered macronutrients or micronutrients for organisms (Cu, Co, Zn, P,...) may show a toxic effect at high concentrations, generate important changes in the population dynamics, produce alterations in soil functions and properties, and modify the biogeochemical cycles.

Among human activities, mining shows a high economic and social relevance, but also generates a greater impact on the environment. Extractive activities of coal, minerals or rocks are of major importance in mining. In the last decades, more efficient extraction techniques and processing operations has been developed, although the impact generated by mining activities is still important. These impacts can be direct, such as loss of land or decrease of ecological functions, or indirect, such as contamination of the two most sensitive compartments in the environment, air and water, or affection to biodiversity. The nature of the impact and its magnitude depends on numerous factors, including geological material, extraction technique, particle size, content of reactive materials and environmental conditions.

There are numerous techniques to mitigate or attenuate mining impacts on soils and water systems. These techniques can be *ex situ* or *in situ*, with the latter being the most common for decontamination of large areas. Among the remediation techniques, the most relevant are those employing chemical correctives or amendments, such as the addition of

organic matter, alkaline materials, biochars or pyrogenic materials, nanoparticles and Technosols. The use of phytotechnologies, especially phytostabilization, it is also relevant. All the technologies have advantages and disadvantages, and their use and application method depend, among other factors, on the nature and concentration of the contaminant, and the conditions of the medium (pH, Eh, electrical conductivity,...).

Nowadays, the use of low cost and highly effective technologies, promoting aspects of the circular economy, is key for an adequate environmental recovery processes. Taking into account these aspects, the main objective of this Doctoral Thesis was to evaluate the effectiveness of the use of Technosols and biochars for soil and water remediation in areas contaminated by the presence of inorganic contaminants. To assess and to better understand the behavior of these materials against inorganic contaminants (cations and anions), the following specific objectives were proposed:

i. To characterize the environmental status of soils and waters in a mining system, identifying the main contaminant factors and the limitations for the rehabilitation process. This will allow establishing an adequate remediation methodology to each specific problem.

ii. To determine the physico-chemical characteristics and mechanisms involved in the immobilization of metallic cations in biochars. This will be evaluated for water treatment in both discontinuous and continuous systems.

iii. To evaluate the ability of Technosols with andic properties for the retention of phosphate in aqueous systems under different environmental and operational conditions, in order to determine their applicability under field conditions in reactive wetlands or geochemical barriers.

iv. To analyze the efficiency of an andic-eutrophic Technosol in the rehabilitation of the physico-chemical and biological characteristics of mine tailings with polymetallic contamination and of the chemical quality of the leachates generated. To determine the potential decrease of ecotoxicological effects after 20 months of application under field conditions.

v. To establish methodological guidelines for the management and mitigation of impacts generated by anions or other toxic elements in surface systems.

To fulfill the objectives proposed in this Doctoral Thesis a series of studies that are summarized below, along with the corresponding results, were conducted. In the first study, the environmental quality of the soils and waters of the Fé mine in Saelices el Chico (Salamanca, Spain) was determined, which allowed assessing the initial situation and the recovery alternatives (Chapter 2). For this purpose, soil samples developed on different mine wastes and host rocks, natural soils from the area adjacent to the mine (used as control) and water samples from the tailings were collected in the mining area. Soil samples were classified taxonomically and chemically analyzed to determine their quality and risk. Moreover, the main characteristics and properties of the mine soils and natural soils, key for the rehabilitation strategy, were determined and comparison between both was established. The water samples were characterized to evaluate their quality and degree of contamination, and a thermodynamic analysis was conducted to assess their evolutionary behavior. The results of the analysis of the soil samples showed that the mine soils have very low organic matter content, are predominantly acidic and present high concentrations of potentially toxic elements that can generate a high risk for the ecosystem and human health. These soils were classified as different spolic (sulfuric, salic or haplic), urbic and ekranic Technosols. On the other hand, the natural soils adjacent to the mine showed a great anthropic influence, as a consequence of the nearby mining activities or other activities of intensive use (livestock and agriculture). These soils were classified as Leptosols (lithic or haplic) or Cambisols (leptic or haplic). The most evolved horizon was a B horizon cambic, with little thickness and low degree of chemical-mineralogical evolution, in which the dominant solid phases were originated from the starting material.

The mine waters analyzed are hyperacid, hyperconductive and hyperoxidant. They have a variable chemical composition due to the seasonal hydrological variations, although they are always characterized by high concentrations of sulfates and different potentially toxic elements (Al, Cd, Mg, Fe and Mn). The results of the thermodynamic modeling, carried out by the PHREEQC program, indicate that most metals are forming ionic pairs with sulfate. The presence of sulfate ions regulates the chemistry of these waters. As a result of the oxidation of the mineral sulfides, strong acidity is originated, as well as the presence of ionic species with high toxicity Al^{3+}, Mn^{2+}, Zn^{2+}, Ni^{2+} y Cu^{2+}.

Taking into account the limiting conditions in the soils and waters of the mine, and in those present in the mine surroundings, it is essential to act on these anthropic soils in order to reduce the oxidation of the sulfides and to improve soil fertility. The main objective should be to establish a vegetation cover and to stimulate pedogenesis and biogeochemistry processes, such as the nutrient cycle, which will consequently improve the physico-chemical quality of the water.

In Chapter 3 the suitability of different biochars for the removal of cationic contaminants from aqueous effluents is evaluated. The metal considered for this study was copper. For this purpose, batch tests (discontinuous systems) were conducted with six biochars derived from different materials: chicken manure, acacia, eucalyptus, corncob, olive residue and rice husk. These biochars, obtained by pyrolysis at 300-400 ºC, were characterized to determine the physico-chemical parameters that influence the retention of copper. Also, the reaction mechanisms were established. The results showed that the different biochars have a high retention capacity and that this capacity is mainly conditioned by adsorption, precipitation or co-precipitation mechanisms. The retention capacity of the biochars is directly related to the O/C ratio, the P content and the ash content of these materials. The copper retention sequence for the different biochars was as follows: rice husk biochar > chicken manure biochar > olive waste biochar > acacia biochar > eucalyptus biochar > corncob biochar. Additionally, the distribution of this contaminant in the different phases (Cu-Biochar, Cu-dissolved organic carbon, and free Cu^{2+}) is also dependent on the nature of the biochar. This is an important criteria when selecting which material will be used for water decontamination treatment. The effect of the pH of the system on copper retention was also evaluated, and it was found that the biochar retention capacity increases with the increase of pH, independently of the feedstock material used for the biochar preparation.

To evaluate the potential use of biochars in reactive barriers or fixed bed columns, the copper removal efficiency of biochars was studied in continuous flow systems (Chapter 4). This study was carried out with biochars derived from different raw materials: chicken manure, eucalyptus, corncob, olive waste and pine sawdust. Firstly, the effect of the flow rate (2.5, 5.0, 7.0 y 13 mL min^{-1}) on the copper retention capacity was analyzed for the corncob biochar. This parameter strongly influences the copper retention capacity of the biochar, since a decrease from 5.51 to 3.48 mg Cu g^{-1} is observed when the flow rate decreases from 13 to 2.5 mL min^{-1}, respectively. Secondly, the retention capacity of the different biochars was evaluated at constant flow rate (7 mL min^{-1}) using the modified Bohart-Adams model. Copper retention capacity ranges between ~ 1.3 and 26 mg Cu g^{-1}, following the sequence: chicken manure biochar > olive waste biochar >> corncob biochar > pine sawdust biochar. The physico-chemical characteristics of the biochars determined their copper retention capacity and the corresponding immobilization mechanisms. The biochars that present high ash content show a greater copper retention capacity, and therefore are the most suitable for water treatment systems intended to the removal of metallic cations. Finally, the sorption parameters obtained here were compared with the parameters previously obtained in discontinuous systems (Chapter 3), finding a good correlation between both. This good correlation allow us to predict the behavior of different biochars and to optimize the operational conditions with a minimum number of sorption experiments.

In Chapter 5, the effectiveness of Technosols with andic properties for the removal of phosphate from water systems was determined. For this purpose, batch experiments were conducted, allowing higher contact times between the aqueous effluent and the Technosol. These conditions will be similar to those found in wetlands and in systems employing reactive geochemical barriers. The sorption kinetics, sorption isotherms, pH effect (from 4 to 9) and effect of the presence of different anions (bicarbonate, sulfate, chloride, chromate and molybdate) were evaluated in the batch assays. The results of these experiments indicated that the highest percentages of phosphate sorption are found at high pH values. The main mechanism of phosphate removal at pH above 7 is precipitation (as Ca-P solid phases), which was corroborated by thermodynamic calculations using PHREEQC. For this purpose, saturation indices were obtained for different Ca-P solid phases: hydroxyapatite, $Ca_3(PO_4)_2$ (beta), $Ca_4H(PO_4)_3 \cdot 3H_2O$, $CaHPO_4$ y $CaHPO_4 \cdot 2H_2O$. On the other hand, at pH values between 4 and 6 the main mechanism of phosphate retention on the Technosol is surface adsorption, although surface precipitation may not be ruled out. The retention capacity of the phosphate varied when other anions are present in the system. At pH 4, the presence of bicarbonate, sulfate or chloride did not modify the retention capacity of Technosol. However, the presence of chromate led to an increase in phosphate retention by more than 50 %, while the addition of molybdate produced a strong reduction in the phosphate retention as both ions competed for the Technosol surface sites. At pH 9, the presence of sulfate, chloride and chromate did not affect the phosphate retention, while the presence of molybdate (> 0.1 M) produced a decrease of the phosphate retention, although to a lesser extent than that observed at acid pH. The presence of bicarbonate led to a significant reduction in the phosphate retention capacity due to bicarbonate-phosphate competition.

In this Chapter 5 sorption experiments were also carried out using fixed bed columns, evaluating the effect of different variables: flow rate, reactive layer thickness, pH of the influent solution and material reuse. The immobilized phosphate concentration in the Technosol was calculated using the modified Bohart-Adams model. The increase of the flow rate produced a decrease in the breakthrough and saturation times, as well as in the amounts of phosphate retained by Technosol, from 6.19 to 2.37 mg PO_4 g^{-1} when the flow rate changed from 1.5 to a flow of 5 mL min^{-1}. Larger contact times favor sorption processes (surface adsorption, precipitation or surface precipitation) and consequently higher retention capacities of the Technosol. A reduction of the amount of Technosol, from 11.20 g to 5.60 g, while maintaining the other parameters constant (pH, flow rate), led to a 65 % decrease in the breakthrough time and to a 14 % reduction in the amount of phosphate immobilized. On the other hand, the retention capacity of the Technosol was increased from 2.37 to 6.21 mg PO_4 g^{-1} when the pH of the influent decreased from 5.5 to 3.0. At pH < 6.0, the main retention mechanism is surface adsorption, process that is more favorable at acid pH values. Finally, the possible reuse of Technosol was evaluated through several cycles of sorption-desorption. After the first cycle, Technosol loses a 40 % efficiency for the retention of phosphate. However, subsequent sorption-desorption cycles do not produce additional reduction and the retention capacity remains constant. This allows to conclude that the Technosol can be reused in water treatment systems after a washing cycle. The leachates obtained in the washing procedure could be used to produce a liquid fertilizer. Finally, when the Technosol is saturated, it could be recycled as a phosphate-rich amendment.

In Chapter 6, a study that evaluates, at a physico-chemical, biological and ecotoxicological level, the efficiency of a Technosol with andic and eutrophic properties for the rehabilitation of mine tailings, composed of a mixture of rich-sulfide materials and host rocks, is presented. A pilot assay was conducted at the Fé mine (Saelices el Chico, Salamanca), where a 20 cm surface layer of Technosol was applied to a tailing (over an area of 625 m^2). Twenty months after the application, samples of Technosol, treated tailing (located under the Technosol layer) and non-treated tailing were collected. These samples were analyzed to determine the elements in the pseudototal fraction (*aqua regia*), in the available fraction (soluble + interchangeable) and in the leachates. At the biological level, the activity of four enzymes (dehydrogenase, β-glucosidase, acid phosphatase and urease) was determined. The presence of these enzymes, which are involved in the C, P and N cycles, indicates the state of the microbial community. Additionally, the quality and metabolic capacity of the different microbial communities was determined following the changes in the concentrations of CO_2 and CH_4, by continuous soil respirometry analysis for 450 hours. Finally, the different materials and their corresponding leachates were evaluated at ecotoxicological level using two commonly recommended plants for revegetation by ISO recommendations , *Lollium perenne* L. and *Trifolium pratense* L. Three bioassays were then performed: filter paper, hydroponic test and soil test under germination conditions in a growth chamber (25 ± 1 ºC, 16 hours light + 8 hours darkness). Microcosms tests under greenhouse conditions were also conducted. To evaluate these bioassays, visual aspects, germination rate, aerial and root shoot elongation, and dry biomass of seeds and seedlings exposed to the materials and their leachates were analyzed. In the microcosm test, visual aspects, percentage of coverage and aerial dry biomass were evaluated.

The characterization of the materials and their leachates showed that the non-treated tailing presents a considerable environmental risk due to its pH (moderately acidic), poor soil structure and high concentrations of potentially toxic elements. Significant differences were found between the non-treated tailing and the treated tailing. The ecotoxicological effect evaluated by the different bioassays for both plant species was not conclusive, whereas some differences were found in the microcosms test, where the germination of *Trifolium pratense* was inhibited and the germination and development of the *Lollium perenne* was limited. The application of Technosol significantly improved the physico-chemical and biological characteristics of the tailing materials (treated tailing). There was a decrease in the total concentration of potentially toxic elements (Co, Mg, Mn, Ni and Pb), between 17 and 55 % depending on the chemical element, and an increase in the concentration of nutrients, Ca and P. The organic matter content and nutrient concentration in the leachates and in available forms were also increased. This promotes a greater stimulation of the microbial activities and a good development of both plant species in the bioassays and microcosms test. The Technosol, after 20 months of application, still presented adequate characteristics for the rehabilitation of the mine tailing, as well as for ensuring the ecological functions of the system and its vegetal cover. On the other hand, the Technosol did not present ecotoxicological effects and the microcosms test indicated the high potential that the Technosol has for revegetation with grass. Nevertheless an analysis of the consequent grassland is needed in order to evaluate that there is no risk for livestock.

As a general conclusion of the thesis (Chapter 7), it is indicated that the use of Technosols, both in the laboratory and in the field, constitutes a suitable technological solution for the recuperation of contaminated soils or tailings. Reusing these materials produce an economic profit after the remediation process. In contaminated waters, the use of Technosols can contribute to the rehabilitation in non-dynamic or static systems, such as wetlands, and in dynamic systems, using them as reactive geochemical barriers. The use of biochars for the treatment of contaminated water showed high efficiency, both in batch and continuous systems. Its use represents a sustainable alternative that can be used in geochemical barriers and sorption columns, or it can be also a reactive constituent of the Technosols.

INTRODUCCIÓN

1. CONTAMINACIÓN: FUENTES Y PRINCIPALES IMPACTOS

En las últimas décadas el aumento acelerado de la población trajo consigo el incremento de actividades industriales, minería y agrícolas con el fin de abastecer sus necesidades. Como resultado de esto, se incrementó el contenido de contaminantes de origen antrópico en el medio ambiente, presentando una serie de impactos negativos sobre los suelos y las aguas, con procesos tales como: acidificación, salinización, erosión, eutrofización, incremento de la concentración de metales y aniones potencialmente tóxicos, etc.

Dentro de los contaminantes antrópicos, los inorgánicos, tanto cationes como aniones, constituyen un gran problema dado que, al contrario de los contaminantes orgánicos, estos no se degradan permaneciendo en los diferentes compartimentos biogeoquímicos de los ecosistemas. Aunque algunos de estos elementos químicos (ej. Cu, Ni, Zn, Co, Fe, P, N) son nutrientes esenciales para los diferentes organismos (desde la microbiota del suelo a los animales y plantas superiores), en dosis elevadas pueden ejercer un efecto nocivo o tóxico (Adriano, 2001; Kabata-Pendias, 2011). De hecho, distintos autores indicaron una disminución de la actividad microbiana (Hinojosa et al., 2008; Santos et al., 2016) o la alteración de procesos fisiológicos en algunas plantas (Santos et al., 2009; Arenas-Lago et al., 2016) en suelos contaminados o en suelos naturales con anomalías geoquímicas de concentración. Elevadas concentraciones de estos nutrientes conducen a alteraciones en los procesos químicos y/o propiedades en suelos y aguas. Por ejemplo, un exceso en Na y/o K en los suelos conlleva un aumento de salinidad y pérdida de estructura en los suelos (Menneer et al., 2001), mientras que el exceso de N causa la acidificación de suelos y acelera la descomposición de la materia orgánica (Högberg et al., 2006; Ju et al., 2009; Tian et al., 2012; Yang et al., 2014). En aguas, el incremento de N y P es la principal causa del proceso de eutrofización, el cual promueve la proliferación y el crecimiento excesivo de algas, así como cambios importantes en la dinámica de las comunidades acuáticas (Kappler, 1991; Prepas and Chartette, 2005).

Las actividades mineras se encuentran entre aquellas actividades humanas que presentan una mayor importancia económica y social, si bien también generan un mayor impacto al medioambiente. Dentro de este tipo de actividades se encuentran las actividades extractivas de carbón, minerales o rocas (Tiwary, 2001; Lottermoser, 2010; Neri and Sánchez, 2010;

FAO and ITPS, 2015). En la actualidad se han desarrollado técnicas extractivas más eficientes (Reichl et al., 2016; USGS, 2017), si bien el impacto de estas actividades continua siendo significativo. En general, las actividades mineras presentan impactos directos sobre el terreno, por ejemplo, la pérdida del suelo y de sus funciones ecológicas, e impactos indirectos con la contaminación del aire y el agua, así como una disminución de la biodiversidad (Wong, 2003; Clemente et al., 2004; FAO and ITPS, 2015). El tipo y magnitud de los impactos generados es dependiente de numerosos factores, entre otros, el tipo de material extraído, la metodología de extracción, el tamaño de partícula generado, el contenido de materiales reactivos presentes en el material geológico asociado y las condiciones ambientales (regímenes de humedad y temperatura, topografía) (Moore and Luoma, 1990; Sengupta, 1993; Langer, 2001; Wong 2003).

En los proceso de extracción y procesamiento de las materias primas se generan grandes volúmenes de escombreras, constituidas por diferentes materiales con una granulometría variada, desde pequeños diámetros a grandes bloques, lo que también condiciona su reactividad y estabilidad física. El riesgo de estas escombreras está asociado a las elevadas concentraciones totales de elementos potencialmente tóxicos, volúmenes de escombreras, bajo pH, posibilidad de erosión, cantidad de elementos que puedan ser lixiviados, y cuando existen materiales reactivos, como los sulfuros, la generación de drenaje ácido de mina (Monterroso et al., 1998; Álvarez-Valero et al., 2007; Abreu et al., 2010; Jamieson, 2011). Las escombreras que no presentan una adecuada cobertura vegetal contribuyen a una mayor dispersión de elementos potencialmente tóxicos, no sólo por el material particulado, sino también por sus lixiviados.

La exposición a la intemperie de aquellas escombreras que contengan sulfuros origina la oxidación de los mismos, lo que conlleva la generación del drenaje ácido (Blowes et al., 2003; Abreu et al., 2010). De hecho, los sulfuros sólo son estables en condiciones fuertemente reductoras o anóxicas, condiciones muy similares a las que permiten la estabilidad del C nativo o de la necromasa más lábil. Oxidantes tales como O_2, NO_3^-, Fe^{3+}, Mn^{4+} e incluso algunas formas de C recalcitrante (Figura 1) pueden actuar como aceptores de electrones procedentes de los sulfuros en condiciones oxidantes, subóxicas e incluso en algunas condiciones anóxicas y favorecer la formación de sulfatos (Alpers et al., 2000; Schippers and Jørgensen, 2002; Blowes et al., 2003; Chandra and Gerson, 2011). Dentro de estos, el O_2 y el Fe^{3+} son los oxidantes más importantes de los sulfuros metálicos en aguas, siendo el Fe^{3+} el más agresivo y reactivo a todos los valores de pH (Nordstrom and Alpers, 1999a; Chandra and Gerson, 2011).

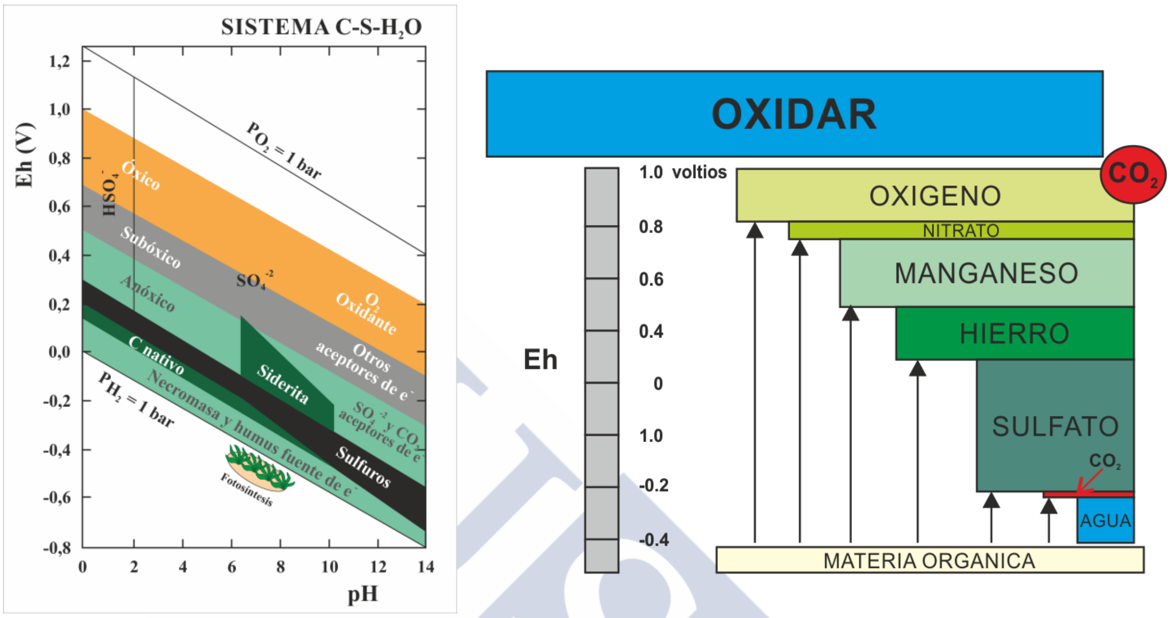

Figura 1. *Campo de estabilidad de los sulfuros (izquierda) y agentes oxidantes en diferentes condiciones Eh-pH (derecha).*

Los mecanismos de oxidación de los sulfuros son extremadamente variables, tanto en sus componentes reactivos como en la cinética y productos de las reacciones. Estos mecanismos dependen de factores tan diversos como la composición del material de partida, el tamaño de partícula, el grado de cristalinidad o las condiciones en que se produce el propio proceso oxidativo, i.e. pH, Eh, temperatura, presencia o ausencia de microorganismos (Alpers et al., 2000; Blowes et al., 2003).

Existe numerosa literatura sobre las reacciones de la oxidación de piritas, especialmente con respecto a la oxidación química o geoquímica abiótica y biótica (Lowson, 1982; Nordstrom, 1982; Nordstrom and Alpers, 1999a; Alpers et al., 2000; Jacobs et al., 2014). Este proceso se puede describir de forma general en dos fases bien diferenciadas:

i) La oxidación de Fe^{2+} por medio del O_2, con formación de Fe^{+3} acuoso en un medio hiperácido (Ecuación 1) o de $Fe(OH)_3$, ferrihidrita, a pH > 4.0 (Ecuación 2), se produce mediante la siguientes reacciones:

$$2\ Fe^{2+} + 1/2\ O_2 + 2\ H^+ \leftrightarrow 2\ Fe^{3+} + H_2O \quad (1)$$

$$Fe^{3+} + 3\ H_2O \leftrightarrow Fe(OH)_3(s) + 3H^+ \quad (2)$$

ii) La oxidación de la pirita en un medio óxico o subóxico. La reacción inicial, cuando el oxígeno es el agente oxidante (Ecuación 3), es lenta y fácilmente controlable por la presencia de reductores o compuestos neutralizantes de la acidez (carbonatos, silicatos,...). Cuando las condiciones son fuertemente ácidas el oxidante principal será el Fe^{+3} acuoso (Ecuación 4). Este ión actúa oxidando a los sulfuros con formación de un ión Fe^{2+}, el cual a continuación se oxida a Fe^{3+} (proceso catalizado por la presencia de bacterias) recuperando de esta forma el agente oxidante. Este ciclo continúa hasta la completa eliminación de los sulfuros o hasta que se reduzca la actividad de Fe^{+3}. Las reacciones de oxidación de los sulfuros a sulfatos se presentan a continuación:

$$2\ FeS_2 + 7\ O_2 + 2\ H_2O \leftrightarrow 2\ Fe^{2+} + 4\ H^+ + 4\ SO_4^{2-} \quad (3)$$

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \leftrightarrow 15\ Fe^{2+} + 16\ H^+ + 2\ SO_4^{2-} \quad (4)$$

Las reacciones de generación de drenaje ácido de mina presentan cinéticas muy variadas relacionadas con los organismos que biocatalizan la oxidación del Fe^{2+} a Fe^{3+}, los cuales actúan en diferentes condiciones de Eh-pH (Figura 2). Entre los organismos que catalizan este proceso destaca el *Acidithiobacillus ferrooxidans*, que puede oxidar los sulfuros minerales tanto en condiciones óxicas como anóxicas (Okibe et al., 2003; Schippers, 2004; Baker et al., 2006).

Por lo general, las aguas generadas en estos sistemas son hiperácidas ($pH < 3.5$), hiperoxidantes ($Eh > 650$ mV) e hiperconductoras, presentando concentraciones elevadas de elementos potencialmente tóxicos (Tabla 2), tanto en formas catiónicas (Al^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+},Hg^{+2}) como en formas aniónicas (AsO_4^{3-}, AsO_3^{3-}, SeO_4^{2-}) (Sengupta, 1993; Macías, 1996; Monterroso et al., 1998; Blowes et al., 2003; Abreu et al., 2010). El drenaje ácido de mina conlleva numerosos impactos negativos sobre aguas y suelos, afectando a la vida de los organismos terrestres y acuáticos y produciendo cambios en las funciones del ecosistema (Yadav, 2010; Simate and Ndlovu, 2014; Liao et al., 2016). Estos impactos son generados principalmente por la acidez del sistema y la concentración elevada de elementos tóxicos (As, Al, Cd, Co, Cu, Hg, Pb,…).

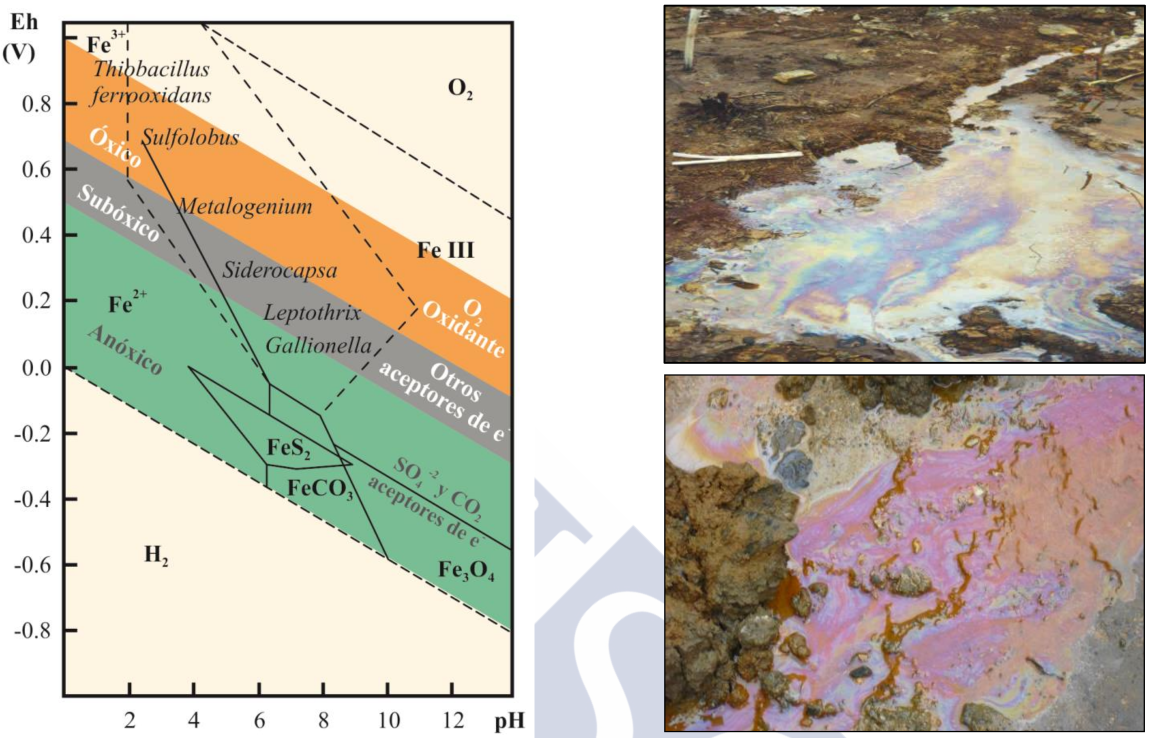

Figura 2. a) Microorganismos que realizan biocatálisis oxidativas de los sulfuros de Fe y condiciones Eh-pH óptimas para su mayor eficiencia (modificado de Grant and Long, 1985); b) Bacterias catalizadoras que forman colonias con un aspecto mucilaginoso característico en el que son frecuentes irisaciones similares a las producidas por la presencia de hidrocarburos.

Tabla 2. Composición de drenajes ácidos de mina en distintas regiones o distritos mineros.

Áreas mineras		g/L		mg/L		
	pH	SO_4^{2-}	Fe	As	Cu	Zn
FPI (España)[a,b]	0.6-4.2	0.3-134	4.0-74.2	1.0-303	0.5-1945	<LD-1440
FPI (Portugal)[c,d,e]	1.0–3.9	0.7-49.9	$7.9 \cdot 10^{-3}$-82.5	<ld-388	0.1-111	$1.5\text{-}49 \cdot 10^3$
Richmond Mine, Iron Mountain, USA[f,g]	-3.6-1.51	14-760	2.7-111.0	3-850	218-4760	$50\text{-}23 \cdot 10^3$
Ducktow District Tennessee [h]	2.2–3.1	0.6–2.0	$6.2 \cdot 10^{-3}$-0.68	-	0.3-13.0	$17 \cdot 10^3$- $38 \cdot 10^3$

[a] Sánchez-España et al., 2005; [b] Sánchez-España et al., 2008; [c] Abreu et al., 2010; [d] Ferreira da Silva et al., 2015; [e] Martins et al., 2011; [f]Nordstrom and Alpers, 1999b; [g]Nordstrom et al., 2000; [h] Lee et al., 2002. ld: límite de detección. FPI: Franja Piritica Ibérica.

Los contaminantes inorgánicos presentes en los drenajes ácidos tienen la capacidad de persistir por largos períodos en el ecosistema. Por otra parte se pueden acumular en los tejidos de animales y plantas, causando alteraciones en sus funciones metabólicas, generando daños celulares y afectando al crecimiento, y produciendo cambios en la fisiología y morfología de las plantas (Gardeatorresdey et al., 2005; Yadav, 2010; Akpor and Muchie, 2010; Jiwan and Kalamdhad, 2011; Singh et al., 2011). El efecto de una exposición crónica a bajas concentraciones de contaminantes conlleva normalmente alteraciones en la reproducción, deformaciones y lesiones en los órganos, mientras que una exposición corta a altas concentraciones puede producir la muerte de los organismos (Yadav, 2010; Singh et al., 2011).

Las condiciones hiperácidas en estos sistemas conllevan la generación de precipitados en forma de óxidos o hidróxidos de Fe que cementan los lechos de los ríos, los fondos de embalses u océanos. La presencia de estos precipitados puede afectar a los organismos bentónicos, así como producir cambios en la especiación química de los iones en el agua y efectos en la respiración, influyendo principalmente en especies sensibles, como los salmónidos, los cuales se ven rápidamente afectados por cambios en elpH del medio. En suelos, los cambios de pH afectan directamente a la biodisponibilidad de los nutrientes, afectado de esta forma al crecimiento de las plantas y microorganismos (Adriano, 2001; Kabata-Pendias, 2011). A valores bajos de pH, la disponibilidad de N, P y K para las plantas disminuye, así como la de cationes básicos (Ca^{2+}, Mg^{2+}), mientras que se incrementan la disponibilidad los cationes ácidos (Al^{3+} y H^{+}) en el complejo de cambio y la disponibilidad de elementos tóxicos (Schrock et al., 2001; White, 2013b).

2. EL SUELO Y SUS MECANISMOS DE ATENUACIÓN DE CONTAMINANTES

El suelo es uno de los componentes fundamentales de la biosfera, y es la interfase entre la atmosfera, la litosfera y la hidrosfera. Está constituido principalmente por tres fases: sólida (materia mineral y orgánica), acuosa (agua) y gaseosa (aire). El contenido, distribución, propiedades y características de cada una de estas fases están determinados por la combinación de los factores físicos, químicos y bióticos que actuaron sobre los materiales orgánicos y minerales durante la edafogénesis (Mirsal, 2008; White, 2013a).

La fase acuosa, conocida como la disolución del suelo, constituye un 20-50 % del suelo y contiene solutos orgánicos e inorgánicos tanto nutrientes como contaminantes, así como la fracción coloidal (diferentes tipos de arcillas, óxidos de Fe o Al, y coloides orgánicos con tamaño menor a 500 nm) que controla su disponibilidad y movilidad. La fase gaseosa del suelo constituye un 10-25 %. Esta fase se crea en los espacios entre las partículas del suelo donde se acumula aire cuya composición principal es similar a la de atmosfera, N_2 y O_2, aunque con contenidos de CO_2 más elevados y diferentes gases derivados del metabolismo microbiano (White, 2013a). La fase sólida constituye un 40-50 % del suelo, la cual se constituye por una fracción inorgánica y otra orgánica. La fracción inorgánica o mineral está constituida principalmente por los productos de alteración del material geológico de partida, destacando la presencia de aluminosilicatos y oxihidróxidos, los cuales a su vez son constituyentes de la fracción coloidal (partículas con un tamaño menor a 2 μm). Dentro de esta fracción mineral se encuentran filosilicatos de tamaño arcilla más o menos cristalinas (montmorillonita, vermiculita, caolinita, haloisita, alofanos,…), óxidos (hematita, magnetita, ferrihidrita,…) y oxihidróxidos (gibbsita, goethita,…) (Evangelou, 1998). Estos componentes coloidales constituyen la fracción más reactivas en el suelo, participan en numerosos procesos físico-químicos (adsorción, intercambio catiónico, precipitación,…) y determinan la capacidad de amortiguación frente a impactos y la productividad vegetal de los suelos. Su reactividad está determinada por una elevada área superficial y, en algunos, una carga superficial variable (positiva o negativa en función del pH del medio) (Sparks, 2003). La fracción orgánica está constituida principalmente por el humus o sustancias húmicas, las cuales se originan a partir de la descomposición de los residuos vegetales y animales, así como de las sustancias orgánicas producidas por los organismos del suelo. La materia orgánica natural contribuye a la mejora de las propiedades químicas, físicas y biológicas del suelo: suministra nutrientes (N, P y S), promueve la estructura y la aireación del suelo, favorece la retención de humedad. Su porosidad, carga superficial y capacidad de intercambio catiónico le confiere una gran reactividad, de tal forma que se considera buen adsorbente de contaminantes, tanto inorgánicos como orgánicos (Bohn et al., 2001).

Las propiedades físico-químicas (área superficial, carga superficial, pH, Eh, cationes de cambio…) y mecanismos de reacción (adsorción, precipitación o co-precipitación, complejación, intercambio iónico, reacciones redox) de los componentes inorgánicos y orgánicos del suelos son la base de los procesos de amortiguación y de las tecnologías de rehabilitación ambiental. A continuación se describen los principales mecanismos de atenuación o reacción de estos componentes:

i) La complejación órgano-metálica es un proceso de interacción entre la materia orgánica natural con los cationes metálicos presentes en disolución, estableciéndose un enlace covalente entre ambos (Tipping, 2002). El empleo de enmiendas orgánicas, además de aumentar la capacidad de acumulación de agua en el suelo, permite aumentar el contenido de C y nutrientes, favorece la estructura física y produce una disminución en la biodisponibilidad de cationes potencialmente tóxicos (Adriano, 2001; Wong, 2003; Larney and Angers, 2012; Bolan et al., 2014). La aplicación combinada de enmiendas orgánicas y materiales alcalinizantes en escombreras conlleva la acumulación de material orgánica, el desarrollo de microestructura y el aumento de la microbiota en los suelos (Zanuzzi et al., 2009; Arocena et al., 2012). Por otro lado, no todo tipo de material orgánico se comporta de igual forma. Dependiendo del tipo de C y sus propiedades, se favorece la retención de un elemento u otro, pudiendo incluso llegar a movilizar contaminantes a la disolución, como por ejemplo el As (Kumpiene et al., 2008; Bolan et al., 2014).

ii) La precipitación o co-precipitación es la formación de una fase sólida a partir de los componentes presentes en la fase acuosa. Estos procesos están controlados por las condiciones de pH, Eh y T^{a}, así como por la concentración de elementos en el medio. La precipitación se emplea para inmovilizar contaminantes a través de la adición de materiales encalantes (calizas, dolomitas, cenizas), lo que favorece la formación de fases sólidas con diferentes solubilidades, i.e. carbonatos, fosfatos, sulfatos y óxidos o hidróxidos metálicos (Kumpiene et al., 2008; Bolan et al., 2014). En ambientes con generación de drenaje ácido la aplicación de esta solución es temporal, ya que se favorece el proceso opuesto, la disolución de las fases minerales o se generan fases con una mayor solubilidad (Pérez-López et al., 2009; Santos et al., 2014).

iii) Los procesos de intercambio iónico controlan la concentración de nutrientes y de elementos tóxicos presentes en la disolución del suelo. Este proceso, especialmente relevante en el caso de arcillas 2:1 y de la materia orgánica natural, se refiere al intercambio de un ión presente en la superficie por otro de ión de igual carga presente en la disolución (White, 2013b). Por ejemplo, el uso de enmiendas orgánicas favorece los procesos de intercambio en suelos contaminados y escombreras, siendo un proceso importante en el control de nutrientes y elementos contaminantes (Adriano, 2001; Madeira et al. 2012; Bolan et al., 2014).

iv) La adsorción es uno de los procesos físico-químicos de mayor importancia en suelos y aguas, ya que controla la movilidad, transporte y disponibilidad de nutrientes y contaminantes en el medio (Essington, 2005). La retención o inmovilización de nutrientes y contaminantes en suelos a través de este proceso, viene dado por la presencia de la materia orgánica natural y los óxidos o hidróxidos minerales (Fe, Al o Mn) (Sparks, 2003). Las reacciones de adsorción entre los componentes en disolución y la fase sólida implica mecanismos físicos y químicos, entre otros la formación de complejos superficiales, interacciones electrostáticas o interacciones hidrofóbicas (Sparks, 2003; White, 2013b). Cambios en las condiciones físico-químicas del medio (pH, Eh y T^{a}) o la presencia de otros elementos en disolución puede favorecer la adsorción o producir la desorción de aquellos elementos inicialmente adsorbidos, pasando nuevamente a la fase acuosa con los consiguientes efectos negativos sobre el ecosistema (Antelo et al. 2005; Kanematsu et al., 2013; Antelo et al., 2015; Otero-Fariña et al., 2017)

v) Las reacciones de oxidación-reducción son procesos de gran importancia en suelos y aguas, ya que definen la especiación química, dinámica y peligrosidad de las especies químicas presentes. La adición de enmiendas (materia orgánica, materiales alcalinos, óxidos minerales) pueden producir cambios en el potencial redox y el pH en el medio, y consecuentemente en la disponibilidad o movilidad de las especies químicas (Adriano, 2001; Guha et al., 2001; Fernandes et al., 2002).

3. TÉCNICAS DE RECUPERACIÓN DE SUELOS Y AGUAS

3.1. Enmiendas

La aplicación de enmiendas o correctivos para la recuperación de suelos y aguas, se basan principalmente en un único mecanismo de retención. El uso de enmiendas contribuye con numerosos efectos positivos sobre los suelos, por ejemplo, la adición de materia orgánica favorece la agregación y la estructura, o incrementa el contenido de nutrientes; la aplicación de enmiendas alcalinas, como las calizas o cenizas, favorece el incremento de pH y la retención de contaminantes catiónicos mediante precipitación, o la adición de óxidos de Fe o Fe (0) favorece la inmovilización de contaminantes (Kumpiene et al., 2008; Tiberg et al., 2016). Por otro lado, la aplicación de enmiendas también puede generar efectos negativos, como las transformaciones de Cr (III) o As (V) a Cr (VI) y As (III) con el aumento de pH producido por la adición al suelo de cenizas u otros materiales encalantes; o la agregación por cementación o cambios en la porosidad derivados de la aplicación en dosis elevadas de Fe (0) (Kumpiene et al., 2008; Bolan et al., 2014) (Figura 3).

Figura 3. Efectos *positivos y negativos que pueden derivarse de la aplicación de diferentes enmiendas sobre los suelos en algunas condiciones.*

El uso combinado de varios tipos de enmienda en una única dosis puede aumentar su eficiencia, ya que contribuyen con la mejora de diversas características al mismo tiempo (de Varennes et al., 2010). Sin embargo la aplicación de enmiendas, tanto individualmente como en mezcla, sólo influye positivamente en algunos procesos biogeoquímicos y pueden presentar una efectividad a corto o medio plazo (Macías, 2004; Macías et al., 2011). De este modo sería necesario aplicar las enmiendas de forma periódica, lo cual encarecería inevitablemente los procesos de recuperación (Pérez-de-Mora et al., 2011).

Una alternativa al empleo de las enmiendas tradicionales, es la aplicación de materiales o tecnologías que integren diferentes procesos para la retención o inmovilización de contaminantes, tales como las nanopartículas, los biocarbones (biochar) y los Tecnosoles. La aplicación de este tipo de materiales conlleva a un aumento en la efectividad en el tratamiento y recuperación de suelos y aguas (Monterroso et al., 1998; Macías et al., 2011; Beesley et al., 2011; Xu et al., 2013; Ahmad et al., 2014; Bolan et al., 2014; Santos et al., 2014).

3.2. Biocarbones

Los biocarbones son materiales ricos en carbono que se obtienen a partir de la degradación térmica en ausencia de oxígeno de distintos materiales orgánicos, tales como residuos agrícolas y forestales, estiércoles, restos de animales, lodos de depuradora y otros tipos de materiales (Regmi et al., 2012; Méndez et al., 2012; Ahmad et al., 2014; Lu et al., 2017). Se caracterizan por presentar una alta porosidad, elevada superficie específica y una densidad de grupos funcionales reactivos alta. La capacidad que presentan los biocarbones para eliminar contaminantes metálicos (Pb, Cu, Zn, Cr, Ni,….) en aguas ha sido demostrada en numerosos estudios (Chen et al., 2011; Kolodyńka et al., 2012; Kim et al., 2013; Li et al., 2013; Xu et al., 2013; Trakal et al., 2014; Wang et al., 2015). Así mismo también presentan un elevado potencial para la recuperación de suelos contaminados (Beesley et al., 2011; Ahmad et al., 2014; Bolan et al., 2014). Entre principales mecanismos de reacción o interacción de los biocarbones se pueden citar las interacciones electrostáticas, intercambio iónico, sorción vía π electron desplazado del carbono, precipitación o co-precipitación superficial, y la adsorción (Cao et al., 2009; Cao and Harris, 2010; Sohi et al., 2010; Uchimiya et al., 2011; Xu et al., 2013; Puga et al., 2016) (Figura 4).

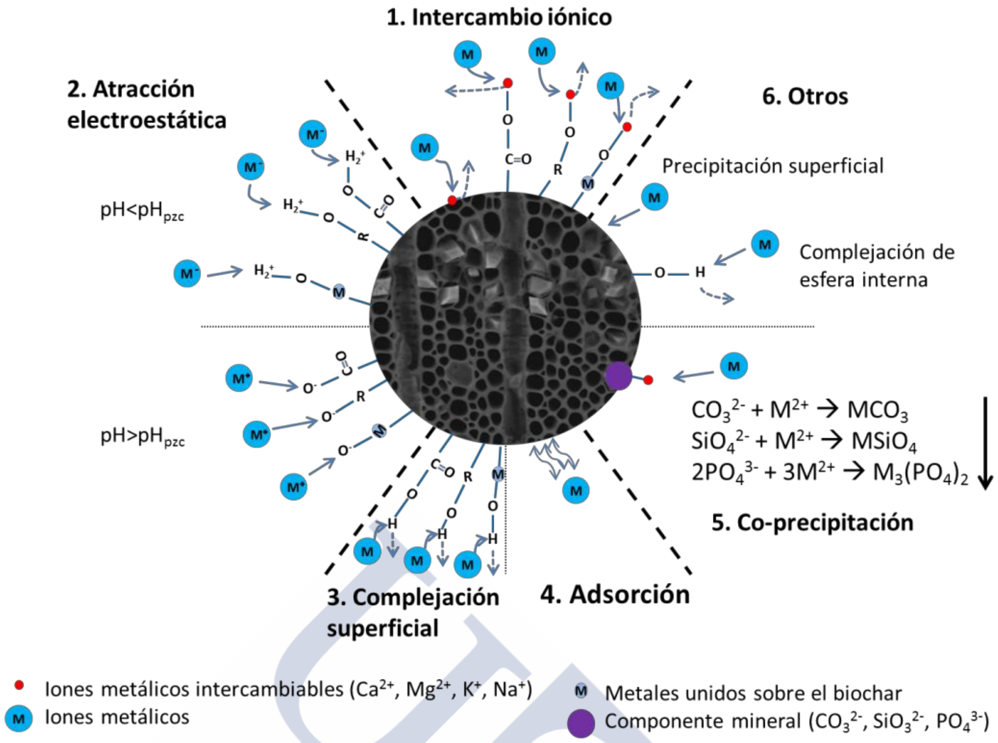

Figura 4. Diversos mecanismos por los que se puede producir la retención de elementos metálicos en los biochars (modificado de Tan et al., 2015)

3.3. Tecnosoles

Los Tecnosoles son otra tecnología novedosa que se emplea en numerosos trabajos de recuperación de suelos y aguas. Son definidos como suelos cuya formación y propiedades están influenciadas por las actividades humanas, incluyendo suelos derivados de residuos antrópicos (IUSS Working Group WRB, 2015). Estos suelos son derivados de residuos, tales como escombreras, lodos o cenizas, entre otros, cuya formación y propiedades dependen de su origen técnico (IUSS Working Group WRB, 2015). Además, pueden generarse de manera artificial a partir de diversos residuos, a imagen de los suelos existentes en la naturaleza (Camps-Arbestain et al., 2008), y diseñados bajo un concepto de edafo-ingeniería. Su diseño se basa en el entendimiento de las características y el comportamiento de los residuos y de los componentes que lo van a formar, de tal modo que los Tecnosoles puedan presentar patrones de evolución similares a lo de los suelos naturales (Macías, 2015). Las cantidades relativas de los distintos componentes que constituyen el Tecnosol son ajustadas a las condiciones de las áreas degradadas sobre la que se aplicarán, de tal forma que se diseñan Tecnosoles específicos al problema a solucionar. Así mismo, la aplicación de Tecnosoles se basa en crear y estimular los procesos biogeoquímicos y de edafogénesis, permitiendo que existan efectos complementarios de sus distintos componentes y facilitando un proceso de rehabilitación a medio-largo plazo (Macías, 2004; Macías et al., 2007; Macías-García et al 2009; Macías et al, 2011; Santos et al., 2014, 2016). Estos efectos a medio-largo plazo se consiguen al promover las características y funciones en los suelos degradados a varios niveles: físico, mejorando la estructura y textura de los suelos; químico, a través del incremento de materia orgánica, nutrientes y reduciendo la disponibilidad de elementos tóxicos; y biológico, con el aumento de la cobertura de plantas y la microbiota del suelo. La eficacia de esta tecnología en la recuperación de sistemas contaminados fue analizada en estudios de microcosmos (Santos et al., 2014. 2016; Rodríguez-Vila et al., 2016) y en condiciones de campo (Monterroso et al., 1998; Macías-García et al., 2009; Macías et al., 2011; Asensio et al., 2013; Bolaños et al., 2015).

3.4. Fitotecnologías

Las fitotecnologías son una alternativa basada en el empleo de la capacidad de plantas y microorganismos presentes en la rizosfera para atenuar o inmovilizar los contaminantes a través de distintos procesos, entre los que destacan la fitoestabilización, fitoextracción, fitovolatilización y fitodegradación (Pulford and Watson, 2003; Favas et al., 2014) (Figura 5). En suelos o sedimentos con contaminación polimetálica la técnica que presenta más ventajas y un menor riesgo es la fitoestabilización (Tordoff et al., 2000; Mendez and Maier, 2008; Abreu and Magalhães, 2009). Esta técnica consiste en el empleo de especies vegetales tolerantes para estabilizar o reducir la disponibilidad de contaminantes a través de la incorporación de los mismos a la pared celular de la raíces, en las vacuolas celulares, formando placas extra-radiculares o formando quelatos con los exudados radiculares (Figura 6), es decir, mediante mecanismos de absorción/acumulación y mecanismos de precipitación, complejación o reducción en la rizosfera (Tordoff et al., 2000; Wong, 2003; Mendez and Maier, 2008; Ali et al., 2013; Favas et al., 2014).

La fitoestabilización ocurre de forma natural en las plantas espontaneas y colonizadoras de las áreas degradadas, siendo un proceso de recuperación lento. Sin embargo, debido a las características adversas de los suelos y aguas presentes en estas áreas (falta de nutrientes, pedregosidad, acidez, elevados contenidos de contaminantes, aridez,…), el desarrollo y expansión de estas comunidades vegetales por si solas es difícil. Por lo tanto, es necesaria normalmente la aplicación de enmiendas que favorezcan su supervivencia y desarrollo, es decir combinando esta técnica con otras tecnologías, como enmiendas o empleo de Tecnosoles, que fortalecen y aceleran el proceso de recuperación (Santos et al., 2014).

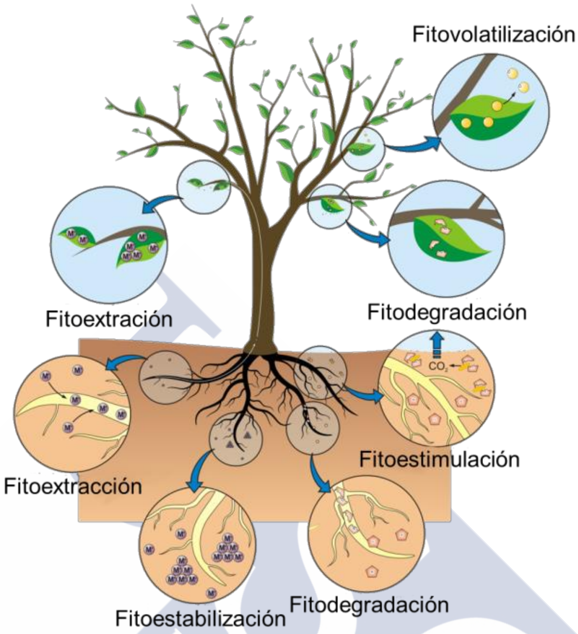

Figura 5. Representación de las diferentes técnicas que engloba la fitorremediación (modificado de Favas et al., 2014)

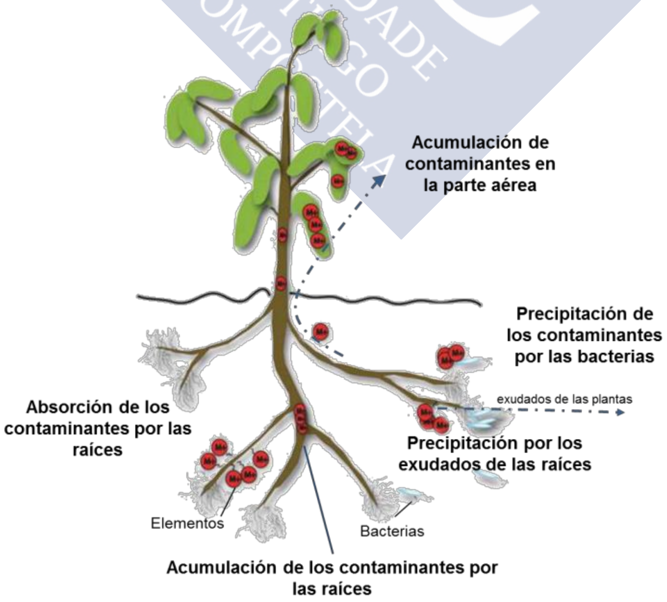

Figura 6. Esquema de los principales procesos que ocurren en la Fitoestabilización (modificado de Mendez and Maier, 2008)

4. MODOS DE APLICACIÓN DE LAS TÉCNICAS DE RECUPERACIÓN

Las diferentes tecnologías de recuperación *in situ* mencionadas en la sección anterior se emplean para el tratamiento de suelos/escombreras y aguas contaminadas por compuestos orgánicos e inorgánicos. Estas tecnologías pueden aplicarse de diferente modo, en función a las necesidades de cada problema y con el fin de garantizar un tratamiento más eficaz. La aplicación de enmiendas, como la adición de materia orgánica, biocarbones, materiales alcalinizantes (calizas, cenizas,…) u óxidos metálicos, en el tratamiento de suelos contaminados o escombreras se realiza superficialmente. Estas enmiendas solas o en combinación se aplican en la superficie del suelo o escombrera y posteriormente se realiza un mezclado con su capa superficial (máximo 40 cm) para evitar pérdidas del material por lavado o dispersión por el viento, así como para garantizar la recuperación del suelo en la capa en la que se establecerá la vegetación.

La aplicación de los Tecnosoles en suelos o escombreras es ligeramente diferente. Se pueden emplear como las enmiendas, mezclándolos con la capa superficial del suelo o escombrera, pero normalmente esta aplicación es en una capa superficial o combinación de varias (Figura 7). Esto es debido a que lo que se añade es un suelo bien estructurado y con las características y propiedades físico-químicas adecuadas, no solo para el tratamiento y corrección del problema, sino también para un establecimiento de una cobertura vegetal diversificada (herbácea, arbustiva y/o arbórea). El tratamiento mediante esta tecnología se basa en gran parte en un correctivo en profundidad, a través de los lixiviados producidos por el Tecnosol y del particulado que es eluviado. Tanto el uso de Tecnosoles como de otro tipo de enmiendas puede estar asociado al empleo de fitotecnologías que complementen y aceleren los procesos de rehabilitación de las áreas degradadas.

Para el tratamiento de aguas contaminadas, el empleo de enmiendas, biocarbones o Tecnosoles se puede realizar de diferentes formas: a través de su uso en columnas o bioreactores, en humedales reactivos/*wetland* (Figura 8), en barreras geoquímicas, o la combinación de varias (Figura 9) (Blowes et al., 2003; Khan et al., 2004; Johnson and Hallberg, 2005; Bolaños et al., 2015). La selección del modo de empleo de estos materiales estará condicionada, no sólo por las condiciones físico-químicas de las aguas y los contaminantes presentes, sino también por otras características, como las condiciones ambientales (precipitación, temperatura) o condiciones hidrológicas (caudal, volumen…).

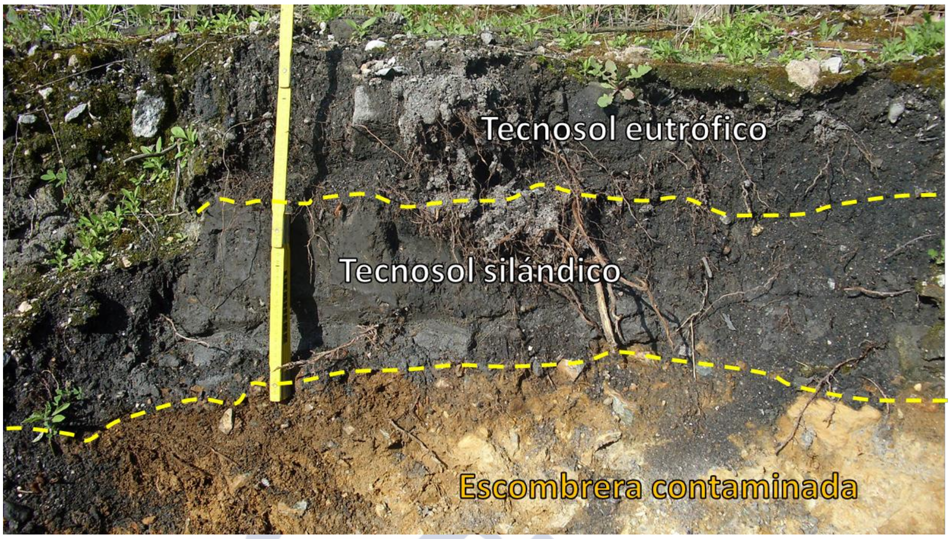

Figura 7. Aplicación de dos Tecnosoles combinados para el tratamiento de una escombrera contaminada en la mina de Touro. Modificado de Macías (2015)

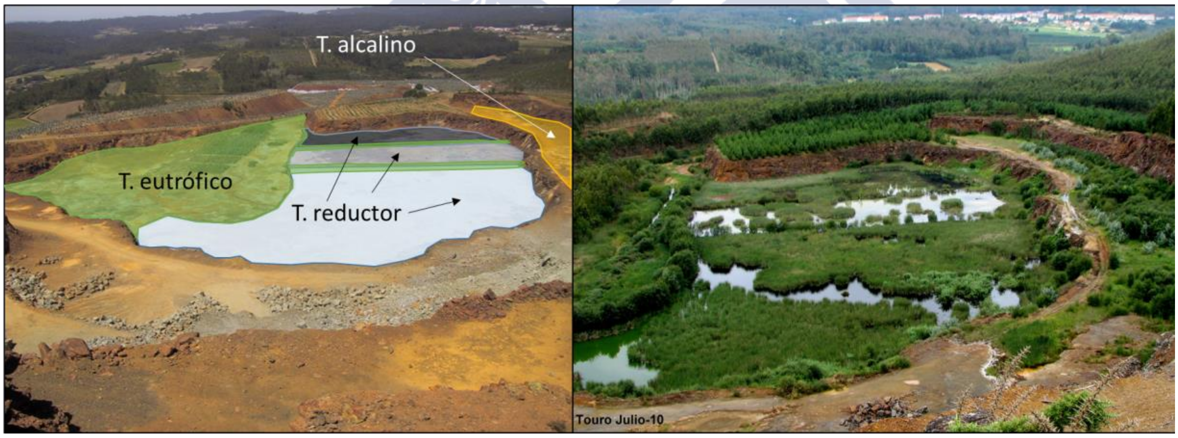

Figura 8. Establecimiento de un humedal reactivo compuesto por diferentes Tecnosoles para el tratamiento de aguas ácidas provenientes de las cortas de la mina de Touro (A Coruña, España). Autor: Felipe Macías.

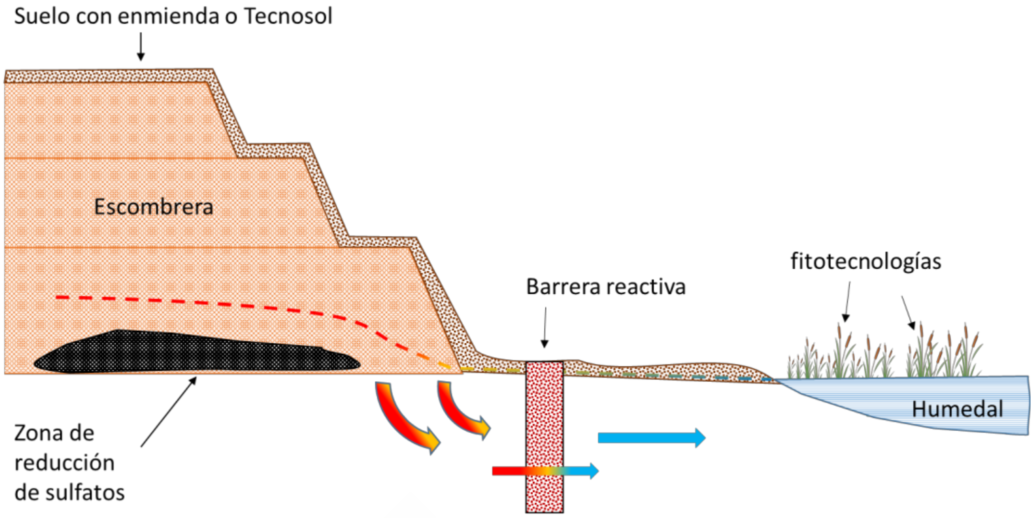

Figura 9. Diagrama esquemático de las diferentes tecnologías y modos de aplicación combinados para el tratamiento de los suelos y aguas contaminados en una actividad minera. Adaptado de Blowes et al. (2003).

5. OBJETIVOS Y ESTRUCTURA

La contaminación inorgánica derivada de las actividades antrópicas genera efectos negativos e importantes impactos sobre suelos y aguas, y por lo tanto existe una necesidad de recuperación de estos sistemas para mitigar sus efectos sobre el ecosistema. Existen diversas tecnologías de recuperación *in situ* para el control y atenuación de la contaminación multielemental, sin embargo, la selección de tecnologías de bajo coste, elevada efectividad y que promuevan aspectos de la economía circular son puntos clave a tener en cuenta en los procesos de recuperación ambiental. Teniendo en cuenta este marco, el objetivo de la presente Tesis Doctoral fue evaluar la eficacia del empleo de Tecnosoles y biocarbones en la recuperación ambiental, de suelos y aguas en zonas contaminadas. Para llevar a cabo esta evaluación y entender cuál es su comportamiento de estos materiales ante contaminantes de carácter inorgánico (cationes y aniones) se propusieron los siguientes objetivos específicos:

i. Caracterizar el estado ambiental de los suelos y aguas de un sistema minero, determinando las principales afecciones al medio y sus limitaciones de recuperación, lo que permitirá establecer metodologías de recuperación ajustadas a cada problema específico.

ii. Determinar las características físico-químicas y mecanismos que intervienen en la inmovilización de cationes metálicos en biocarbones, tanto en sistemas en discontinuo como en sistemas en continuo típicos para el tratamiento de aguas.
iii. Evaluar la capacidad de Tecnosoles con propiedades ándicas para la eliminación de fosfato en sistemas acuosos bajo diferentes condiciones del medio y operacionales, con el fin de determinar su aplicabilidad en condiciones de campo, a través humedales reactivos o barreras geoquímicas.
iv. Analizar la eficacia de un Tecnosol ándico-eutrófico en la recuperación de las características físicas, químicas y biológicas de los materiales de una escombrera con contaminación polimetálica, así como de la calidad química de los lixiviados generados tras 20 meses de aplicación en condiciones de campo y determinar la disminución del efecto ecotoxicológico.
v. Establecer pautas metodológicas para la gestión y mitigación de los impactos generados por aniones u otros elementos tóxicos en los sistemas superficiales.

Para realizar y cumplir los objetivos marcados en esta Tesis Doctoral se realizaron una serie de estudios cuyos resultados se distribuyen entre los Capítulos 2 y 6. En el Capítulo 2, se determinó el estado ambiental de los suelos y aguas presentes en la mina Fé (Ciudad Rodrigo, España). Se realizó una comparativa en la calidad de los suelos derivados de materiales de préstamo presentes en la mina, así como de los suelos naturales del entorno. Todos los suelos se clasificaron taxonómicamente, así como en función de sus aptitudes y limitaciones de uso. En las aguas generadas por los componentes mineros se evaluó su calidad físico-química y los riesgos que presentan. Por último, en este capítulo se determinaron las limitaciones existentes y se establecieron prioridades de actuación para la recuperación ambiental de la mina.

En los Capítulos 3 y 4, se evalúo la eficacia del empleo de distintos biocarbones como materiales adecuados para la inmovilización de contaminantes metálicos en aguas. Utilizando sistemas en discontinuo se determinó qué características químicas de los biocarbones influyen en la capacidad de inmovilización del cobre, así como los mecanismos de reacción y su relación con el material de partida. La evaluación y determinación de la aplicación de estos materiales, en sistemas en continuo, así como la influencia de diferentes condiciones operacionales en la eliminación del cobre de un efluente acuoso se presentan en el Capítulo 4.

En el Capítulo 5 se determinó el potencial que tienen los Tecnosoles con propiedades ándicas para la inmovilización de fosfato en aguas contaminadas. Para ello, se analizó el efecto que tienen el pH y la presencia de distintos aniones en el medio (sulfatos, cloruros, carbonatos,…) sobre la retención de fosfatos, así como su cinética de retención. Por otro lado, se determinó la eficiencia que tienen los Tecnosoles en sistemas en continuo, evaluando el efecto que tienen distintos parámetros (pH, flujo, cantidad de material) sobre su capacidad de eliminación de fosfato del sistema acuoso.

En el Capítulo 6, se determinó la eficacia de la recuperación de escombreras con contaminación polimetálica mediante la aplicación de una capa de Tecnosol con propiedades ándicas y eutróficas. El proceso de recuperación se evaluó a nivel físico-químico (pH, conductividad eléctrica, concentración multielemental,…), biológico (respiración basal y actividad enzimática) y ecotoxicológico (bioensayos directos e indirectos según las directivas de la OCDE y ensayo en microcosmos en condiciones de invernadero), tanto en los materiales como en sus lixiviados.

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CALIDAD AMBIENTAL DE LOS SUELOS Y AGUAS DE LA MINA FÉ (SALAMANCA): SITUACIÓN INICIAL Y ALTERNATIVAS DE RECUPERACIÓN

1. INTRODUCCIÓN

Las explotaciones mineras son consideradas una actividad importante para el desarrollo socioeconómico de la sociedad moderna. Los principales impactos originados por la minería son consecuencia no sólo de las actividades extractivas (degradación paisajística, alteración de la estructura del suelo o de los flujos de escorrentía), sino también de las características mineralógicas y físico-químicas de las escombreras que se acumularon en el área minera. Estas escombreras, generalmente, presentan baja estabilidad estructural y fertilidad, así como elevadas concentraciones de elementos potencialmente tóxicos (Wong, 2003). Por otra parte, la presencia de fases sólidas reactivas en los materiales de escombrera, como son los sulfuros, y el cambio en las condiciones de potencial redox respecto a su situación original, aumenta la capacidad de generación de drenaje ácido (pH < 3) y potencia graves problemas ambientales por el incremento de la movilidad y biodisponibilidad de diferentes elementos de riesgo (As, Se, Cd, Cu, ...) que pueden encontrarse asociados a los sulfuros (Monterroso y Macías, 1998a, 1998b; Monterroso et al., 1998; Abreu et al., 2010; Sánchez-España et al., 2005; Nodstrom, 1982). La composición de los drenajes ácidos de mina está determinada por el tipo de material que atraviesa el agua de lluvia y la disolución del suelo, así como los tiempos de residencia o interacción propios de cada sistema (Monterroso y Macías, 1998). En general, los suelos desarrollados sobre residuos de minería y metalurgia presentan baja calidad físico-química y biológica, si bien en algunos casos puedan ser colonizados por vegetación espontánea y tolerante. Así, el problema ambiental presente en muchas áreas mineras se relaciona no sólo con las características extremas de las escombreras y suelos desarrollados sobre estos materiales, sino también con el potencial de generación de drenaje ácido.

Debido a la complejidad de las escombreras y suelos de las áreas mineras, principalmente las que presentan sulfuros, es esencial una evaluación holística de los riesgos medioambientales asociados a cada área minera. Esta evaluación permite conocer los verdaderos problemas, así como delinear y gestionar el programa de rehabilitación más adecuado y sostenible para cada situación ambiental y socio-económica. Es fundamental poseer la máxima información, no sólo del problema (distribución de la contaminación, composición química de los materiales,…), sino también de la caracterización y condiciones específicas de cada lugar (geología, climatología y geomorfología) (Bech et al., 2014).

El objetivo de este trabajo es evaluar las características físico-químicas de los suelos de una mina de uranio (mina Fé, Saelices el Chico, Salamanca, España), así como conocer la calidad química de las aguas de escorrentía de los suelos de la mina. Esto permitirá realizar un diagnóstico de la problemática ambiental existente y de las potenciales intervenciones de recuperación a aplicar.

2. MATERIAL Y MÉTODOS

2.1. Área de estudio

La mina Fé está localizada en Saelices el Chico (29T 702113 4501299), en las proximidades de la Ciudad Rodrigo (Salamanca, España). Tiene una superficie de aproximadamente 320 ha (3.2 km^2). La región en la que se localiza la mina presenta condiciones climáticas de tipo mediterráneo, con una fuerte influencia continental (tipo CSA en la clasificación de Koppen). La precipitación media anual es de 503 mm, principalmente en el invierno, y las temperaturas varían entre 4 y 30 ºC. Los regímenes de humedad y temperatura del suelo son xérico y mésico, respectivamente.

Esta mina explotó el depósito de uranio más importante en España, con una reserva de más de 16000 Mg de U_3O_8, el cuál fue originado por un sistema de procesos hidrotermales complejos hace 34.8 millones de años (Both et al., 1994). El origen de la mineralización en este yacimiento se atribuye a una re-movilización y transporte del uranio contenido en los metasedimentos del complejo esquisto-grauváquico, principalmente pizarras ampelíticas, y su posterior deposición por el complejo uranil-carbonatado en zonas fracturadas de los esquistos (Arribas, 1985). Según este autor, las especies que presentan uranio en este yacimiento son principalmente uraninita y pechblenda (UO_2), así como fases sólidas secundarias de composición variable, como por ejemplo iantinita ($U^{4+}(UO_2)_5O_7 \cdot 10H_2O$), autunita ($U^{4+}(UO_2)_2(PO_4)_2 \cdot 11H_2O$), y kasolita ($Pb(UO_2)(SiO_4) \cdot H_2O$), que están asociadas a diferentes sulfuros, principalmente de Fe como la pirita o marcasita, pero también de Pb, Zn y Cu. La extracción minera y concentración de uranio se realizaron entre los años 1975 y 2000 por la empresa ENUSA.

Después del cese de las actividades de extracción se inició un plan de recuperación para evitar el riesgo de radiactividad en la zona, el cual consistió en encapsular los residuos radioactivos bajo una capa de Arcosa con un espesor de 30 cm (Figura 1). Sobre esta capa se depositó una mezcla heterogénea de material de escombrera sin radioactividad y de roca de la zona con sus respectivos suelos en un espesor de aproximadamente 30 cm y, por encima de esta, una capa de "tierra vegetal" de 30 cm. Estas acciones modificaron en mayor o menor medida la dinámica del sistema hídrico, ayudando a favorecer los procesos de escorrentía superficial y delimitando la infiltración a capas profundas.

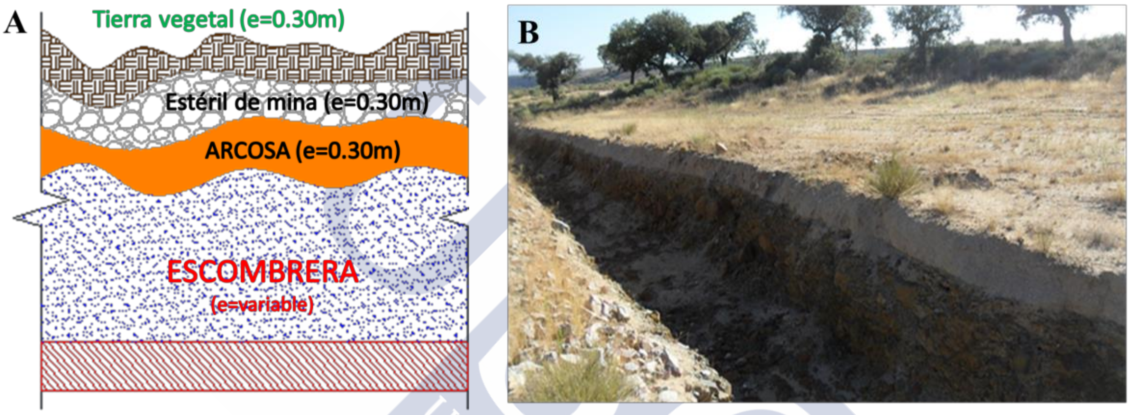

Figura 1. A) Esquema conceptual del perfil del plan de recuperación establecido en la mina Fé para mitigar a la radioactividad. B) Fotografía del perfil presente en los suelos de la mina Fé, siguiendo el esquema del plan de recuperación.

2.2. Caracterización química de suelos y aguas

En el área minera se recogieron un total de 59 muestras de suelos en septiembre de 2015. Estas muestras son representativas de suelos localizados en el área minera ($n = 46$), los cuales se desarrollan sobre distintos residuos de mina y rocas encajantes en diferentes proporciones, así como de suelos naturales de la zona adyacente a la mina ($n = 13$). La clasificación de los suelos fue realizada de acuerdo con sus características físico-químicas, las observaciones obtenidas en campo y las directrices de la World Reference Base, WRB (IUSS Working Group, 2015).

En cada punto de muestreo se recogió una muestra compuesta de suelo (≈ 2 kg) hasta una profundidad de 20 cm, correspondiente al horizonte superficial. Las muestras de suelo se secaron al aire y fueron homogeneizadas y tamizadas. En la fracción < 2 mm se analizaron: pH en H_2O y KCl (1:2.5 m: *V*), P extraíble (método Olsen), y contenidos totales de C, N y S (TruSpec CHN-1000, LecoSC-144DR). La capacidad de intercambio catiónica efectiva se determinó con una solución de NH_4Cl 1 M siguiendo el método de Peech et al. (1947). El contenido total de elementos se extrajo de las muestras de suelo (fracción < 2 mm) con *aqua regia* sometidas a presión en un digestor microondas (ETHOS Plus, Milestone). Las disoluciones obtenidas tras la digestión del suelo se acidificaron y almacenaron a 4 ºC hasta su análisis químico.

Para evaluar la calidad de las aguas del área de explotación se recogieron un total de 11 muestras de aguas, entre noviembre de 2014 y julio de 2015, de una poza denominada "Caldera" en la que convergen las aguas que emergen del hueco de explotación y las aguas de escorrentía de las escombreras adyacentes. El análisis de la calidad química de estas aguas, en contacto con los residuos mineros, permite evaluar la situación ambiental actual y predecir, mediante modelos termodinámicos de equilibrio, las tendencias de evolución del sistema y, consecuentemente, establecer los principales puntos de enfoque del sistema de recuperación ambiental.

En el momento de recogida de las muestras de agua se midieron *in situ* el pH, potencial redox y conductividad eléctrica. Todas las muestras fueron filtradas en el campo (< 0,45 µm) y divididas en dos sub-muestras para llevar a cabo distintos análisis químicos. Una sub-muestra fue acidificada a pH < 2 con HNO_3 concentrado, mientras que la segunda sub-muestra se conservó sin acidificar. Todas las muestras fueron almacenadas a 4 ºC hasta su análisis químico.

En los extractos obtenidos tras la digestión de las muestras de suelo y en las muestras de agua se determinó el contenido de Al, Ca, Mg, Na, K, Co, Cu, Fe, Mn, Ni, Pb, y Zn mediante espectroscopia de absorción atómica de llama (FAAS, Perkin Elmer 1100B); As y Cd mediante espectroscopia de absorción atómica en horno de grafito (GFAAS; Perkin Elmer 4110ZL); y fosfato mediante el método de azul de molibdeno (Murphy y Riley, 1962). En las muestras de agua se determinó también la concentración de Cr y Si por FAAS; Sb y Se por GFAAS; sulfatos, nitratos y cloruros mediante cromatografía iónica (Dionex series 4500i); nitritos y amonio mediante un analizador de flujo (Third generation continuous flow analyser 2000); y fluoruros mediante electrodo selectivo (MetroHM 692 pH/ION METER).

En el período seco (mayo-octubre) se forman eflorescencias salinas de evaporitas en la superficie de los materiales, las cuales fueron recogidas. Estas sales se almacenaron en recipientes herméticos a temperatura ambiente y protegidos de la luz. El análisis mineralógico de las evaporitas se realizó en muestras de polvo (< 45µm), previamente seleccionadas tras análisis con un microscopio binocular según color y morfología, mediante difracción de rayos X (XRD) usando radiación Cu Kα. Para la identificación mineralógica se consideró, además de las difracciones obtenidas por DRX, la composición elemental, pH de los lixiviados, así como la temperatura y humedad relativa del área en el campo. Después de ser analizadas por XRD las muestras de sales se disolvieron en agua (1:20 m: *V*), se agitaron hasta su completa disolución y su composición química (a pH < 3.5) se determinó mediante FAAS y GFAAS.

El control de calidad interno incluyó el uso de muestras de referencia certificada (SO-2 Soil simple-CANMET, NIST 2782 Industrial Sludje) y soluciones estándar certificadas, así como réplicas analíticas de las muestras, blancos y estándares de laboratorio.

2.3. Análisis de datos

Con los resultados analíticos de las muestras de agua se llevó a cabo la modelización termodinámica usando el software de especiación PHREEQC (Parkhurst y Appelo, 2013), para conocer así las actividades de las principales especies químicas presentes y las tendencias de evolución mineralógica. El análisis estadístico se realizó con el programa Statistica versión 8.0 para Windows (StatSoft, Inc., 2007). Para evaluar las diferencias entre los dos grupos de suelos (suelos de mina *vs* suelos naturales) se utilizó el test no paramétrico de Mann-Whitney a $p < 0.05$. Tanto para los análisis estadísticos como para la modelización termodinámica, los resultados por debajo del límite de detección fueron asumidos como la mitad del valor de dicho límite.

Para la evaluación de los condicionantes limitantes de las muestras de suelo se asignaron una serie de valores críticos a cada uno de los parámetros físicos-químicos siguiendo el procedimiento para la Clasificación de Capacidad de Fertilidad del Suelo (Buol et al., 1975, modificado por Calvo de Anta et al., 1992), y teniendo en cuenta los límites de los elementos potencialmente tóxicos (NGR, establecidos para Galicia y materiales Hercínicos) que pueden generar riesgos ambientales (Macías y Calvo de Anta, 2008).

3. RESULTADOS

3.1. Caracterización y clasificación de los suelos

Las principales características químicas de los suelos naturales adyacentes a la mina Fé y de los suelos de mina se recogen en las Tablas 1 y 2. De un modo general, los suelos de mina presentan gran heterogeneidad en sus características, comparativamente a los suelos naturales, debido a los materiales de partida sobre los que se desarrollaron. Esto se refleja en la ausencia de diferencias significativas para muchas de las características químicas analizadas. La textura de los suelos naturales es principalmente franco-arenosa, mientras que los suelos de mina tienen texturas desde arenoso-franca hasta franco-arcillo-arenosa (Figura 2).

Los suelos naturales presentaron un pH ácido o débilmente ácido (pH_{H2O} = 5.06-6.68), con un predominio de las cargas negativas (Tabla 1). Los suelos de mina mostraron una mayor variabilidad en la reacción del suelo, desde neutra a ácida, con frecuentes valores de pH en agua y KCl menores a 3.5 (reacción hiperácida). Estos valores de pH se diferencian significativamente de los valores obtenidos para los suelos naturales (Tabla 1).

El contenido total de C y N fueron muy bajos (Tabla 1), especialmente en las muestras correspondientes a los suelos de mina, encontrándose diferencias significativas entre ambos grupos de muestras. Estos valores se traducen en un bajo contenido de materia orgánica del suelo, lo que conlleva una baja estabilidad estructural, menor capacidad de retención de agua y menor resistencia a los procesos erosivos, así como una escasa actividad biológica en los suelos (FAO y ITPS, 2015). El contenido total de S no presentó diferencias entre los dos grupos de suelos, si bien se encontró una mayor variabilidad en los suelos de mina, con valores máximos de 78.0 g kg^{-1} (Tabla 1). El contenido total de P tampoco mostró diferencias entre ambos grupos de muestras. Sin embargo para la fracción disponible de P (P_{Olsen}) si se encontraron diferencias, siendo mayor la cantidad de P disponible en los suelos de mina (Tabla 1).

Tabla 1. Características químicas de los suelos naturales y suelos de mina de la mina Fé. Se presenta el rango de valores mínimo y máximo, así como los valores de mediana y media (entre paréntesis).

	Suelos Naturales (*n*=13)	Suelos de mina (*n*=46)
pH_{H2O}	5.06 - 6.68 (5.51; 5.68 *)	3.25 - 6.95 (5.20; 5.04 *)
pH_{KCl}	3.41 - 5.97 (4.58; 4.72 *)	3.13 - 6.43 (3.84; 4.06 *)
	g kg⁻¹	
C_{total}	3.00 - 47.80 (29.90; 26.80 *)	2.50 - 55.40 (9.20; 13.0 *)
N_{total}	0.03 - 3.20 (2.00; 1.70 *)	0.03 - 4.50 (0.30; 0.70 *)
S_{total}	0.17 - 0.60 (0.30; 0.30)	0.04 - 78.0 (0.40; 3.40)
	mg kg-1	
P_{total}	132.81 - 585.08 (328.27; 330.62)	80.21 - 750.53 (388.32; 375.33)
P_{Olsen}	1.04 - 6.25 (2.49; 2.77 *)	0.03 - 35.83 (4.24; 6.78 *)
	cmoles (+) kg-1	
pH	3.89 - 7.24 (4.72; 5.00 *)	3.04 - 6.09 (4.10; 4.24 *)
H^+	—	0.02 – 10.30 (0.36; 1.16)
Al^{3+}	<0.123 – 3.15 (0.20; 0.92 *)	0.14 – 13.98 (1.61; 2.72 *)
Ca^{2+}	1.27 – 21.64 (9.91; 9.19)	0.20 – 315.3 (7.31;15.31)
Mg^{2+}	0.38 – 2.92 (1.18; 1.26 *)	0.23 – 55.56 (2.64; 4.72 *)
Na^+	0.02 – 0.11 (0.07; 0.06)	0.01 – 0.44 (0.06; 0.07)
K^+	0.13 – 0.91 (0.27; 0.31)	0.00 – 1.07 (0.22; 0.25)
CICe	1.83 - 23.29 (11.90; 11.16)	3.44 - 315.90 (13.20; 23.02)

CICe: Capacidad de intercambio catiónico efectiva. *Los datos del mismo parámetro seguidos de asterisco indican diferencias significativas entre los dos grupos de suelos ($p < 0.05$).

Se observó una gran variabilidad en la capacidad de intercambio catiónico efectiva (CICe) de los suelos de mina, debido fundamentalmente a la gran variación en el contenido de arcillas (Figura 2). A pesar de no observarse diferencias significativas en los valores de CICe para ambos grupos de suelos, si se encontraron para los contenidos de Al y Mg intercambiable, siendo los suelos de mina aquellos que presentaron porcentajes de saturación máximos del 60 % y 70 % para el Al y Mg intercambiable, respectivamente (Tabla 1).

Para los contenidos totales de elementos no se encontraron diferencias entre los dos grupos de suelos, con la única excepción del Pb (Tabla 2). Sin embargo, de forma general los suelos de mina presentan mayores concentraciones totales de los elementos. Aunque la heterogeneidad de los suelos es relativamente grande, el contenido total de los distintos elementos es menor que el observado para otros suelos de mina (y suelos agrícolas adyacentes) localizados en la misma franja de la mina Fé (Abreu et al., 2007, 2014a,b; Ferreira da Silva et al., 2013; Ávila et al., 2017; Neves et al., 2012). Para estos suelos de mina, este hecho puede estar relacionado con la dilución de la contaminación al mezclar materiales de escombreras con suelos naturales en el proceso de cierre.

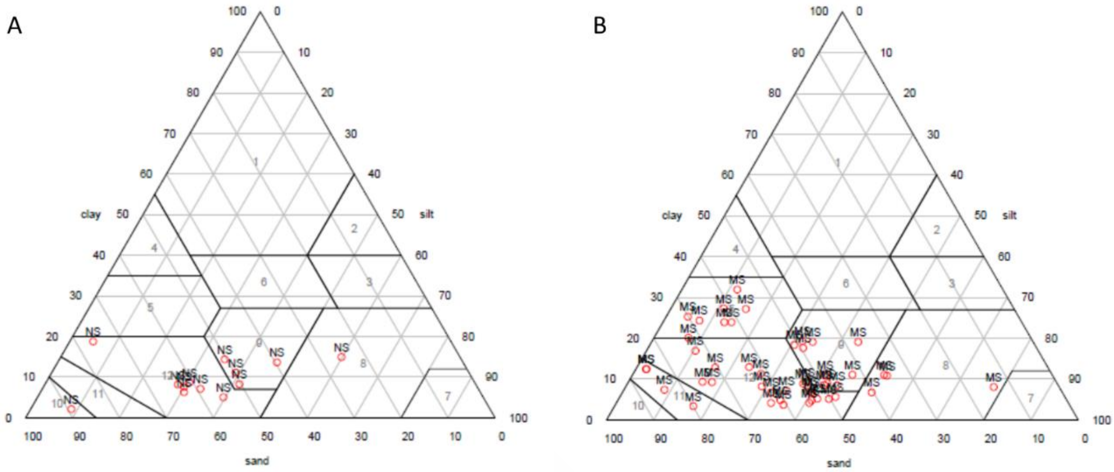

Figura 2. Clases texturales de los suelos naturales (A) y de mina (B): 1-Arcilloso; 2-Arcillo limoso; 3-Franco arcillo limoso; 4-Arcillo arenoso; 5-Franco arcillo arenoso; 6-Franco arcilloso; 7-Limoso; 8-Franco limoso; 9-Franco; 10-Arenoso; 11-Arenoso franco; 12-Franco arenoso.

La concentración total de elementos químicos en el suelo es considerado un indicador del grado de contaminación, siendo utilizado en muchos países como un parámetro de la legislación para la protección y calidad del suelo (Santos et al., 2017). Debido a que la Comunidad Autónoma en la que se sitúa el área minera no dispone de legislación ni valores máximos admitidos, se usaron los valores genéricos de referencia de Galicia (DOGA, 2009) para los diferentes usos del suelo y los valores del nivel de fondo edafogeoquímico (NGR) establecido por Macías y Calvo de Anta (2008). Estos valores pueden considerarse totalmente válidos pues están basados en las variaciones naturales (fondo edafogeoquímico) de los suelos de Galicia, dentro de la misma zona del macizo hercínico que el yacimiento de Saelices el Chico. Se seleccionaron como referencia los materiales esquistosos y pizarreños, debido a que las características geológicas de éstos materiales son similares a los del complejo esquisto grauváquico de la zona estudiada. Así, se observó que una gran parte de las muestras de los suelos de mina tienen contenidos que exceden los valores máximos de As, Co, Cu, Mn, Ni y Pb establecidos para diferentes usos y protección de la salud humana (DOGA, 2009). Por otro lado, los suelos naturales, también presentan contenidos de As, Mn y Zn que superaron, en algún caso, el fondo edafogeoquímico indicado en Macías y Calvo de Anta (2008) (Tabla 2).

Tabla 2. Concentración total de los elementos químicos de los suelos naturales y de la mina Fé (Mínimo – máximo; ((mediana; media)), y Niveles Genéricos de Referencia (NGR) y de fondo edafoquímico (DOGA, 2009; Macías y Calvo de Anta, 2008).

	Suelos naturales (*n*=13)	Suelos de mina (*n*=46)	NGR de Galicia para diferentes usos ($mg{\cdot}kg^{-1}$)			
	$mg{\cdot}kg^{-1}$		*Industrial*	*Urbano*	*Otros*	*Base Edafoquímica*
Al	7210.5 - 37420 (25100; 24696.2)	7200 - 54820 (31140; 29821.3)	-	-	-	-
As	3.00 – 64.0 (10.0; 18.3)	3.54 - 141 (19.5; 35.8)	50	50	50	45
Ca	374 – 17360 (819.5; 2344)	40.70 - 81200 (652.0; 2792)	-	-	-	-
Cd	0.08 - 0.24 (0.12; 0.15)	0.01 - 2.09 (0.20; 0.36)	20	4	2	0.25
Co	2.50 - 27.00 (15.00; 13.38)	2.50 – 45.0 (15.00; 17.27)	150	50	40	40
Cr	6.00 - 42.00 (19.00; 21.38)	2.50 – 44.0 (24.50; 21.73)	300	100	80	80
Cu	2.50 - 40.0 (15.00; 16.35)	2.50 – 70.0 (21.0; 24.2)	200	100	50	45
Fe	3060 - 36400 (20780.00; 19892.31)	6140 - 46800 (23100.0; 25018.7)	-	-	-	-
K	1360 - 6760 (3710.00; 3983.10)	1070 - 17060 (4380.0; 4819.9)	-	-	-	-
Mg	780 – 10400 (3200; 3646.2)	1220 - 11400 (5300; 5703.0)	-	-	-	-
Mn	44.0 - 1980 (680; 698.4)	30.0 – 2260 (448.5; 537.0)	2000	1500	850	850
Na	115 – 605 (240; 252.2)	84.0 – 413 (214.5; 212.4)	-	-	-	-
Ni	7.00 – 64.0 (32.0; 29.23)	6.00 – 97.0 (32.5; 36.6)	200	100	75	65
Pb	12.5 – 35.0 (12.5; 18.9 *)	10.0 – 316 (29.0; 40.7 *)	500	100	100	55
Zn	14.0 – 113 (60.0; 58.5)	18.0 – 223 (72.0; 83.0)	1000	500	300	100

** Los datos del mismo parámetro seguidos del asterisco indican diferencias significativas entre los dos grupos de suelos ($p < 0.05$)*

En los suelos de mina, en los que el contenido de materia orgánica es muy bajo y las reacciones son predominantemente ácidas, las elevadas concentraciones totales de elementos potencialmente tóxicos pueden generar un elevado riesgo para la salud humana y el ecosistema al favorecerse condiciones de mayor disponibilidad de estos elementos. Únicamente aquellos elementos presentes en la fracción disponible del suelo (fracción soluble e intercambiable) afectan directamente a los organismos y procesos edafoquímicos (Adriano, 2001; Kabata-Pendias, 2001). Por otro lado, los suelos naturales estudiados indican una gran influencia antrópica, como consecuencia de la actividad minera cercana o la dispersión de partículas por el viento. Estos suelos también pueden verse influenciados por otro tipo de uso intensivo, como la ganadería. Esta influencia, así como las labores de mezclas y cubriciones realizadas en la fase de recuperación, podría explicar la similitud de las características químicas entre los dos grupos de suelos.

De acuerdo con los resultados obtenidos (observaciones de campo y datos analíticos), se pueden diferenciar cuatro grupos de suelos de referencia de acuerdo con el sistema de la WRB (IUSS Working Group, 2015), los cuales están cartografiados en la Figura 3. Los suelos naturales se generaron a partir de la alteración de materiales metamórficos, pelitas grises y negras (IGME, 1990) bajo condiciones climáticas xerofíticas dando origen a un horizonte A ócrico, con saturación superior al 50%, de escasa profundidad y, en ocasiones, un delgado horizonte de alteración (B cámbico) en materiales metamórficos. En materiales sedimentarios, como las rañas o depósitos de terrazas pleistocénicas puede aparecer un horizonte árgico de mayor o menor espesor. La evolución de la edafogénesis a partir de estos materiales metamórficos sigue la secuencia Leptosol lítico - Leptosol háplico - Cambisol léptico - Cambisol háplico, de modo que el horizonte más evolucionado encontrado es un horizonte B de tipo cámbico, con escaso espesor y bajo grado de evolución químico-mineralógico, en el que predominan las fases sólidas heredadas del material de partida.

Los suelos de mina están muy modificados por las actividades mineras y la construcción de las infraestructuras de recuperación y contención de la radioactividad, caracterizándose por un alto contenido de “artefactos” (> 20%), lo que permite clasificarlos como Tecnosoles espólicos. Dentro de este grupo se diferencian algunos suelos debido a sus propiedades y/o condiciones específicas. Así, en las zonas afectadas por drenaje ácido de mina se originan horizontes sulfúricos, dando lugar a Tecnosoles espólicos sulfúricos (Figura 4A), mientras que en las zonas con elevadas concentraciones de eflorescencias salinas se originan Tecnosoles espólicos sálicos (Figura 4B). Los suelos recogidos en áreas con actividades urbanísticas se clasificaron como Tecnosoles úrbicos y ekranicos.

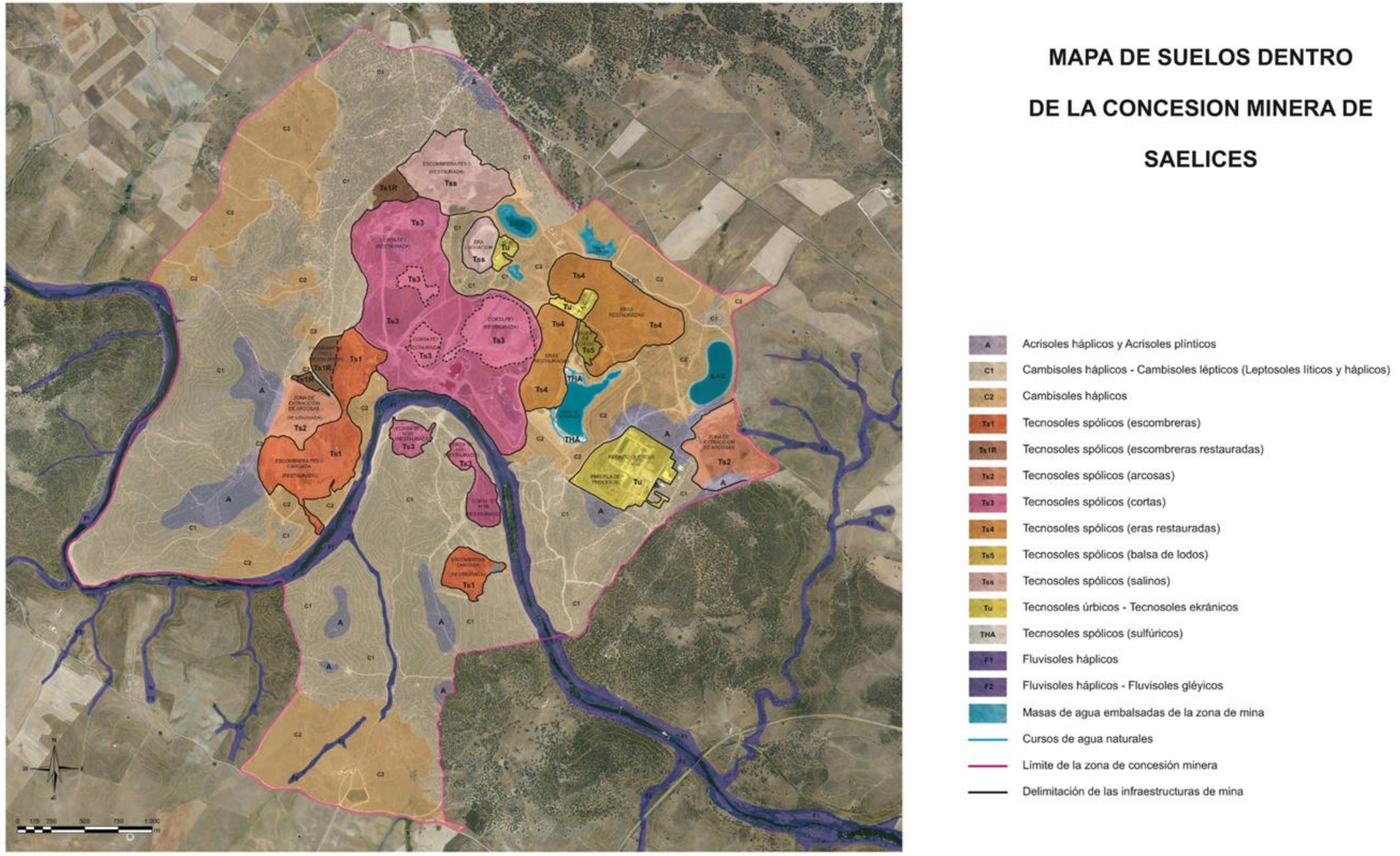

Figura 3. Cartografía de las diferentes unidades edafológicas identificadas en la mina Fé según la WRB (IUSS Working Group, 2015).

En el período seco, cuando la temperatura atmosférica es más alta y la humedad relativa es baja, se empiezan a formar sales evaporíticas con una elevada solubilidad. El espesor de estas costras superficiales de sales varía desde poco milímetros a aproximadamente 50 cm (Figura 5). Como consecuencia de la alta concentración de sulfatos en las aguas, así como otros elementos (Al, Mg y Fe), se puede formar distintos sulfatos y oxihidroxisulfatos. Mediante análisis por DRX se identificaron los minerales *epsomita* ($MgSO_4 \cdot 7H_2O$) y diferentes sulfatos de Al y Fe, como la *halotricita* ($Fe^{2+}Al_2(SO_4)_4 \cdot 22H_2O$) y la *rhomboclasa* ($H_5Fe^{3+}O_2(SO_4)_2 \cdot 2H_2O$), y en menor medida sulfatos de Cu y Ni, como la *bonattita* ($CuSO_4 \cdot 3H_2O$) y la *morenosita* ($NiSO_4 \cdot 7H_2O$). Pueden existir otras fases minerales, sin bien no son detectables mediante DRX debido a su baja concentración o cristalinidad. La composición química de las sales (Tabla 3) coincide con las fases sólidas identificadas.

Debido a que estos sulfatos son altamente solubles, los episodios de precipitación llevan a la redisolución (principalmente cuando forman costras finas) de muchas de estas sales eflorescentes acumuladas durante el período seco y, consecuentemente, a la dispersión de elementos potencialmente tóxicos a zonas adyacentes. De hecho, las concentraciones de algunos de estos elementos en el primer mes de lluvia son mayores. Se puede considerar entonces que estos sumideros de sulfato y elementos potencialmente tóxicos son temporales.

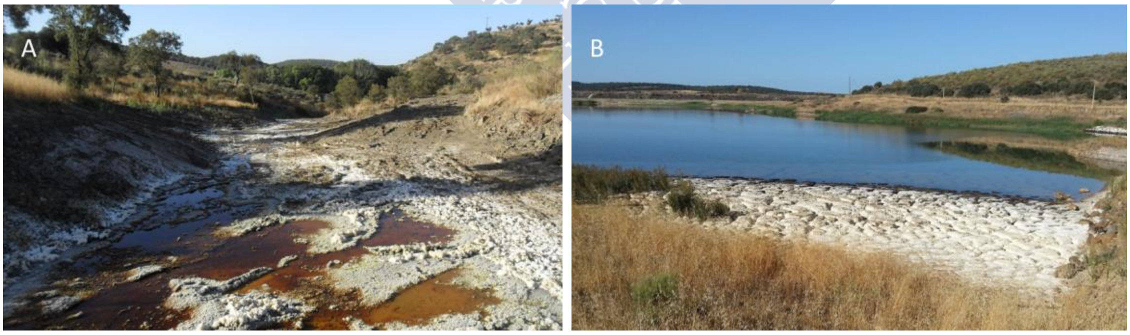

Figura 4. Tecnosoles espólicos sulfúricos (A) y Tecnosoles espólicos sálicos (B) de la mina Fé

Figura 5. Sales evaporiticas formadas sobre los Tecnosoles espólicos sálicos de la mina Fé.

Tabla 3. Composición química de sales evaporíticas presentes en la mina Fé.

	Muestra 1	Muestra 2
	$g\cdot kg^{-1}$	
C	2.50	2.30
N	<0,05	<0,05
S	127.2	123.4
	$mg\cdot kg^{-1}$	
P	9.79	6.53
Al	13060	4600
As	0.20	0.42
Ca	358	360
Cd	8.41	3.91
Co	320	303
Cr	<5.00	<5.00
Cu	33.0	17.0
Fe	844	735
K	175	84.0
Mg	23000	74800
Mn	8820	9140
Na	835	1545
Ni	18.0	18.0
Pb	<25.0	<25.0
Zn	1020	690

3.2. Caracterización físico-química de las aguas y modelización termodinámica

Las principales características químicas de las muestras de agua de la Caldera (Figura 6) se recogen en la tabla 4 y la especiación resultante de la modelización termodinámica en la tabla 5. Las aguas muestreadas son hiperácidas ($pH < 3.5$), hiperoxidantes ($Eh > 600$ mV) e hiperconductoras “de tipo salmuera” ($CE > 10\ mS\cdot cm^{-1}$) e hiperoxidantes ($Eh > 650$ mV). La composición química de estas aguas es variable a lo largo del año (datos no mostrados), debido a las variaciones hidrológicas estacionales. Este hecho es relevante para el manejo y entendimiento del sistema y consecuentemente para su recuperación (Monterroso y Macías, 1998b).

Las muestras de agua presentan concentraciones elevadas de sulfato disuelto (que en algunos casos alcanzan valores próximos a $34\ g\ L^{-1}$) y de varios elementos potencialmente tóxicos (Al, Ca, Mg Fe y Mn), lo que explica su elevada conductividad eléctrica. Esto se debe a la alteración de los sulfuros minerales presentes en el área minera, cuya oxidación contribuye a la formación continua de lixiviados ácidos y consiguiente liberación de elementos químicos (Monterroso y Macías, 1998a, Sánchez–España, 2005). Así, las aguas de drenaje ácido de las escombreras de la mina Fé representan un medio de dispersión de elementos potencialmente tóxicos y un foco de contaminación para suelos adyacentes. Esto conduce a la reducción del establecimiento de vegetación, incluso de la considerada tolerante, y decrecimiento de la biodiversidad específica, así como alteración de la actividad de varias enzimas de los suelos asociadas al ciclo de los nutrientes (Abreu et al., 2010; Santos et al., 2016).

En general, la composición química de estas aguas está en el mismo rango que la de otros drenajes ácidos de áreas mineras ricas en sulfuros de la península Ibérica (Abreu et al., 2010, Sánchez-España et al., 2005). Los resultados de la modelización termodinámica indican que la mayoría de los metales están formando pares iónicos con el sulfato, siendo este anión el que regula la química del agua. Dado su elevada actividad como SO_4^{-2} libre ($\approx 10^{-2}$ M), este ión presenta una gran tendencia a unirse a los cationes metálicos presentes en el medio formando fases sólidas estables. Por otro lado, la fuerte acidez de estas aguas origina la presencia de especies de elevada toxicidad entre las que destacan el Al^{3+}, Mn^{2+},

Zn^{2+}, Ni^{2+} y Cu^{2+}, con actividades que varían entre 10^{-4} y 10^{-6} M dependiendo de la especie (Tabla 5).

Tabla 4. Características químicas de las aguas de contacto con los suelos de mina (Control) recogidos en la mina Fé (n=11).

	Mínimo - máximo	Media
pH	2.73 – 2.97	2.80
E.C ($mS \cdot cm^{-1}$)	11.4 – 16.0	12.8
Eh (mV)	709 – 841	759
	$mg \cdot L^{-1}$	
F^-	0.15 – 0.34	0.23
Cl^-	33.9 – 152	82.7
SO_4^{-2}	22929 – 33908	30145
$PO4^{-3}$	<DL	<DL
NO_3^-	1.00 – 23.8	10.5
NO_2^-	0.03 – 1.92	0.50
NH_4^+	0.03 – 1.85	0.75
Al	207 – 372	291
Ca	516 – 688	578
Mg	1850 – 2375	2067
Na	46.8 – 290	118
K	5.82 – 7.31	6.27
Co	7.34 – 9.00	8.37
Cr	0.07 – 0.08	0.08
Cu	0.36 – 0.70	0.52
Fe	104 – 175	133
Mn	284 – 348	310
Ni	17.5 – 19.2	18.7
Pb	0.48 – 0.61	0.55
Si	25.9 – 30.8	29.1
Zn	2.68 – 25.4	19.9
	$\mu g \cdot L^{-1}$	
As	1.00 – 159	54.4
Cd	81.3 – 336	202
Sb	3.00 – 6.00	4.67
Se	2.75 – 48.0	18.1

EC: Conductividad eléctrica; DL: límite de detección.

Tabla 5. Actividad de las especies dominantes, en molar, para las aguas de escorrentía y aguas subterráneas de contacto de los suelos de mina (Control) recogidos en la mina Fé (n=11).

Especies dominantes	Media	Desviación estándar
$Al(SO4)_2^-$	3.13E-03	7.74E-04
Al^{+3}	1.47E-04	6.71E-05
$AlSO_4^+$	3.02E-03	1.20E-03
Ca^{+2}	2.26E-03	4.76E-04
Cd^{+2}	1.88E-07	6.41E-08
Cu^+	2.51E-06	1.03E-06
Fe^{+2}	3.95E-04	1.23E-04
H^+	1.71E-03	3.20E-04
H_3AsO_3	7.79E-07	8.40E-07
K^+	1.12E-04	2.52E-05
Mg^{+2}	1.57E-02	2.42E-03
Mn^{+2}	8.65E-04	1.98E-04
Na^+	3.81E-03	2.79E-03
Ni^{+2}	4.93E-05	5.55E-06
Pb^{+2}	1.75E-07	3.10E-08
SO_4^{-2}	1.76E-02	5.48E-03
Zn^{+2}	3.76E-05	9.61E-06

A partir del análisis físico-químico de las aguas muestreadas en la poza de la Caldera (Tabla 4) y la correspondiente modelización termodinámica (Tabla 5), se elaboraron diferentes diagramas de estabilidad para este sistema. Estos diagramas (Figuras 7 y 8) muestran la evolución del sistema, en cuanto a su reacción, tendencias de neoformación y alteración mineralógica.

La primera aproximación se estableció con el sistema SiO_2-Al_2O_3-H_2O (Figura 7), en el que se establecen las relaciones termodinámicas entre los distintos aluminosilicatos generalmente neoformados en los sistemas edáficos y de alteración superficial. Este diagrama de equilibrio pone de manifiesto el importante problema que presentan las escombreras que dan origen a las aguas de la Caldera, pues todas las muestras se encuentran en condiciones de disolución para las fases sólidas consideradas, lo que indica su completa alteración y/o imposibilidad de neoformación mineral.

Por otro lado, hay que considerar la importancia de los sulfatos en el sistema, junto con los silicatos, óxidos y oxihidróxidos de aluminio, evaluando para ello el diagrama de estabilidad del sistema SO_2-SiO_2-Al_2O_3-H_2O (Figura 8). Este diagrama mostró claramente que en la mina Fé el control termodinámico de la concentración de aluminio, sulfatos y sílice no es ejercida por los hidróxidos de aluminio, como la *gibbsita* $Al(OH)_3$, que suele ser lo usual en sistemas no degradados, sino por oxihidroxisulfatos de aluminio, como la *jurbanita* ($Al(SO_4)(OH) \cdot 5H_2O$ y la *alunita* ($KAl_3(SO_4)_2(OH)_6$), siendo esta última la fase sólida más estable. Para el hierro, el diagrama Eh-pH mostró que el sistema se encuentra en el campo de estabilidad de las *jarositas* ($KFe_3(SO_4)_2(OH)_6$) o en equilibrio con la *schwermanita* ($Fe_{16}O_{16}(SO_4)_2(OH)_{12} \cdot 10H_2O$) (Figura 8). Por lo tanto en las aguas de la Caldera la principal fase sólida estable del aluminio es la *alunita*, que junto con las *jarositas (sulfatos de Fe)*, serían las fases minerales hacia las que tiende el sistema termodinámicamente, con disolución de todos las demás fases sólidas (Figuras 8 y 9). Cuando el pH sube estas especies de sulfatos serían sustituidas por los hidroxisulfatos jurbanita y schwermanita respectivamente.

Figura 6. Aguas de la Caldera en la mina Fé.

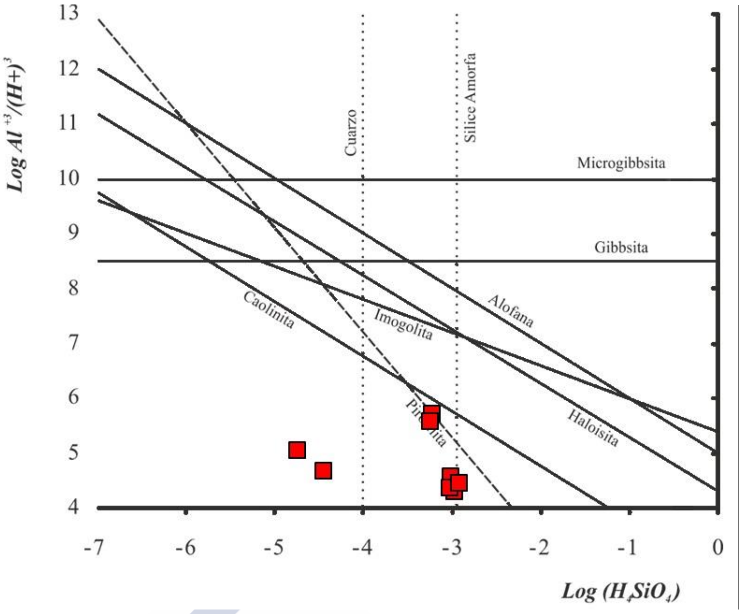

Figura 7. Diagrama de estabilidad del sistema SiO_2-Al_2O_3-H_2O para las aguas de la Caldera.

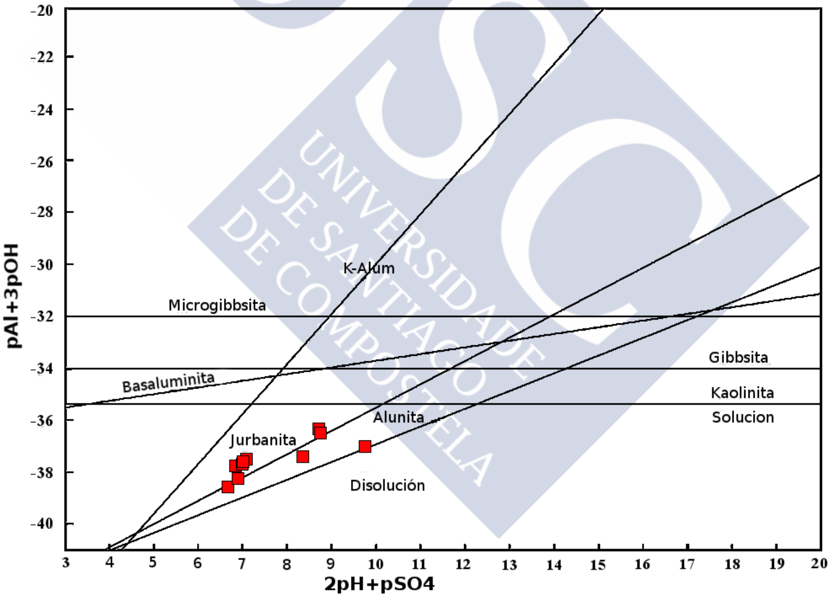

Figura 8. Diagrama de estabilidad del sistema SO_2-SiO_2-Al_2O_3-H_2O para las aguas de la Caldera

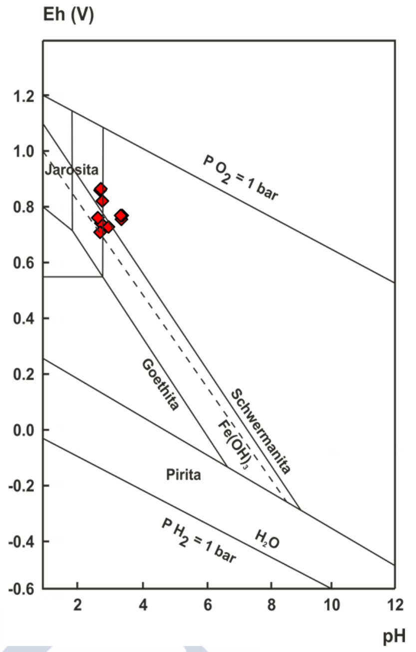

Figura 9. Diagrama Eh-pH para las formas de Fe en las aguas de la Caldera

3.3. Consideraciones para la recuperación ambiental de los suelos

Para la recuperación de los suelos de la mina Fé se evaluaron las condiciones limitantes para el desarrollo de la vegetación y el uso del suelo, siguiendo el procedimiento de la Soil Fertility Capability Classification System (Buol et al., 1975, modificado por Calvode Anta et al., 1992), y teniendo en cuenta los elementos potencialmente tóxicos que pueden generar riesgo (Macías y Calvo de Anta, 2008). Los parámetros específicos evaluados y los criterios empleados se muestran en la Tabla 6.

Para las diferentes unidades establecidas en la cartografía de suelos (Figura 3) se identificaron los limitantes más importantes para el desarrollo vegetativo (Tabla 7). Así con independencia del tipo de suelo (suelos naturales y de mina) existen limitaciones comunes e importantes para el desarrollo vegetativo, como son la prolongada sequía y los bajos contenidos en C, N, P disponible (Tabla 1) y, en la mayor parte de los casos, posiblemente la baja disponibilidad de K (evaluada por la concentración de K en las posiciones de cambio). Es decir son suelos claramente distroficos, con un importante déficit de agua en el periodo de desarrollo vegetativo.

Tabla 6. Parámetros específicos para la evaluación de las limitaciones para la recuperación de suelos siguiendo la metodología de la Soil Fertility Capability Classification System (Buol et al., 1975).

TIPOS TEXTURALES	CONDICIONES MODIFICADORAS
	a: acidez. pH < 5.0 con presencia creciente de Al y H+ cambiable
S: arenoso	b: presencia de carbonato libre (pH superior a 7.3 y efervescencia con HCI)
L: textura franca	w: encharcamiento del suelo por períodos de duración variable; presencia de moteados redox.
C: textura arcillosa	d: Carácter xérico. Más de 3 meses de sequía
	e: Capacidad de cambio de cationes muy baja (< 5 cmol(+)/kg
R: roca u nivel endurecido a menos de 50 cm	h: acidez moderada: 5.0-6.0.
LR: Textura franca con contacto lítico	x : presencia de compuestos no-cristalinos (pH NaF superior a 10)
+: Pedregosidad del 15-30 %	v: carácter vértice (> 35 % arcilla y > 50 % arcillas 2:1 hinchables, o cuando la capa superficial del suelo presenta procesos de contracción e hinchamiento).
*: Pedregosidad > 30%	K1: Déficit absoluto de K cambiable y biodisponible. < 0.2 cmol(+)/kg
	K2.- Limitación de la biodisponibilidad del K por exceso de otros cationes cambiables (Kcambiable < 2% Suma de cationes básicos cambiables).
	Ca: bajo contenido en Ca (< 1.5 cmolc kg^{-1} o relación Ca/Mg < 0.5)
	Mg: Bajo contenido en Mg (menos de 0.4 cmolc kg-1 o relación Ca/Mg superior a 50).
	s: salinidad (conductividad eléctrica en el extracto de saturación > 4 mmhos cm^{-1} a 25°C).
	n: exceso de sodio (saturación de Na > 15 %).
	P: Baja biodisponibilidad de P (< 5 ppm de P Olsen)
	N: Déficit de N disponible (< 0.3%) y C/N > 20.
	C: Déficit de C para la estabilidad de la estructura y la actividad biótica (< 3%)
	(): Valor variable en la unidad cartográfica o taxonómica.

Sin embargo, para los suelos de mina hay, además, otros factores específicos como la fuerte pedregosidad y muy baja capacidad de cambio asociada a los materiales aportados procedente de las rañas o terrazas cuaternarias (Figura 10) que se trasmite a todas las zonas en las que estos materiales han sido aportados por las actividades para el cierre de la explotación. También se destaca, por su importancia, además de los problemas ligados a los materiales portadores de sulfuros, el incremento de la salinidad (evaluada por la conductividad eléctrica), acidez (evaluada por los bajos pH de los suelos) y toxicidad (evaluada por las concentraciones significativas de elementos potencialmente tóxicos) ligadas a las zonas del yacimiento o de los tratamientos a que han sido sometidos los materiales explotados.

Tabla 7. Clases de fertilidad de las unidades de suelos cartografiadas para la mina de Fé.

Grupo de suelos	*Unidad edáfica*	Clase Fertilidad	Otros Limitantes
Suelos naturales	Leptosoles líticos y háplicos	LRdhPk1CN	Bajo espesor efectivo; Erosión
	Cambisoles lépticos y háplicos	Ld(a,h)Pk2CN	Erosión
	Acrisoles plínticos y Leptosoles esqueletales	L*daPk1k2Mg1CN	Bajo espesor efectivo; Elevada pedregosidad
	Fluvisoles háplicos y gleicos		Erosión. Inundación; Hidromorfía
Suelos de mina	Tecnosoles espólicos	L+d(a,h)Pk1k2C, N	Acidificación; Toxicidad por Mn, As, Pb, Zn y Al. Salinidad

Figura 10. Aspecto de la raña caracterizado por una fuerte pedregrosidad.

En base a este diagnóstico se estableció el orden de prioridades de actuación para la recuperación de la mina Fé, teniendo en cuenta los riesgos para la calidad del agua, las posibilidades de vegetación utilizable y la recuperación paisajística. Fueron establecidos tres niveles de actuación (nula, media y prioritaria) en el entorno de la mina Fé (Figura 11).

Las zonas de actuación nula, correspondientes a los suelos naturales, no presentan un riesgo para la salud humana y el medioambiente, si bien tienen limitaciones para el desarrollo de vegetación. Las zonas de actuación media tienen un mayor riesgo para la conservación del suelo y la calidad de las aguas, pero no generan problemas para la salud humana o para a la conservación de los ecosistemas propios de la zona (dehesa). Este nivel corresponde a zonas de extracción de materiales de préstamo y zonas de accesos, los cuales presentan una contaminación más difusa ocasionada por el transporte de materiales dentro de la mina. Por último, se establecieron las zonas de actuación prioritaria, correspondientes a las áreas de mayor mineralización. Aquí los materiales tienen un contenido relativamente alto de sulfuros, presentando un nivel de riesgo elevado derivado principalmente por la presencia de elementos potencialmente tóxicos (Al, As, Mn, Cd) y por la generación de aguas ácidas debido a las condición físico-químicas del sistema (pH y Eh). Estas últimas zonas son las que necesitan una recuperación más rápida, pues la tendencia evolutiva actual conduce a elevados riesgos, con una afección directa sobre aguas y suelos adyacentes.

Como medidas iniciales para la recuperación de los suelos y aguas de la mina Fé sería imprescindible lleva a cabo las siguientes actuaciones:

i) Reducir la entrada de aguas de precipitación a los suelos del área minera, limitando los procesos oxidativos de los sulfuros y la generación de drenaje ácido de mina. Para ello sería necesario la desviación de aguas de escorrentía y su rápida eliminación, incrementando la intercepción y la evapotranspiración mediante el crecimiento vegetativo de especies tolerantes a las condiciones ambientales de la zona (especies del género *Cistus*, *Lavandula, Erica*,...); y el aumento de la capacidad de retención de agua y mejora de la estructura, en los suelos adyacentes, a través del incremento del contenido en materia orgánica.

ii) Mejorar la calidad de las aguas superficiales y freáticas. Esto puede lograrse, parcialmente, a largo plazo a través de la retirada o disminución de las sales evaporíticas de hidrólisis hiperácida que se han acumulado en el sistema minero y con nuevas actuaciones de recuperación más adecuadas. Por supuesto, es imprescindible mejorar la calidad de las aguas freáticas que surgen del hueco minero y de toda el agua de contacto con las escombreras.

iii) Reducir los riesgos de erosión (Figura 12), favoreciendo los procesos de edafogénesis y biogeoquímicos del suelo. Este objetivo se alcanza con el incremento del contenido de materia orgánica, conjuntamente con la implementación de una cobertura vegetal, lo cual producirá la mejora de la estructura del suelo y favorecerá los mecanismos para la retención de agua y la actividad biológica.

Por tanto, para la recuperación de los suelos de la mina Fé se requiere intervenir a través de un conjunto de reacciones químicas y procesos que: i) reduzcan la velocidad de oxidación de los sulfuros, llevando materia orgánica lábil a la zona en la que se encuentran los sulfuros y consumiendo así el oxígeno en los niveles superficiales del suelo, ii) neutralicen la acidez existente y la acidez potencial que no pueda ser evitada o ralentizada por procesos reductores, iii) eliminen el exceso de sulfatos, asociando la remoción de las sales evaporíticas con la adsorción aniónica de los sulfatos, lo que también mitigaría los riesgos existentes de As, Pb y Zn y reduciría la pérdida de cationes neutralizantes de la acidez, y iv) incrementen la fertilidad (especialmente de N, P y K) y de la actividad biótica para que se produzca más biomasa y necromasa in situ, más formas lábiles y recalcitrantes de C y se mantenga estable la estructura del suelo, lo cual reducirá el riesgo erosivo.

La recuperación de los suelos conducirá a la recuperación de las aguas, si bien es necesario realizar también actuaciones específicas en las grandes masas de agua existentes, especialmente en aquellas más ácidas y de elevada conductividad eléctrica, promoviendo asi un sistema de recuperación integrado. La implementación de un sistema de recuperación integrado en el área minera de Fé conllevará beneficios económicos tangibles e intangibles. De modo general, se pueden identificar como beneficios intangibles el aumento del secuestro de C y de la biodiversidad, el control de la erosión y la mejora paisajística. Como beneficios tangibles se pueden citar la mejora de las características físicas, químicas y biológicas de los suelos de mina, así como la disminución de la contaminación en aguas y suelos adyacentes, lo que reducirá considerablemente el elevado coste del tratamiento de las aguas.

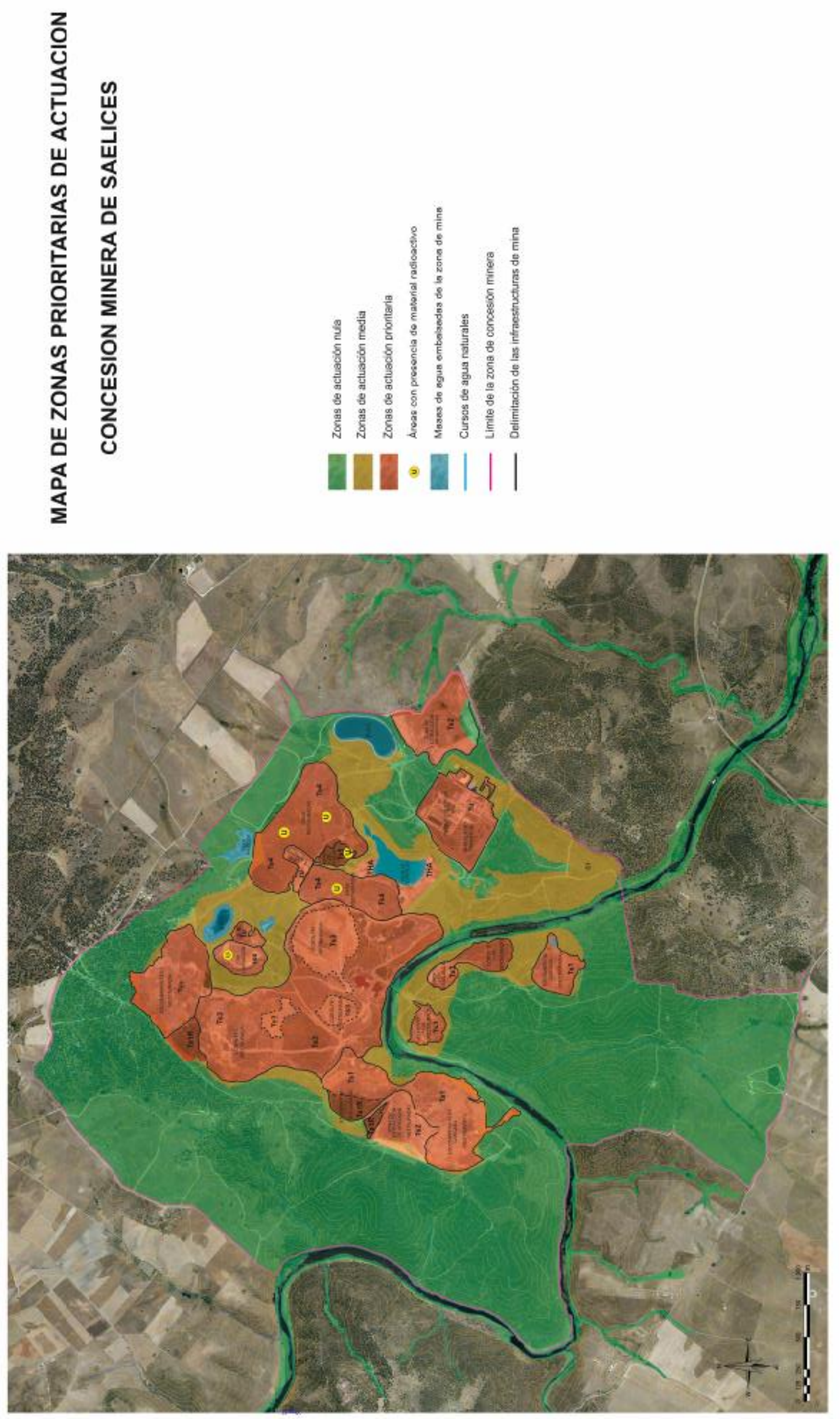

Figura 11. Cartografía de las zonas de prioridad de actuación para la recuperación de los suelos de la mina Fé

Figura 12. Ravinas de erosión hídrica producidas en los suelos del entorno de la mina Fé derivados de rañas o depósitos de terrazas pleistocénicas.

4. CONCLUSIONES

Los suelos de mina están desarrollados sobre diferentes mezclas de material de partida y residuos de mina ricos en sulfuros. Estas mezclas de materiales diluyen el efecto negativo de los materiales de escombrera, ya que las concentraciones totales de los elementos potencialmente tóxicos son similares a los niveles encontrados en suelos naturales. Sin embargo, estos suelos presentan un elevado riesgo, pues generan aguas de drenaje ácido ricas en elementos potencialmente tóxicos y sulfatos. En las épocas cálidas, la evaporación de este drenaje ácido provoca la precipitación de sales evaporíticas que son sumideros temporales de sulfato y metales. Sin embargo, las fases sólidas formadas, esencialmente sulfatos de Mg y Al, tienen baja solubilidad re-disolviéndose con hidrólisis ácida en la época de lluvia y liberando nuevamente los elementos tóxicos al medio.

Por otro lado, los suelos naturales adyacentes a la mina de Fé son pobres en nutrientes y materia orgánica, lo que, junto con las condiciones climáticas de la zona, conlleva un escaso crecimiento vegetativo. Estos suelos tienen una fuerte tendencia erosiva, con predominio de los procesos de rexistasia sobre los de biostasia, que sólo se mantienen de forma muy incipiente en las áreas que conservan una cobertura vegetal permanente.

Teniendo en cuenta las condiciones limitantes de los suelos y el correspondiente riego, es imprescindible actuar sobre estos suelos minimizando la oxidación de los sulfuros y mejorando la fertilidad. El principal objetivo es que se pueda establecer una cobertura vegetal y se estimulen los procesos de edafogénesis y biogeoquímicos asociados, como por ejemplo el ciclo de nutrientes.

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INFLUENCE OF FEEDSTOCK ON THE COPPER REMOVAL CAPACITY OF WASTE-DERIVED BIOCHARS

ABSTRACT

Biochar samples were generated by low temperature pyrolysis of different types of waste. The physicochemical characteristics of the different types of biochar affected the copper retention capacity, by determining the main mechanism involved. The capacity of the biochar to retain copper present in solution depended on the size of the inorganic fraction and varied in the following order: Rice Biochar > Chicken Manure Biochar > Olive Mill Waste Biochar > Acacia Biochar > Eucalyptus Biochar > Corn Cob Biochar. The distribution of copper between the forms bound to solid biochar, dissolved organic matter and free organic matter in solution also depended on the starting material. However, the effect of pH on the adsorption capacity was independent of the nature of the starting material, and the copper retention of all types of biochar increased with pH.

1. INTRODUCTION

Heavy metals can pose a serious risk to human health, even at low concentrations (Mohan et al., 2014). Copper is one of the most commonly used heavy metals in industrial activities and is present in the wastewater generated by the metallurgical, galvanizing, plastics and mining industries (Kolodyńka et al., 2012; Li et al., 2013). It is also widely used in agriculture as a component of fungicides and herbicides (Trakal et al., 2014). Guidelines for drinking water quality propose that concentrations of copper should be below 2 mg L^{-1} (WHO, 2004). However, in a directive aimed at controlling the quality of water to support fish life, the European Council deemed that such waters should contain less than 0.04 mg L^{-1} of soluble Cu (EC, 2006). Numerous processes have been developed to minimize the effects of this metal on the environment: chemical oxidation, precipitation, adsorption, ionic exchange and inverse osmosis. Adsorption-based processes are efficient and cost-effective (Li et al., 2013). In recent years, biochar (BC) has begun to be used as an adsorbent, as a less expensive, efficient alternative to active carbon (which has a limited capacity to remove heavy metals). Biochar is generated by the thermal degradation of organic matter such as agricultural waste, forest waste, manure and other similar types of material, and it is therefore carbon-rich, porous and contains oxygenated functional groups (Regmi et al., 2012). Numerous studies have been carried out in recent years to test the capacity of different types of BC to act as adsorbents for the removal of metallic contaminants (Pb, Cu, Zn, Cr, Ni, etc.) from water (Chen et al., 2011; Xu et al., 2013; Li et al., 2013; Trakal et al., 2014; Wang et al., 2015; Kolodyńka et al., 2012; Kim et al., 2013). The high retention capacity of BC may be due to i) electrostatic interactions, ii) ionic exchange, and iii) sorption via π electrons delocalized from carbon (Sohi et al. 2010). In addition to these mechanisms, surface precipitation or co-precipitation may also lead to the retention of heavy metals in BC containing high amounts of carbonate and phosphate (Cao et al., 2009, Xu et al., 2013; Cao and Harris, 2010).

The use of BC to treat wastewater and other effluents contaminated with heavy metals requires prior assessment of the materials involved. The physicochemical properties of BC derived from raw materials of different origin will affect the adsorption process and associated mechanisms and thus determine the possible forms in which the contaminant of interest are present and, therefore, its mobility and bioavailability. Various studies have shown the existence of a relationship between the BC properties, the retention capacity and the effect on the predominant mechanisms. For example, Cao and Harris (2010) demonstrated that the different conditions under which BC was generated from dairy manure affected the BC properties: the mechanisms underlying lead and anthracene retention were different and the different types of BC had to be used in different ways for remediation purposes. Ahmad et al. (2012) also showed that the adsorption behaviour depended on the physical and chemical properties and established correlations between the adsorption capacity of trichloroethylene (TCE) and the properties of different types of BC, such as the C and O contents, the H/C, O/C and (O+N)/C molar ratios and the surface area.

In this study, we determined the effect of the main physicochemical properties of BC on copper retention. For this purpose, we used different types of BC generated by slow pyrolysis of plant wastes and manure. The specific objectives of the study were as follows: (i) to determine the capacity of the BC to adsorb copper; (ii) to evaluate the chemical speciation and distribution of this trace metal between the BC, dissolved organic matter (DOM) and free copper phases; (iii) to characterize and evaluate the possible mechanisms leading to retention of copper ions; and (iv) to establish any relationships between the properties of the different types of BC and mechanism of adsorption.

2. MATERIALS AND METHODS

2.1. Preparation of the biochar

Biochar (BC) samples were produced from six waste materials of different origin: chicken manure (CMBC), eucalyptus (EBC), acacia (ABC), corn cob (CCBC), olive mill waste (OBC) and rice husk (RBC). Each type of biochar was produced by pyrolysis at 300-400 ^{0}C in an experimental kiln, under oxygen-limited conditions. The duration of pyrolysis depended on the type of raw material: material of plant origin was maintained at this temperature for 2 h and chicken manure, for 6 h. Conversion of raw material at temperatures of between 100 and 1000 ^{0}C for relatively long periods (ranging from a few minutes to several hours) is known as slow pyrolysis and characteristically favours the formation of BC (Brown, 2009; Ahmad et al., 2014). The different types of BC obtained were milled and sieved (< 2 mm) for physicochemical analysis and adsorption assays.

2.2. Characterization of the biochar samples

The total contents of carbon, hydrogen, nitrogen and sulphur (C, H, N, S) in the different types of BC were determined in an element analyser (TruSpec CHN-1000, LecoSC-144DR). The ash content was determined by combustion at 1000 ^{0}C for 6 h (C.H.E.S.A. HT BT S7 RP 1200 ^{0}C). The oxygen (O) content was determined by difference, as follows: % O = 100 – (% C + % H + % N + % S + % Ash). To determine the total content of the most relevant inorganic elements present in the BC materials, 0.5 g of each sample were subjected to microwave-assisted aqua regia digestion (ETHOS Plus, Milestone). The total P was determined by the molybdenum blue method (Murphy and Riley, 1962), while Ca, Mg, K, Na, Fe, Al and Cu were determined by atomic absorption spectroscopy (AAS, Perkin Elmer 1100B). The pH of all samples was measured in distilled water, at a ratio of 1:2.5 (w:v), with a combined glass electrode Radiometer GK-2401C. The surface area (SBET) was determined by N2 adsorption with a Micromeritics Gemini 2360 V2.01 instrument.

The surface functional groups present in each BC were determined qualitatively by infrared spectroscopy (FT/IR-4200 Jasco). The samples were mixed homogeneously and placed on a ZnSe crystal for attenuated total reflection. The FT-IR spectra were obtained at a wavelength interval between 650 and 4000 cm^{-1}, between-data spacing of 0.96 cm^{-1} and a scanning rate of 0.02 cm s^{-1}. The mineral composition of the different BC samples was analysed in an X-ray diffractometer (Burker DRX D2 Phaser) with CuKα radiation. The scanning angle was 5^o to 70^o 2θ and the step size, 0.02^0 2θ. The diffractograms were interpreted using the RRUFF database in the XPowder2004.03.03 software.

2.3. Copper adsorption assays

The adsorption assays were carried out in batch experiments, by varying the initial concentration of copper between 2.5 and 400 mg L^{-1}. A stock solution of copper (10000 mg L^{-1}) was prepared using a nitrate salt: $Cu(NO_3)_2 \cdot 3H_2O$. Suspensions of the different BC samples were prepared at a solid:solution ratio of 1:100 (kg L^{-1}) in 0.1 M KNO_3. The pH of the suspensions was adjusted to pH 5 by addition of 0.1 or 1.0 M HNO_3 or NaOH. The samples were then shaken at 170 rpm in a reciprocating shaker (IKA-HS501 digital) for 24 h, which is a sufficient length of time to reach the adsorption equilibrium. The copper concentration was then determined using different techniques, which revealed the distribution of the metal in the different phases: Cu_{BC} (Cu bound to the solid fraction of the biochar), Cu_{DOM} (Cu bound to the organic matter in solution) and Cu_{free} (free Cu in solution). The concentration of free copper was determined by selective electrode potentiometry with an ELIT 8227 crystal membrane electrode. The suspensions of BC were then filtered through 0.45 µm filters (MF-Millipore, Millex), and the total concentration of copper in solution was measured by AAS. This measure of copper in solution (Cu_{AAS}) includes Cu_{free} and Cu_{DOM}, and the concentration of Cu_{DOM} was therefore determined as the difference between Cu_{AAS} and Cu_{free}. Finally, the Cu_{BC} fraction was determined as the difference between the total amount of copper added and the amount of copper in solution (Cu_{AAS}). The effect of pH on the adsorption capacity was also determined in two BC samples of different origin (plant- and manure-derived) following a similar experimental procedure to that previously described. For this purpose, adsorption assays were carried out at pH 4 – 6, with the CMBC and RBC samples and a total concentration of copper of between 2.5 and 400 mg L^{-1}. In these assays, in addition to copper, the concentrations of Ca and Mg were determined by AAS; the concentrations of Na and K were determined by flame atomic emission spectroscopy, the dissolved organic carbon (DOC) was determined in a continuous flow analyser (Third generation continuous flow analyser 2000), and phosphate was determined by the molybdenum blue method.

The morphology of the different types of BC and the distribution of other major elements (C, O, Cu, Fe, Al, P, Mn, Ca and Mg) were also determined by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) (Zeis EVO LS15 with BSD image detector and an OXFORD detector in the EDX). The working voltage used was 20 KV. The CMBC, OBC and RBC samples were spiked with 400 mg L^{-1} of copper, and the ABC, EBC and CCBC samples with 200 mg L^{-1} of copper. The method used to carry out these adsorption assays was similar to that previously described. The concentrations of copper selected enabled maximal adsorption of each BC under the experimental conditions used. Once the equilibrium was reached, the BC samples were washed twice with distilled water to remove the copper remaining in solution and the electrolyte used to control the ionic strength. The resulting solid was dried at 110 ^{0}C for 12 h, and a small amount of the dry material was stuck to an adhesive tape of carbon over an aluminum circular support for observation and analysis.

2.4. Empirical adsorption models

The data from the copper adsorption assays were fitted to two of the empirical models most commonly used in the descriptive analysis of adsorption processes (Kim et al., 2013; Chen et al., 2011; Xu et al., 2013; Wang et al., 2015):

Freundlich model (F):

$$q_e = K_F * Ce^{1/n}$$

Langmuir-Freundlich model (L-F):

$$q_e = \frac{Qmax * \ (K_{L-F} * Ce)^{\frac{1}{m}}}{1 + (K_{L-F} * Ce)^{\frac{1}{m}}}$$

where q_e is the concentration of copper adsorbed per unit of mass of biochar (mg g^{-1}), C_e is the concentration of copper in solution (mg L^{-1}), K_F is a constant related to the adsorption capacity (mg g^{-1})(L $mg^{-1})^{1/n}$, n is a constant related to the intensity of adsorption and the heterogeneity of the binding sites, Q_{max} is the maximum adsorption capacity of the BC (mg g^{-1}), K_{L-F} is the adsorption constant related to the affinity, and m is a parameter representing the heterogeneity of the system. Values of m close to 0 are indicative of similar behaviour to that described by the Freundlich model, whereas values close to 1 indicate adsorption behaviour similar to that described by the Langmuir model.

3. RESULTS AND DISCUSSION

3.1. Characteristics of the different types of biochar

The different types of BC were generally neutral or basic ($pH_{H2O} > 7$), except for sample EBC, which was slightly acidic (pH 5.19) (Table 1). The most alkaline biochar samples were those with the highest content of KCl, as revealed by the SEM/EDX microanalysis (Fig. S1). These findings are consistent with those of Shinogi and Kanri (2003), who concluded that the increase in pH is due to the removal of alkaline salts from the raw materials during pyrolysis.

The different types of BC were classified into three categories on the basis of the C content (Table 1): high C content, CCBC (85.2 %); intermediate C content, ABC and EBC

(69.7 and 69.3 % respectively); and low C content, CMBC, RBC and OBC (< 50 %). The BC samples with a low C content are characterized by an abundant inorganic fraction, as indicated by ash contents higher than 20 % (Table 1). A high inorganic content is characteristic of raw material such as the shells or husks of grains, herbaceous biomass, straw and animal manure. By contrast, woody material has a low inorganic matter content (Amonette and Joseph, 2009). The N content varied between 0.41 % and 3.02 %, and the S content between 0 % and 0.36 %. The N content of the different types of BC only depends on the characteristics of the raw material and not on the pyrolysis conditions. The same is true for the S content, although little information is available in this respect (Ahmad et al., 2014).

Table 1. Main physicochemical characteristics of the different types of biochar.

	CMBC	RBC	OBC	ABC	EBC	CCBC
pH	7.15	10.50	9.57	7.62	5.19	10.10
%C	32.6	49.6	31.1	69.7	69.3	85.2
%N	3.0	2.3	2.1	0.6	0.4	0.8
%H	3.9	1.5	2.4	4.3	5.1	2.1
%S	0.32	0.36	0.08	<0.01	0.01	0.10
% Ash	46.4	23.3	49.5	3.5	1.9	3.9
%O	13.7	23.0	14.8	22.0	23.2	7.9
O/C	0.32	0.35	0.35	0.24	0.25	0.07
H/C	1.45	0.35	0.94	0.74	0.88	0.29
S_{BET} ($m^2\ g^{-1}$)	1.79	62.60	3.80	1.30	1.60	173.00
P ($g\ kg^{-1}$)	15.30	17.20	3.29	0.53	0.21	0.86

The molar ratios H/C and O/C (Table 1) were used to estimate the aromaticity and polarity of the different types of BC. The degree of carbonization and condensation of the aromatic rings can be described by the H/C molar ratio. The value of this ratio varied between 0.29 and 1.45 in the different types of BC studied. The low values obtained for the CCBC and RBC samples (0.29 and 0.35) are indicative of a high degree of aromatization and are similar to the values of 0.12-0.26 reported for active carbon (Chun et al., 2004, Qiu et al., 2008; Chen et al., 2008). By contrast the values of the ratios were higher than 0.7 in the ABC, EBC and OBC samples. Similar ratios were obtained for BC produced from soybean straw (0.74) and peanut shells (0.67) (Ahmad et al., 2012). High H/C ratios, even higher than 1, indicate a low degree of thermochemical alteration and are associated with high contents of organic residues, such as CH_2 polymers and fatty acids, lignin and cellulose

(Chen et al., 2008). The H/C ratio was highest in CMBC (1.45), possibly because depolymerization did not occur, due to the lack of lignocellulosic compounds in the source material (Ahmad et al., 2014). Similar values were obtained for BC produced, from the same type of waste, at 350 ^{0}C (Uchimiya et al., 2010). Finally, the O/C ratio in the different types of BC varied between 0.07 and 0.35. Low values, such as those obtained for the CCBC, ABC and EBC samples are characteristic of BC with low polarity. These values are similar to the values of between 0.06 and 0.16 reported for active carbon samples (Chun et al., 2004; Chen et al., 2008). Higher O/C ratios, such as those in samples OBC, RBC and CMBC, are indicative of a higher degree of polarity, which is mainly due to the presence of a larger number of functional groups containing oxygen.

The surface area (SBET) of the different types of BC varied greatly (Table 1) and decreased in the order CCBC >>> RBC >> OBC > CMBC > EBC > ABC. Low surface areas of around 5-25 m^2 g^{-1} are common in BC produced under the pyrolysis conditions used (Mohan et al., 2014). The surface area of BC is not only influenced by the structural and morphological characteristics of the feedstock, but also by the pyrolysis conditions, and increases with temperature of the process (Chun et al., 2004; Cao and Harris, 2010). Large differences in the structure and morphology of the different types of BC are observed in the SEM images (Fig. S2). Inorganic components predominated over the organic components in the CMBC and OBC samples, in a highly heterogeneous matrix that generates low surface areas of respectively 1.79 and 3.80 m^2 g^{-1}. The presence of plant cellular structure was more evident in the RBC, although the inorganic content of this BC is also substantial. The carbon matrix of the RBC is highly porous and the pores are of variable size, ranging between 1 and 50 µm in diameter, although many are occluded or are not accessible due to the presence of mineral precipitates that form on the surface of the BC. The cellular structure of ABC and EBC, generated from woody biomass, was distinctive and highly porous. The carbonaceous matrix of sample ABC was characterized by pores of diameter larger than 10 µm, whereas in the EBC sample, the pores were of diameter less than 10 µm, and the surface area of the latter was therefore larger than that of the former. Finally, the surface area of the CCBC (173 m^2 g^{-1}) was much larger than that of the other types of BC. The SEM images of this biochar revealed a well-defined cellular structure, with a large number of pores of diameter less than 10 µm enclosing a network of micropores, which generate the high surface area.

The FTIR spectra (Fig. S3) of the different types of BC show a wide band at around 3400 cm^{-1}, characteristic of O-H vibrations of hydroxyl groups (Chun et al., 2004; Uchimiya et al., 2012; Chen et al., 2011). A band was observed at 2925 cm^{-1}, assigned to $–CH_2$ groups belonging to aliphatic components (Das et al., 2009); an absorption peak at ~1700 cm^{-1} corresponded to the carbonyl of ester groups (Das et al., 2009; Dong et al., 2011); a peak at 1600 cm^{-1} was assigned to the C=O of carboxyl and ketone groups or the C=C of aromatic components (Uchimiya et al., 2012); and a band at between 1500-1400 cm^{-1} corresponded to C-C bonds in aromatic rings. The band at ~1420 cm^{-1}, which was particularly intense in the OBC, CMBC and RBC samples, can be attributed to the presence of carbonate (Cao et al., 2009). Bands at 1209 cm^{-1} and 1110 cm^{-1}, of intermediate intensity, correspond to –OH radicals of cellulose and to the symmetrical stretching of C-O bonds of cellulose, hemicellulose and lignin (Liu et al., 2015). The band close to 1000 cm^{-1} is attributed to the present of phosphate in the BC samples (Cao et al., 2009) and the band at 850 cm^{-1} corresponds to C-H bonds of aromatic compounds (Dong et al., 2011).

Analysis of the X-ray diffractograms (Fig. S4) distinguished two types of samples. Thus, the diffractograms of one group, comprising ABC, EBC and CCBC, showed a high background characteristic of samples of low crystallinity or amorphous character, with peaks at 16^0, 23.7^0 and 44^0 2θ^0, representative of cellulose and lignified structures. The diffractograms of these samples also showed peaks of low intensity, corresponding to the inorganic fraction, mainly comprising quartz (SiO_2) and calcite ($CaCO_3$). The other group, comprising RBC, CMBC and OBC, is characterized by a higher degree of crystallinity. This is consistent with the higher ash content of these samples (Table 1). The inorganic fraction of these types of BC mainly comprises calcite ($CaCO_3$), quartz (SiO_2) and struvite ($MgNH_4PO_4 \cdot 6H_2O$). The results of the XRD analysis, together with the FITR spectra, demonstrate the existence of carbonate- and phosphate-rich species as the main constituents of the inorganic fraction of the BC samples with high contents of ash and total P.

3.2. Adsorption isotherms

The copper adsorption isotherms for the different types of BC are shown in Fig. 1. Maximal retention of copper on the different types of biochar followed the order RBC > CMBC > OBC > ABC > EBC > CCBC. However, analysis of the affinity of the BC for the metal, which is related to the initial slope of the adsorption isotherm, showed that the sequence was RBC > ABC > EBC > CMBC > CCBC > OBC.

Considering the adsorption maxima, two groups of samples were distinguished: one group comprised the RBC, CMBC and OBC, with $q_e > 20$ mg g^{-1}; and the other group comprised ABC, EBC and CCBC, with $q_e < 20$ mg g^{-1}. The difference in the capacity of the different types of biochar to retain copper appears to be related to the physicochemical characteristics. The samples in the first group were characterized by an O/C ratio higher than 0.3 and high ash and phosphorus contents. The O/C ratio was lower in the second group, due to the smaller number of oxygenated groups and the higher degree of carbonization of these types of BC. Another characteristic of the BC samples that appears to influence their capacity to retain copper is the relative content of the inorganic components, indicated by the ash content. Surface precipitation processes due to metal-carbonate and metal-phosphate interactions constitute one of the main mechanisms of retention of heavy metals in BC containing high quantities of ash, as previously highlighted (Cao et al., 2009; Xu et al., 2013). The possible existence of these precipitation processes was investigated in the present study on analysis of the concentration of calcium and phosphate in solution once the adsorption equilibrium was reached. In the BC samples containing more than 10 g Kg^{-1} of P, the calcium content decreased as the concentration of copper added to the system increased, except in OBC, in which the calcium content remained constant (Fig. S5). This can be explained by the more crystalline nature of this BC, in which most of the calcium forms part of the calcite and therefore does not contribute to the exchange between this element and copper. On the other hand, in the RBC sample, the decrease in calcium was accompanied by a decrease in the concentration of phosphate in solution (Fig. S6), which appears to indicate precipitation of copper in the form $Cu_3(PO_4)_2$ or of calcium as hydroxyapatite ($Ca_5(PO_4)_3(OH)$). Formation of the latter would be favoured by an increase in the concentration of calcium in solution due to cation exchange following the addition of copper to the system. Use of the Visual MINTEQ chemical equilibrium model (Gustafsson, 2014) revealed that formation of these compounds is possible under the experimental conditions of the adsorption assay. Post-adsorption SEM-EDX analysis of those samples with high inorganic contents appears to confirm the formation of these compounds containing phosphate, calcium and copper on the surface of the different types of BC, since a close correlation between phosphate and copper was observed in the analysis of the distribution of major elements. This correlation was not observed in the EDX spectra of the samples with low ash contents, although the Cu and O associated with the organic fraction were closely correlated (Fig. S1). This group of BC samples is characterized by low P content (< 1 g Kg^{-1}) and ash content (< 4 %); therefore, the inorganic fraction does not contribute to the retention processes and the predominant mechanisms are complexation with the -COOH and –OH groups, ionic exchange and surface adsorption (Ahmad et al., 2014; Sohi et al., 2010). As the amount of copper retained increased, the concentration of calcium in solution remained constant in the EBC and CCBC, whereas it increased in the ABC. In this case, the concentrations of both elements were linearly correlated, which is indicative of the existence of a cation exchange process (Fig. S7). The ABC showed a higher capacity for retaining copper than the EBC and CCBC due to this exchange and the complexation process.

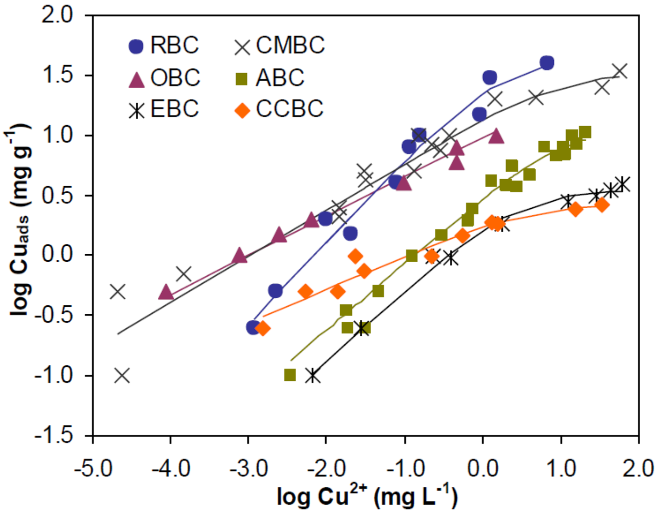


Figure 1. Adsorption isotherms for copper on the different types of BC under study. The lines represent the fit of the Langmuir-Freundlich isotherm to the experimental data

The Langmuir-Freundlich adsorption model provided the best fit to the data, with R^2 values of between 0.993 and 0.999 (Table 2). Although the Freundlich isotherm provided an acceptable fit to the data, the R^2 values were slightly lower, between 0.913 and 0.993. The different types of BC followed the same order of sequence as before in terms of the maximum adsorption capacity, Q_{max}, and the affinity constant, K_{FL}. For the Freundlich model, analysis of parameter K_F, which is also related to the adsorption capacity, revealed the same sequence as obtained for Q_{max}. Regarding parameter m, the values were highest in the BC samples that displayed the highest affinity for copper, indicating similar adsorption behaviour to that described by the Langmuir model. Regression analysis was used to relate the model fits for these parameters to the physicochemical characteristics of the different types of BC, in order to determine which characteristics of the materials had the greatest effect on copper retention.

Table 2. Fitting parameters for the Langmuir-Freundlich and Freundlich isotherms.

	Langmuir-Freundlich				Freundlich		
	K_{LF}	Q_{max}	m	R^2	K_F	n	R^2
RBC	0.57	44.47	0.68	0.996	19.76	1.69	0.959
CMBC	0.17	32.23	0.41	0.995	11.40	2.86	0.913
OBC	0.07	24.10	0.33	0.998	8.67	3.33	0.993
ABC	0.43	9.70	0.74	0.996	2.59	2.02	0.937
EBC	0.37	3.48	0.58	0.999	1.04	2.68	0.942
CCBC	0.13	2.70	0.24	0.993	1.50	4.53	0.920

The maximum adsorption capacity, Q_{max}, is expressed in mg g^{-1}

The physicochemical characteristics identified as most important and the fitted parameters of the empirical adsorption models were then examined by redundancy analysis (RDA). The total P content of the materials, together with the ash content and the O/C ratio explained more than 99.9 % of the variability in the maximum adsorption capacity of the Langmuir-Freundlich model (Q_{max}) (Fig. 2a). Likewise, these three properties of the materials explained the variability in parameter K_F of the Freundlich model (Fig. 2b).

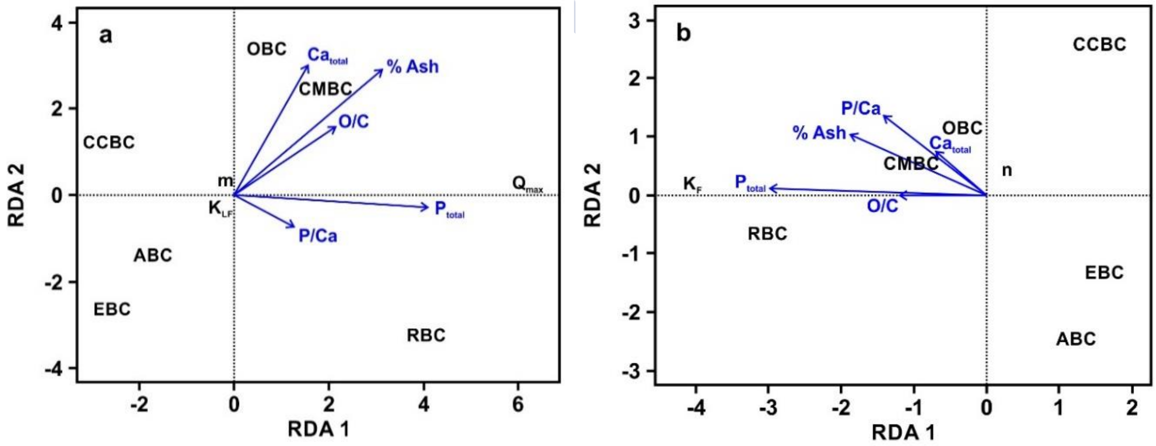


Figure 2. a) Redundancy analysis (RDA) for the parameters of the Langmuir-Freundlich model (a) and Freundlich model (b) for the most closely correlated physicochemical properties (total P, O/C, % ash, total Ca and P/Ca).

Finally, the maximum retention capacities found in the present study were compared with values reported for other types of BC (Fig. 3). In general, the findings are similar to those reported in other studies carried out under comparable experimental conditions. However, the retention capacity of sample RBC was much higher than that of other BC samples produced from the same feedstock. The retention capacity was highest in BC samples of animal origin or derived from shells or husks of grains, grass and straw. As already mentioned, these types of material usually have higher ash contents than other types of material. By contrast, the BC samples derived from woody material, compost and active carbon yielded low to intermediate values of the maximum copper adsorption capacity.

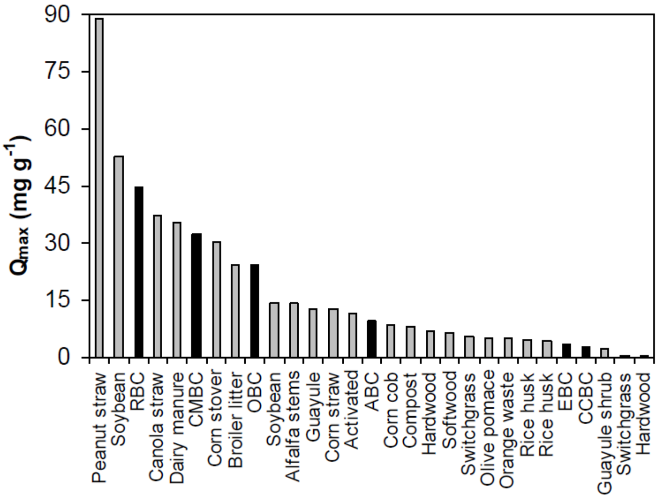
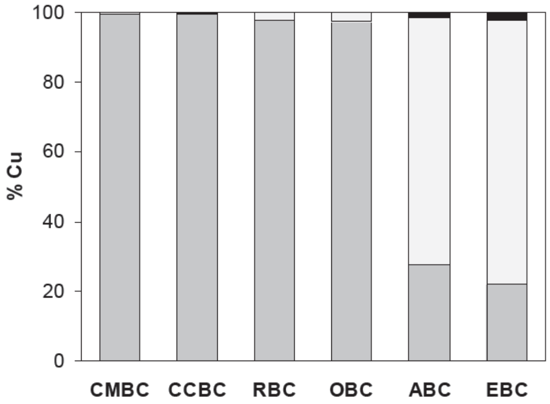


Figure 3. Adsorption capacities of the different types of BC for the removal of copper from solution. The values obtained in the present study are shown in black and those obtained in other published studies, in grey. The numerical values and the references are provided in Table S1 (Supporting information).

3.3. Distribution of copper: solid phase/solution

The distribution of copper between the solid phase (Cu_{BC}) and solution (Cu_{DOM} and Cu_{free}) is shown in Fig. 4. The distribution was very similar for CMBC, RBC, OBC and CCBC, and the fraction retained on the solid phase predominated in all of these samples (Cu_{BC} > 97 %). By contrast, the copper retained on ABC and EBC was mainly associated with organic matter in solution (Cu_{DOM} > 70 %). For both types of BC, a high amount of organic matter remained in solution at the end of the adsorption assays: 12.25 ± 1.90 mg L^{-1} and 18.34 ± 4.09 mg L^{-1} for ABC and EBC respectively. The formation of complexes between the soluble forms of carbon and the copper ion reduces the toxicity of the metal in solution, but maintains it in a mobile form that can be readily assimilated by plants and animals. The increased mobility of copper in soils due to the addition of BC with high contents of DOC has been pointed out in previous studies (Beesley et al., 2010; Park et al., 2011). The DOC content is therefore an important characteristic to take into account in selecting materials destined for decontaminating soils and waters containing heavy metals. Finally, in CMBC, CCBC, RBC and OBC, the content of Cu_{free} in solution was low (Cu_{free} < 0.03 mg L^{-1}) compared with the maximum value recommended in European legislation in regard to quality of water to support fish life, whereas the content was higher in ABC (0.13 mg L^{-1}) and EBC (0.23 mg L^{-1}).



	CMBC	CCBC	RBC	OBC	ABC	EBC
■ Cu_{free}	0.01	0.23	0.11	0.01	1.26	2.30
□ Cu_{DOM}	0.39	0.17	2.06	2.49	71.0	75.7
▨ Cu_{BC}	99.6	99.6	97.9	97.5	27.7	22.0

Figure 4. Distribution of copper in the different fractions for an initial copper concentration of 10 mg L^{-1}: Cu_{BC} (light grey), Cu_{DOM} (dark grey), and Cu_{free} (black).

3.4. Effect of pH on copper adsorption

pH is one of the parameters with the greatest influence on the processes of adsorption in aqueous solution as it affects both ionization and the surface charge of the adsorbent and the degree of ionization and chemical speciation of the adsorbate (Regmi et al., 2012). To test this, we analysed the effect of pH on copper adsorption in two of the biochar samples, RBC and CMBC.

The isotherms obtained at the different pH are shown in Fig. 5, and the fitting parameters are shown in Table 3. For both BC samples, the copper retention capacity increased with the pH of the medium. In the RBC sample, an increase in pH from 4 to 5 produced an increase of 40 % in copper retention, whereas a change in pH from 5 to 6 produced an increase of 53 %. In sample CMBC, the increase in copper retention between pH 4 and 5 was 56 %, and at between pH 5 and 6, it was 20 %. This effect of pH on the adsorption of metals on BC has been observed by other authors (Regmi et al., 2012; Bogusz et al., 2015) and is similar to the effect observed for other carbon rich materials, i.e. humic substances (Kinniburgh et al., 1999) or activated carbon (Wang et al., 2014). This phenomenon may be explained by changes on the surface of the BC, as under acidic conditions, the surface groups are protonated, thus favouring the presence of free metal ions in solution (Bogusz et al., 2015). An increase in pH leads to deprotonation of the surface groups, thus favouring interactions with metal ions. In addition to the changes in the surface of the BC, it is important to take into account the competition between protons and metal, which is favoured at lower pH, i.e. an increase in protons in solution favours a decrease in binding between copper and the BC.

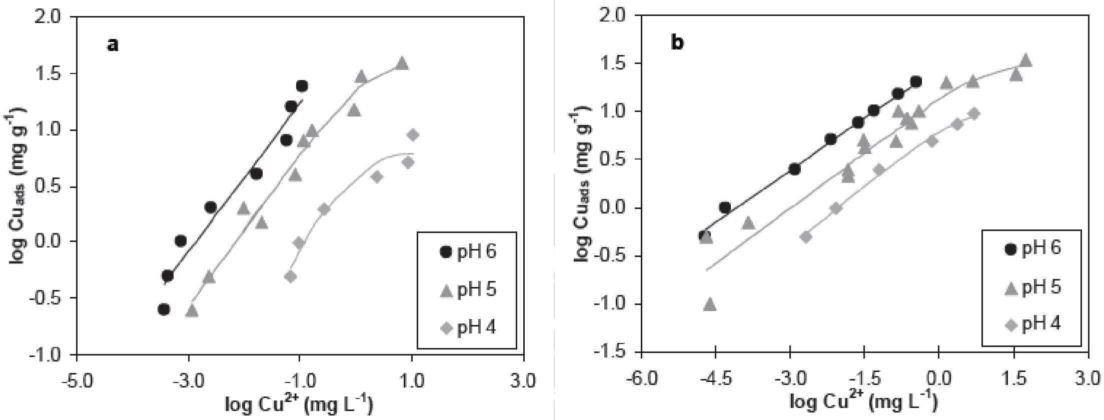


Figure 5. a) Effect of pH on copper adsorption by RBC. The lines represent the fit of the Langmuir-Freundlich isotherm. b) Effect of pH on copper adsorption in CMBC. The lines represent the fit of the Langmuir-Freundlich isotherm.

***Table 3**. Fitting parameters for the Langmuir-Freundlich and Freundlich isotherms.*

		Langmuir-Freundlich				**Freundlich**		
	pH	**K_{LF}**	**Q_{max}**	**m**	**R^2**	**K_F**	**N**	**R^2**
	4	1.48	6.48	1.00	0.981	2.52	2.17	0.929
RBC	**5**	0.57	44.47	0.68	0.996	19.76	1.69	0.959
	6	0.49	94.93	0.61	0.989	80.70	1.50	0.956
	4	0.34	10.69	0.41	0.998	5.55	2.73	0.989
CMBC	**5**	0.17	32.23	0.41	0.995	11.40	2.86	0.913
	6	0.51	38.45	0.36	0.999	29.61	2.77	0.995

The maximum adsorption capacity, Q_{max}, is expressed in mg g^{-1}

The adsorption model that provided the best fit to the experimental data was the Langmuir-Freundlich model, with R^2 values between 0.981 and 0.996 for RBC and between 0.995 and 0.999 for CMBC (Table 3). The Freundlich isotherm provided an acceptable description of the experimental data, although the R^2 values were lower (Table 3). The parameters Q_{max} and K_F, which are both related to the adsorption capacity, increased with pH. The variation may be explained by a greater presence of functional groups with a negative charge due to deprotonation of carboxylic groups (Mohan et al., 2014). Another possible explanation is the coexistence of other retention mechanisms, such as precipitation (Regmi et al., 2012). As already indicated, the formation of copper precipitates in materials with high P contents and large inorganic fractions should not be disregarded.

4. CONCLUSIONS

The BC considered in this study showed a good capacity to retain copper. This capacity was mainly due to adsorption and precipitation or co-precipitation mechanisms, which are influenced by the physicochemical properties of the BC. The most important of these properties in relation to the adsorption capacity were the O/C ratio, the P content and the ash content. Thus, the adsorption capacity increased with increasing values of these properties. Furthermore, the distribution of copper between the different phases depended on the nature of the BC, and prior evaluation of the material is necessary to guarantee efficient retention and immobilization. Finally, the effect of pH on the adsorption process was independent of the nature of the starting material, and the maximum adsorption capacity increased with pH in all types of BC analysed.

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Supplementary materials

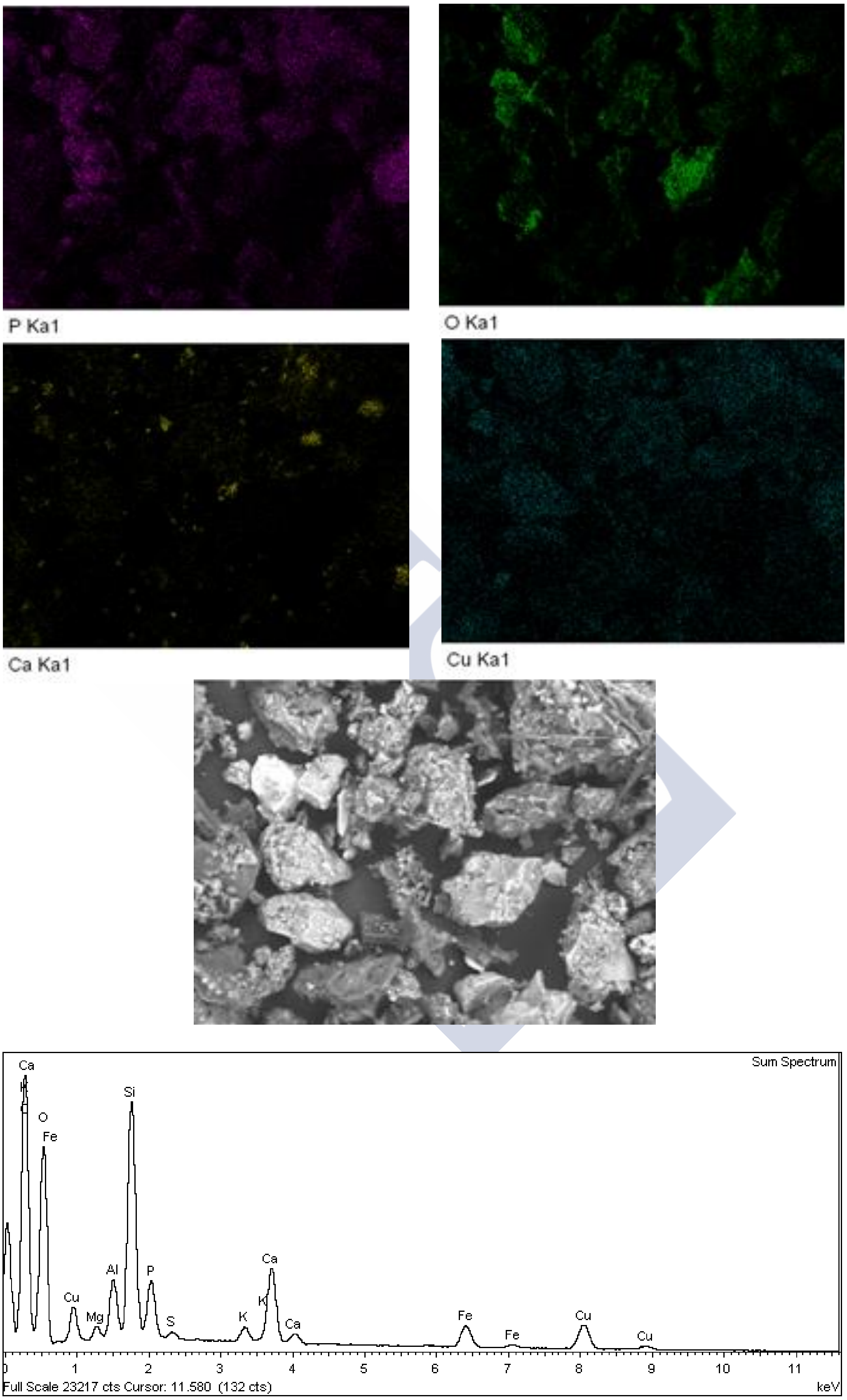

Figure S1-A. Mapping of microelements after copper adsorption on sample CMBC.

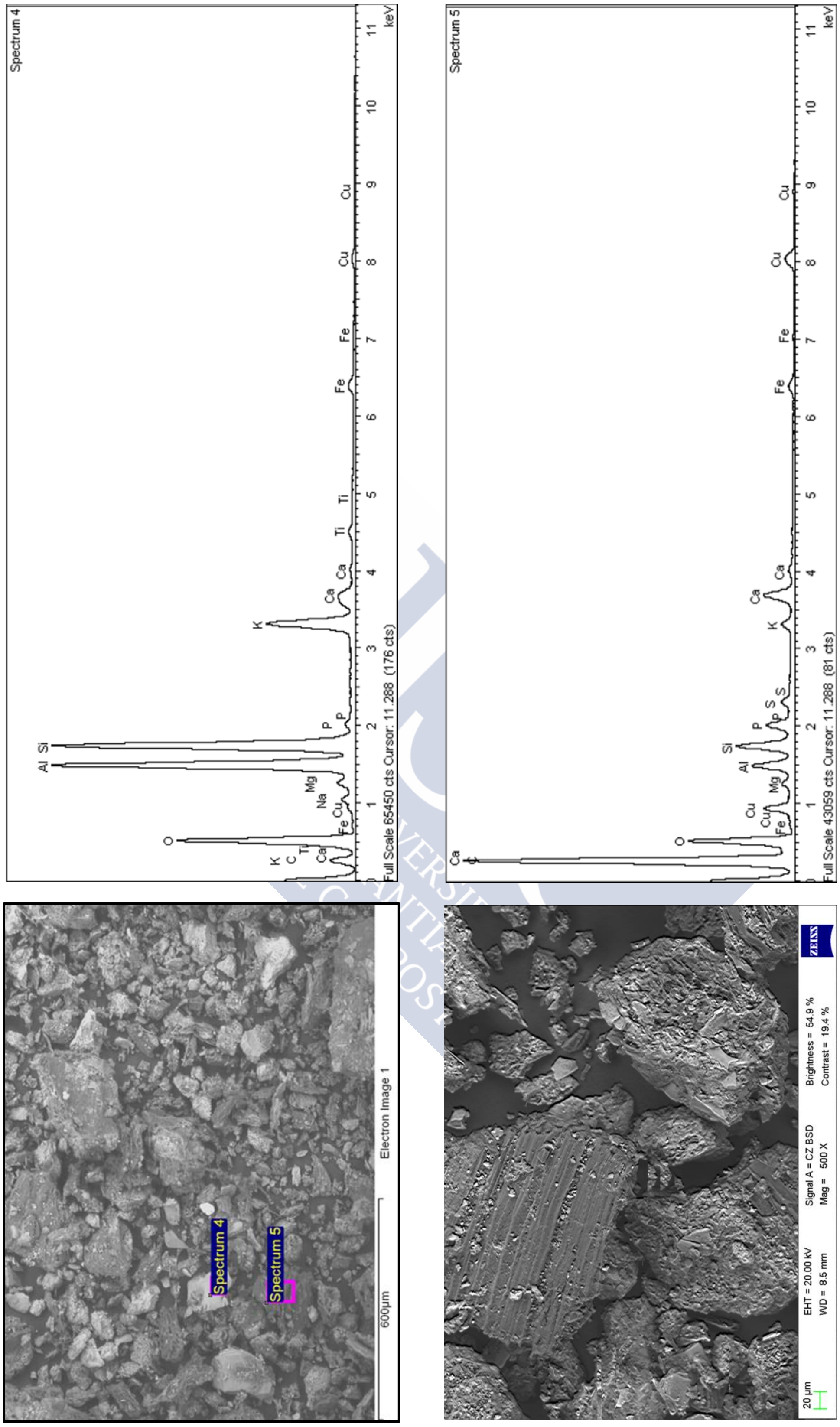

Figure S1-B. SEM-EDX with punctual microanalysis for the sample CMBC.

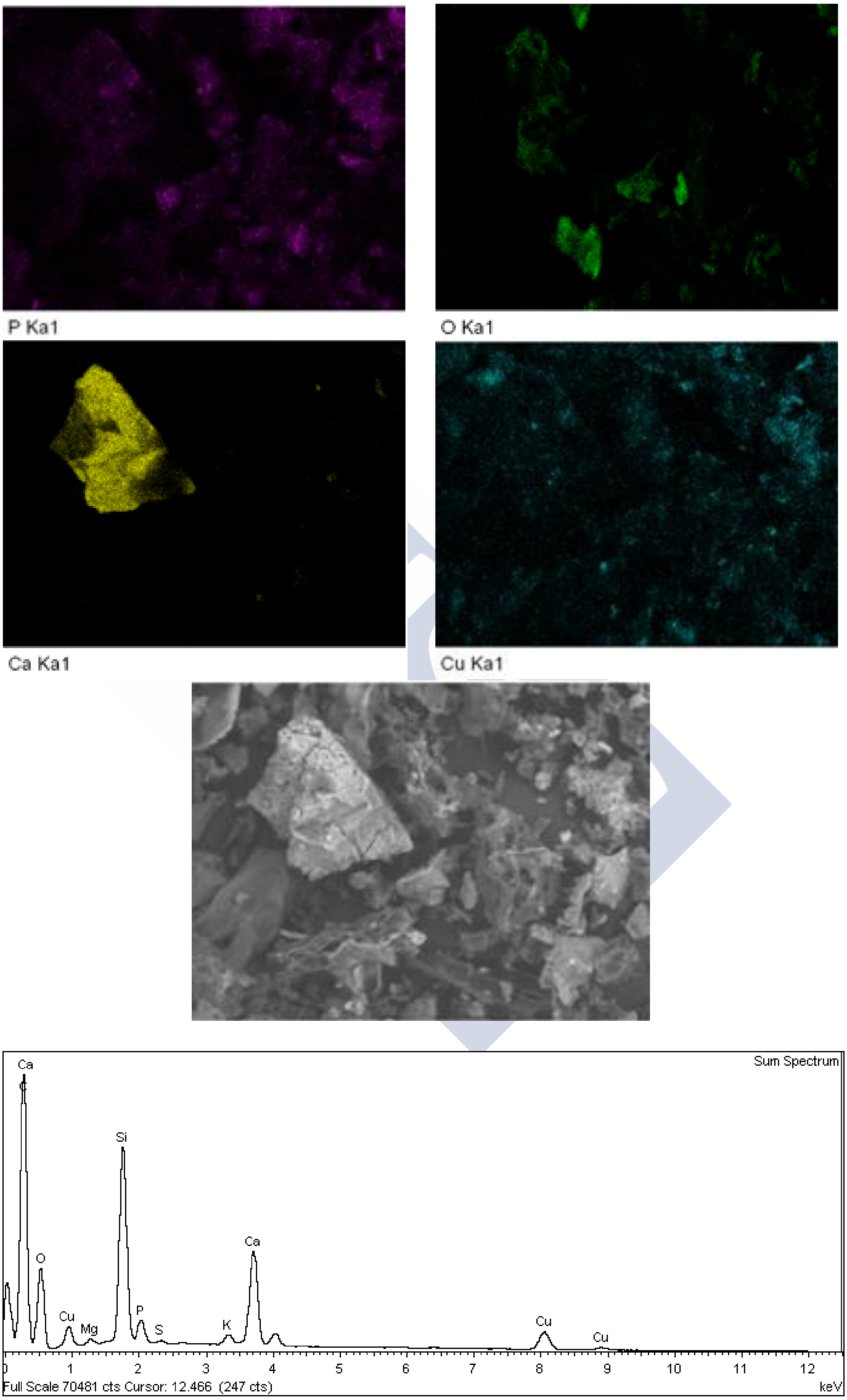

Figure S1-C. Mapping of microelements after copper adsorption on sample RBC.

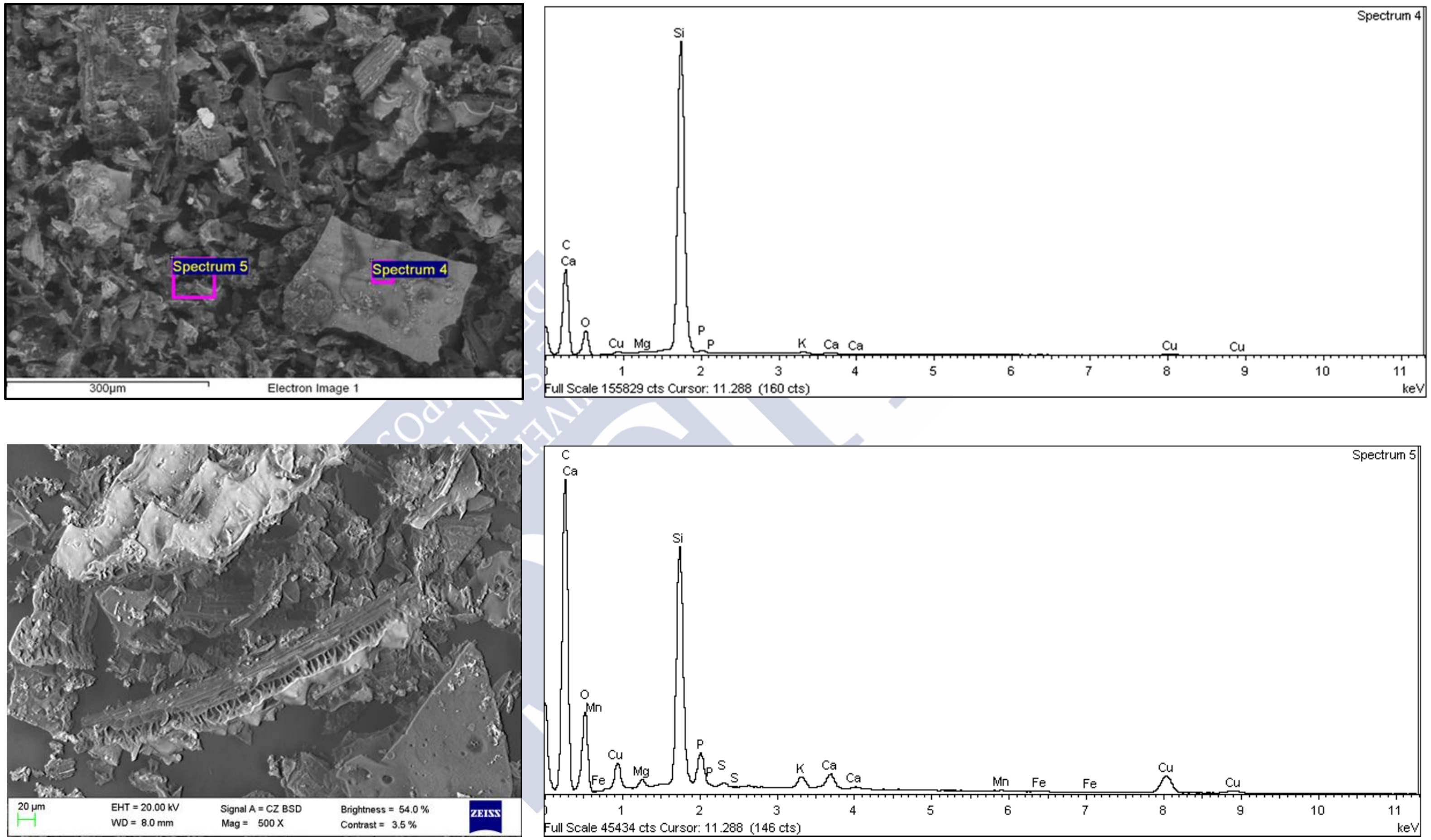

Figure S1-D. SEM-EDX with punctual microanalysis for the sample RBC.

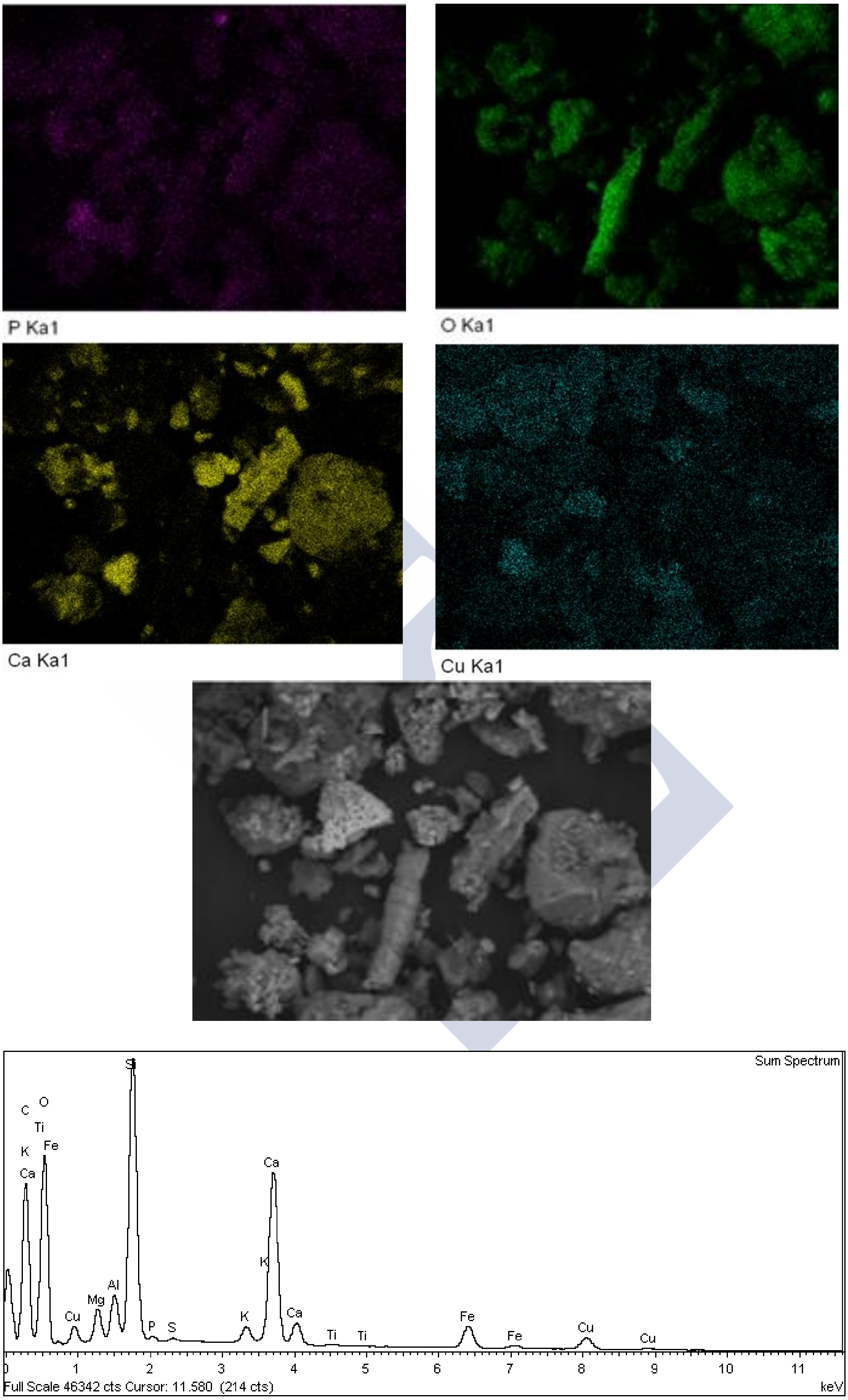

Figure S1-E. Mapping of microelements after copper adsorption on sample OBC.

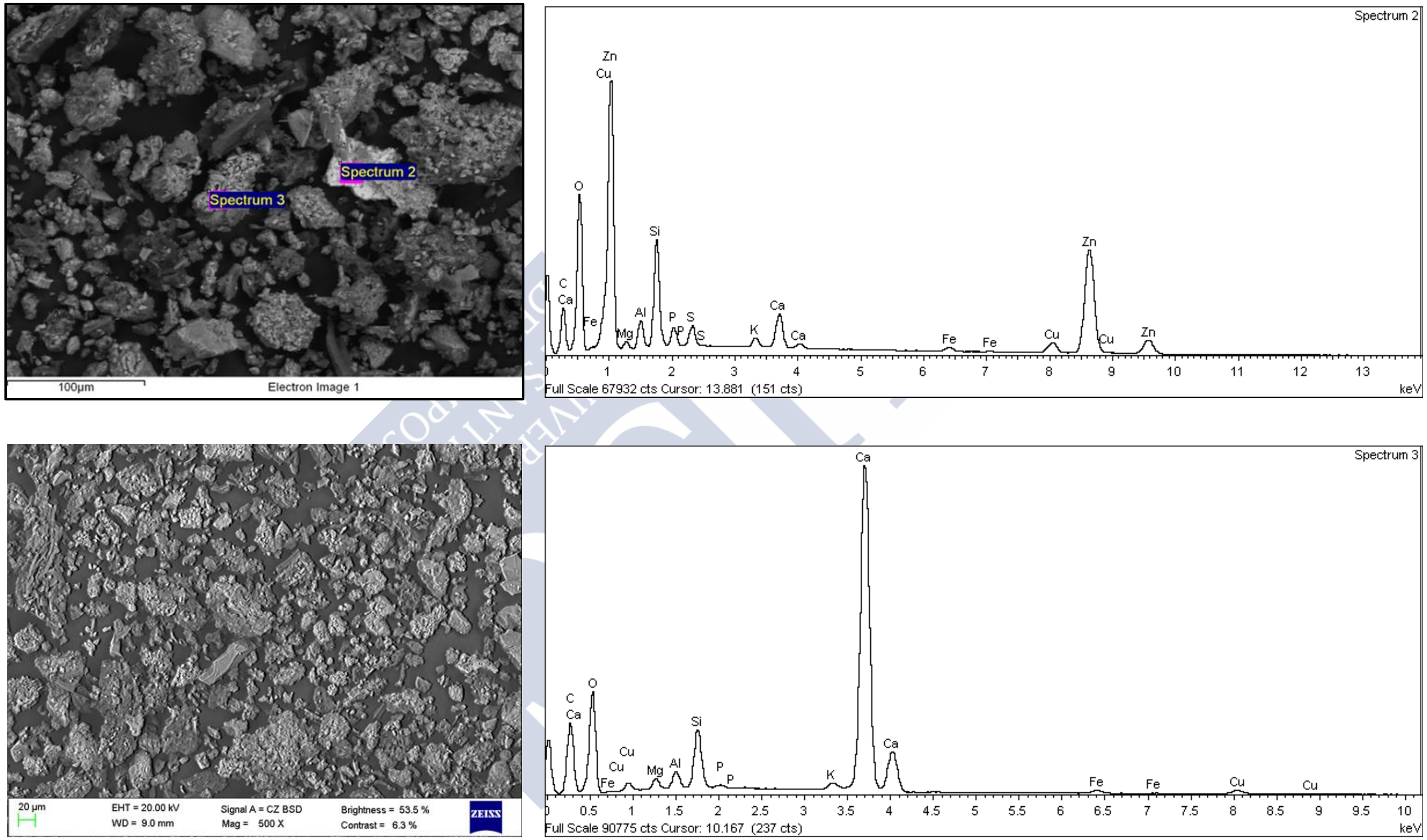

Figure S1-F. SEM-EDX with punctual microanalysis for the sample OBC.

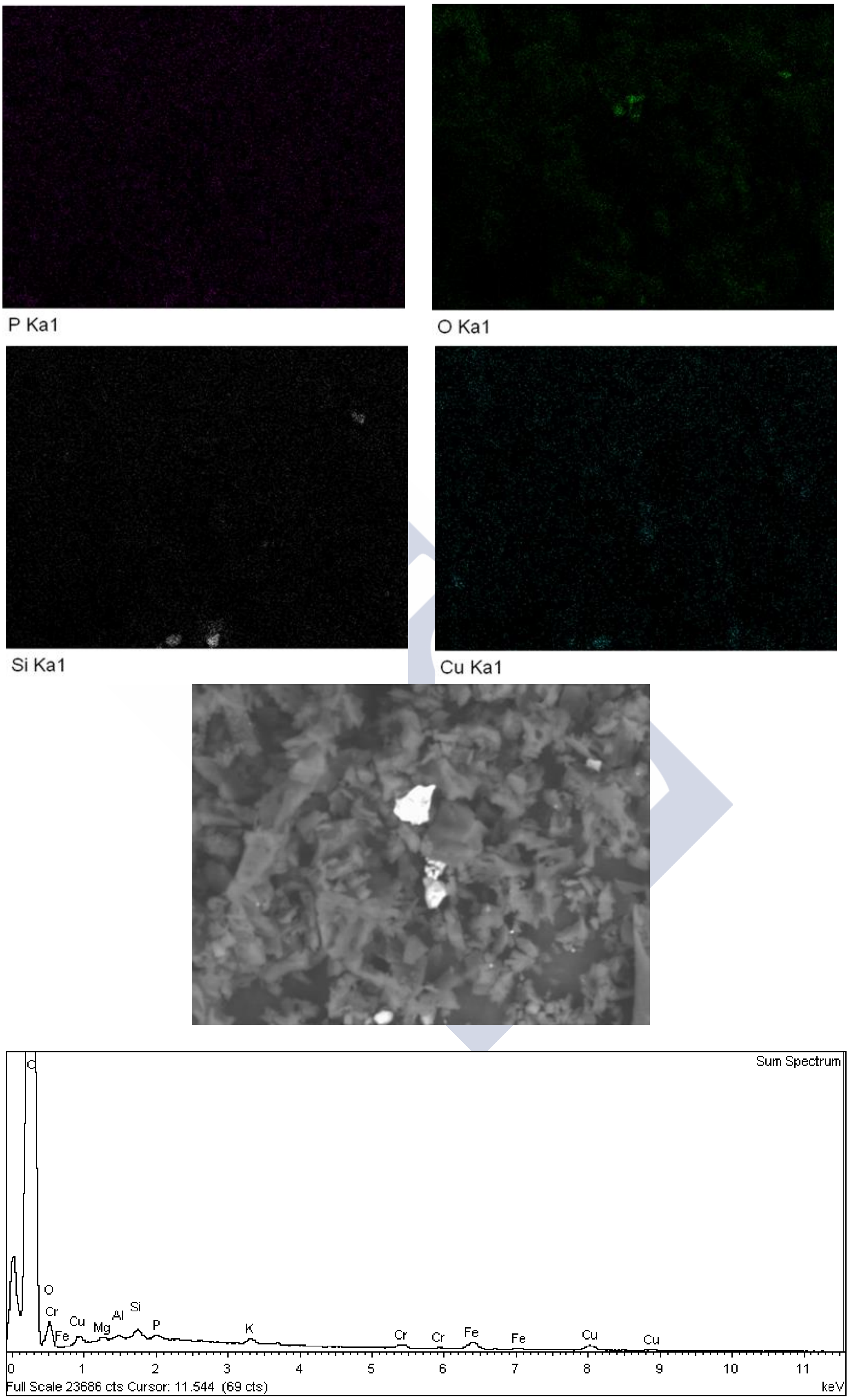

Figure S1-G. Mapping of microelements after copper adsorption on sample CCBC.

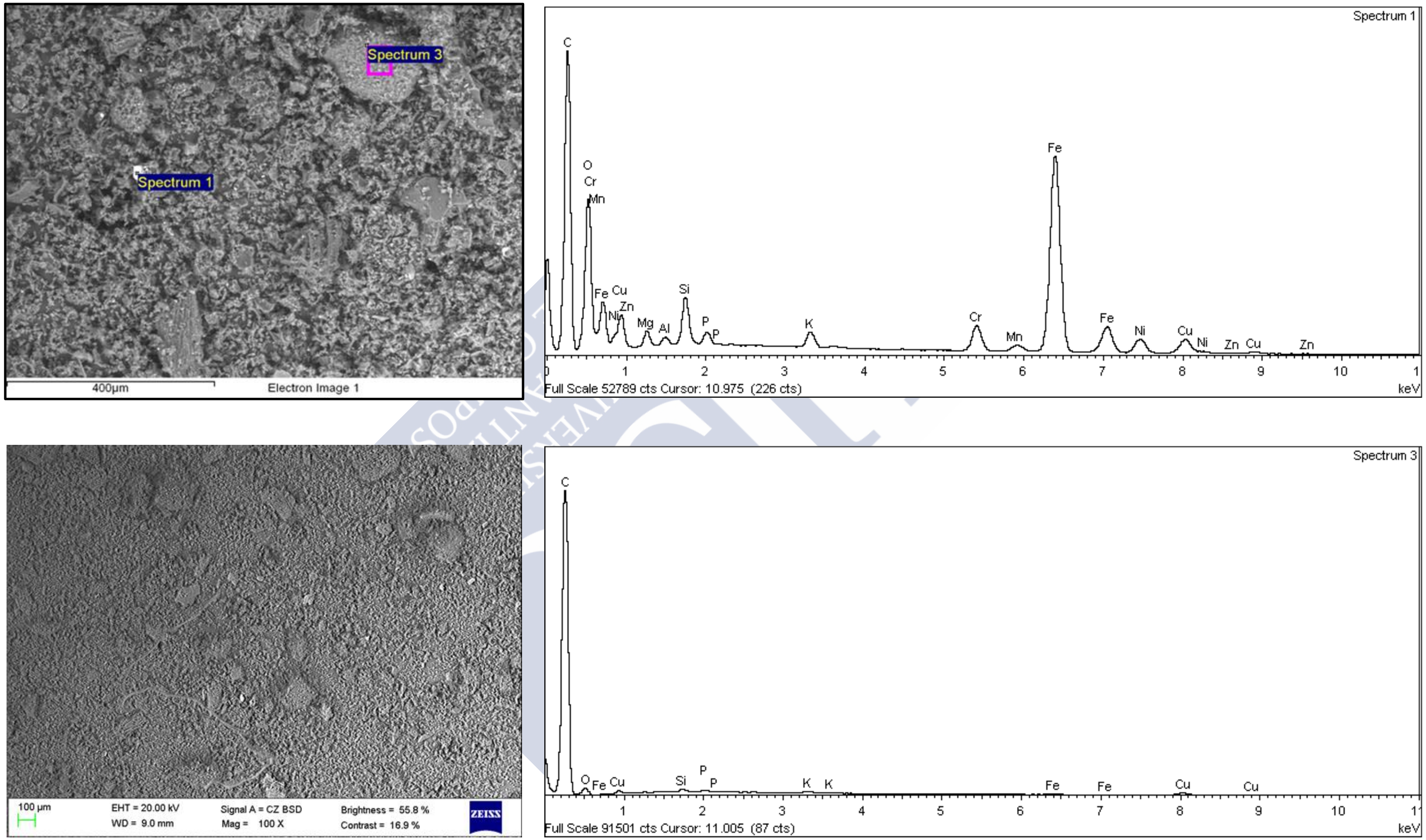

Figure S1-H. SEM-EDX with punctual microanalysis for the sample CCBC.

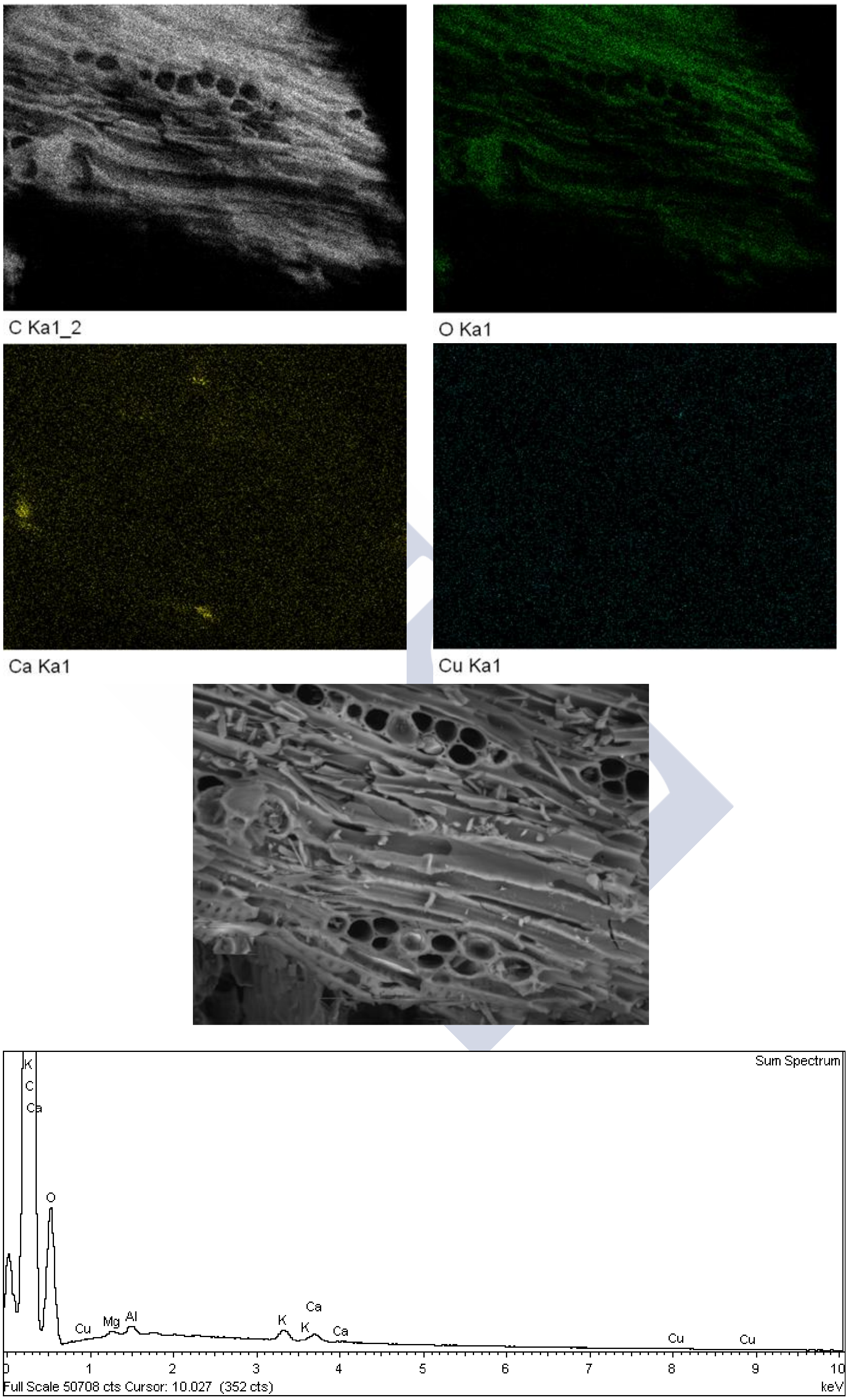

Figure S1-I. Mapping of microelements after copper adsorption on sample ABC.

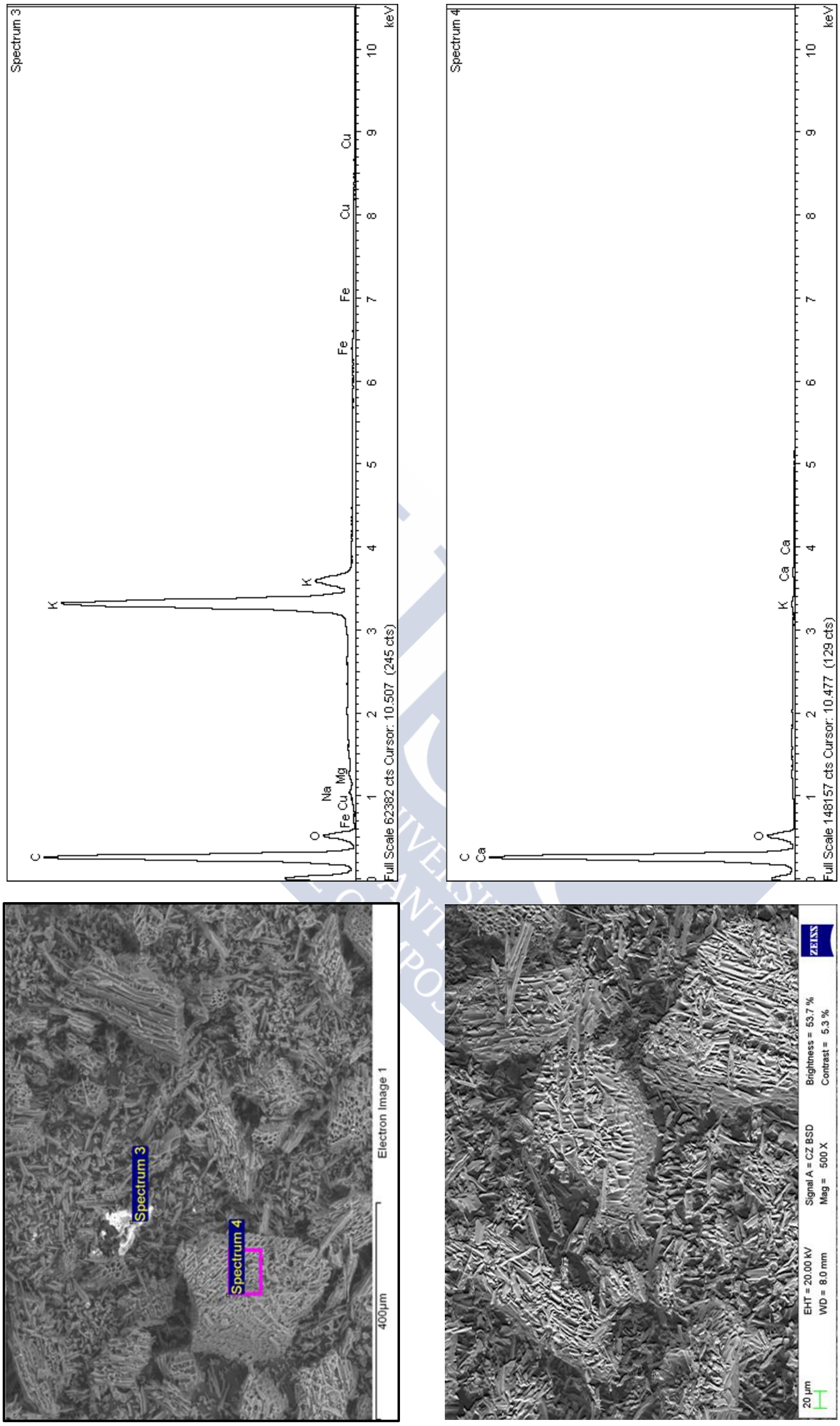

Figure S1-J. SEM-EDX with punctual microanalysis for the sample ABC.

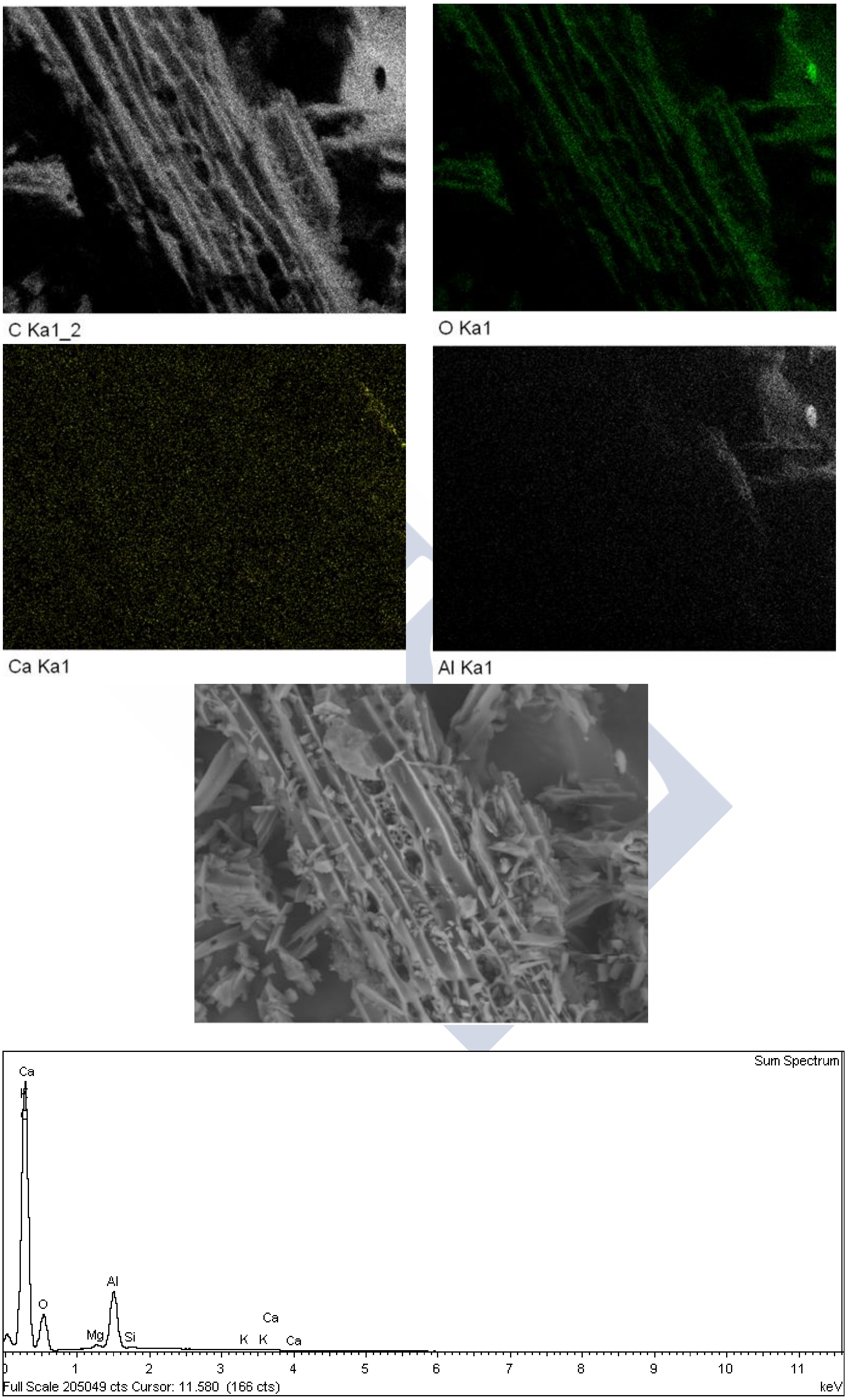

Figure S1-K. Mapping of microelements after copper adsorption on sample EBC.

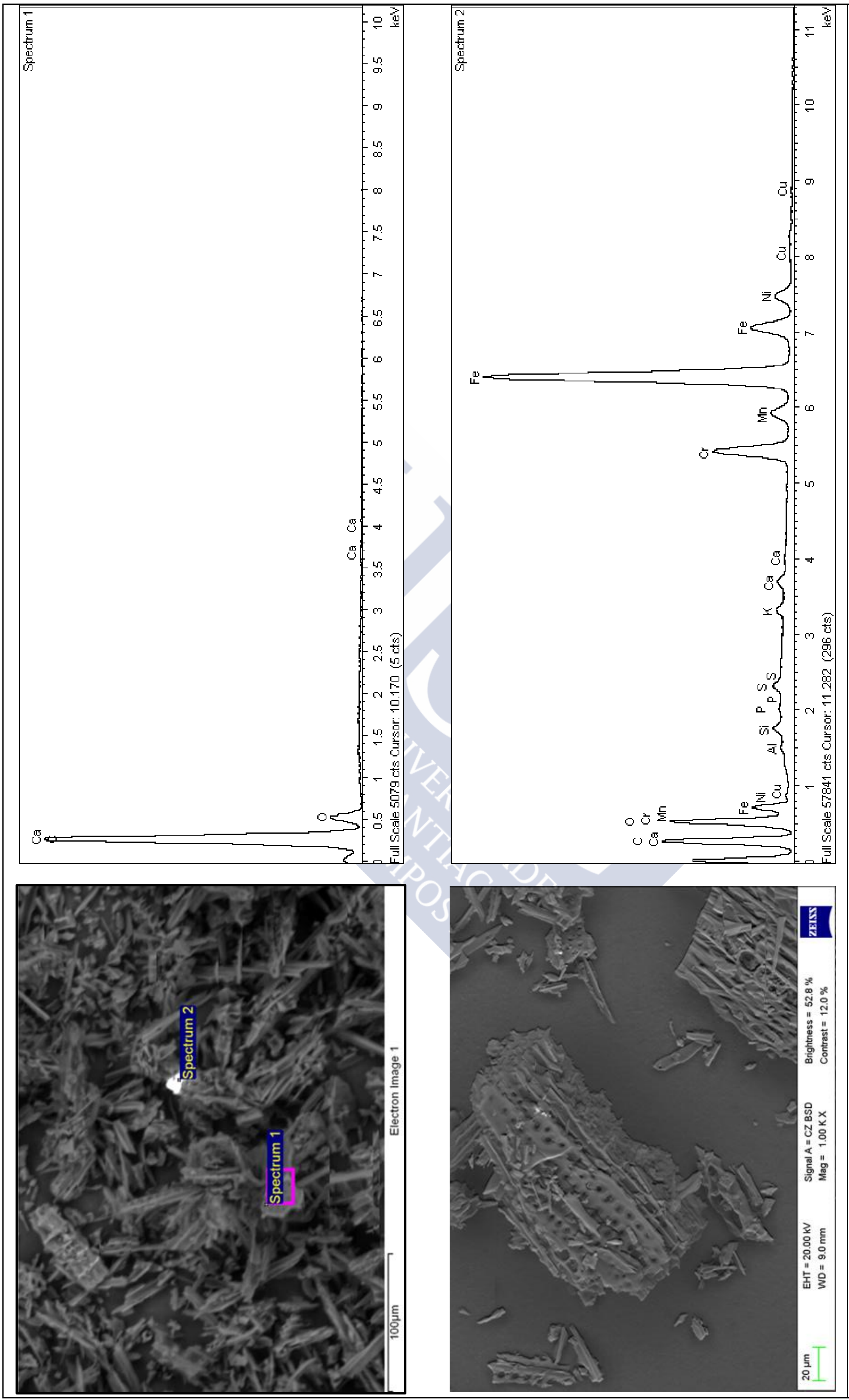

Figure S1-L. SEM-EDX with punctual microanalysis for the sample EBC.

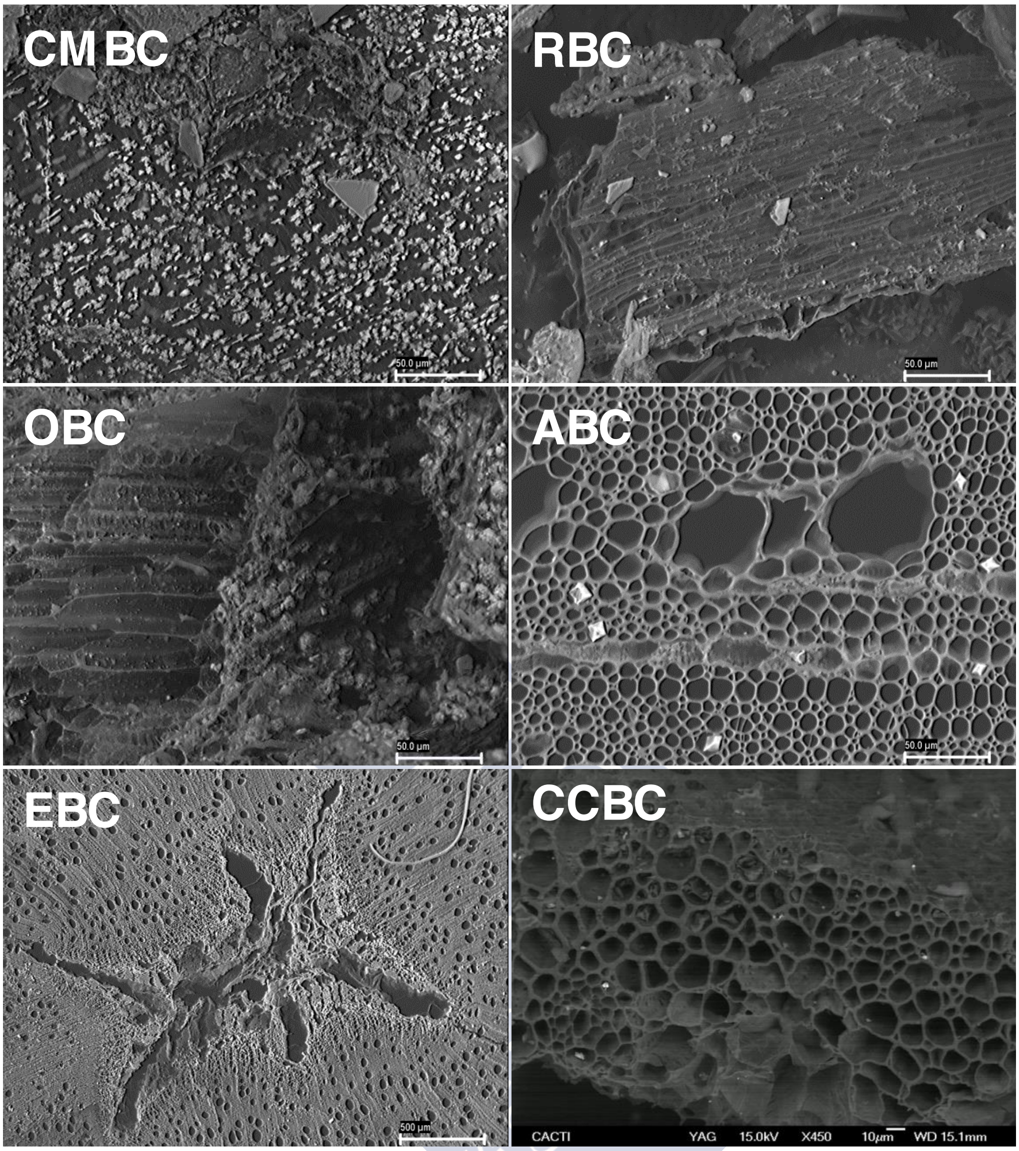

Figure S2. SEM images of the different types of BC.

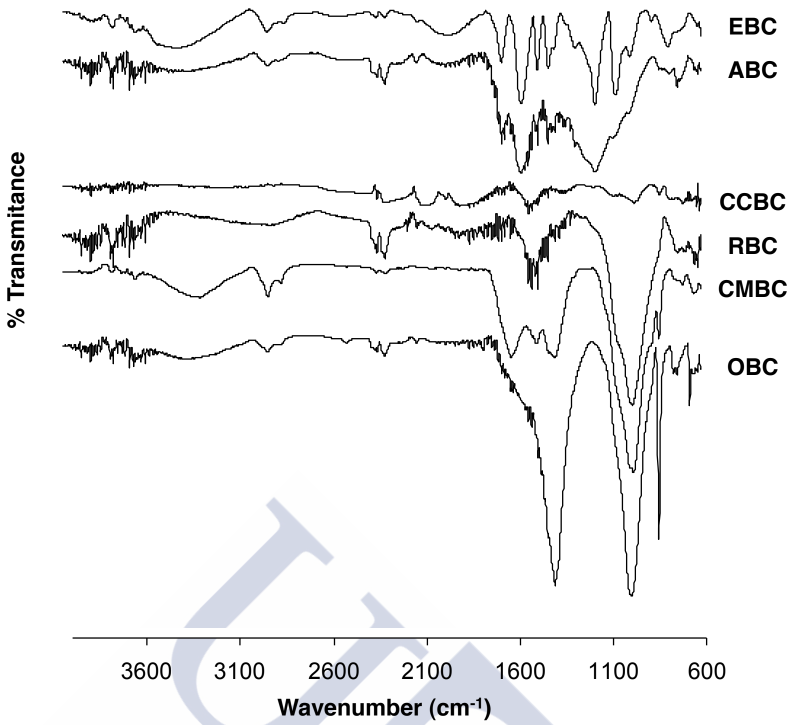

Figure S3. ATR-FTIR spectra for the different types of biochar.

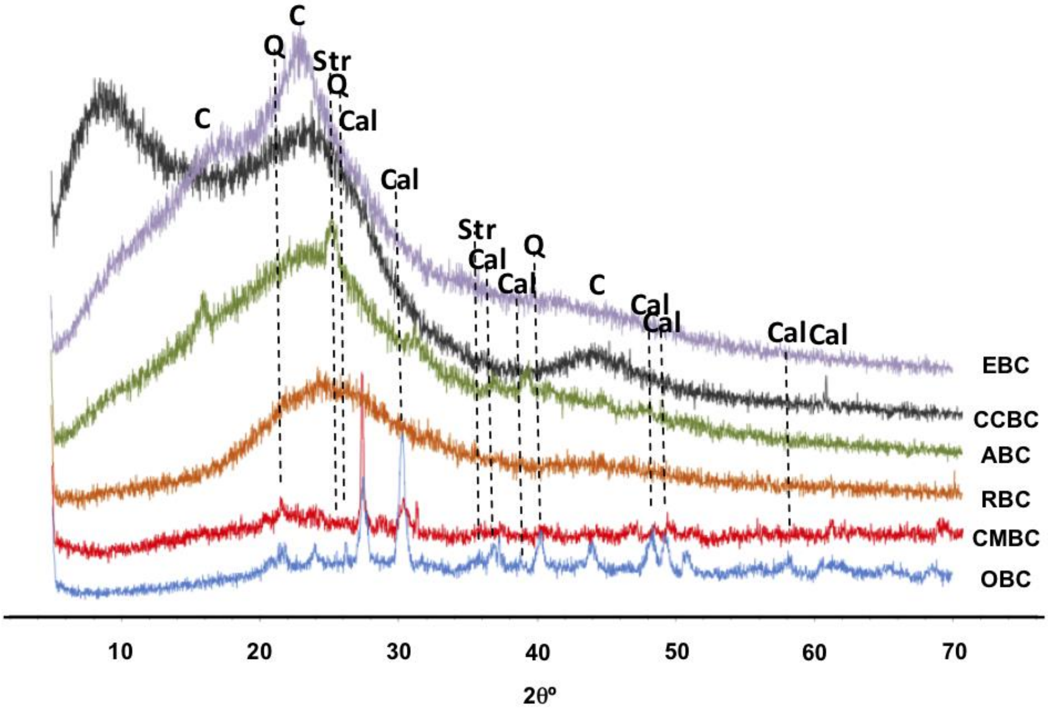

Figure. S4. XRD patterns for the different types of BC under study, C: C-graphite or cellulose; Cal: Calcite; Str: Struvite; Q: Quartz.

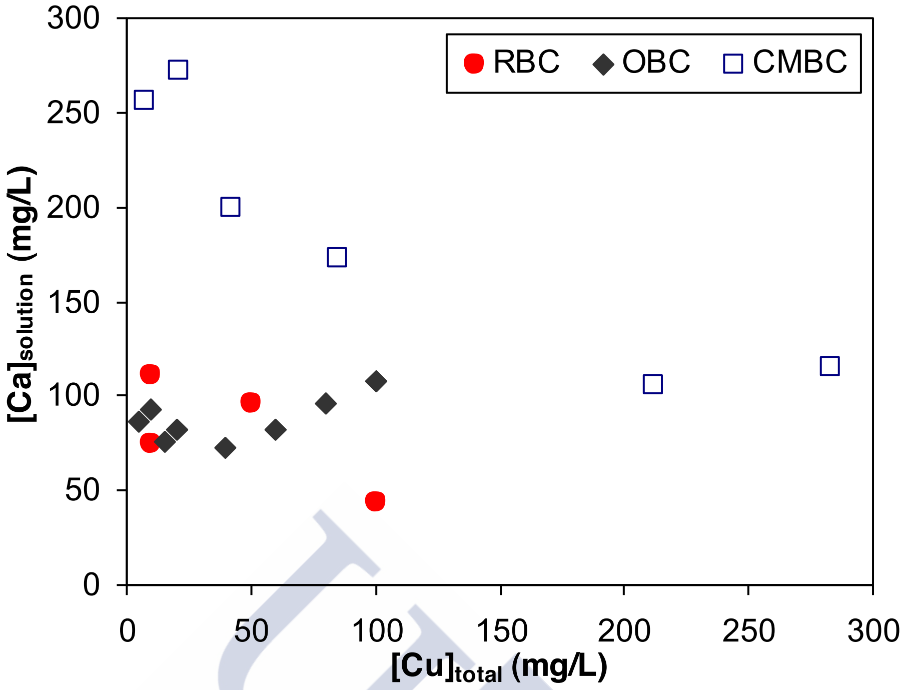

Figure S5. Variation in the calcium content with increasing amounts of copper added to the first group of BC samples.

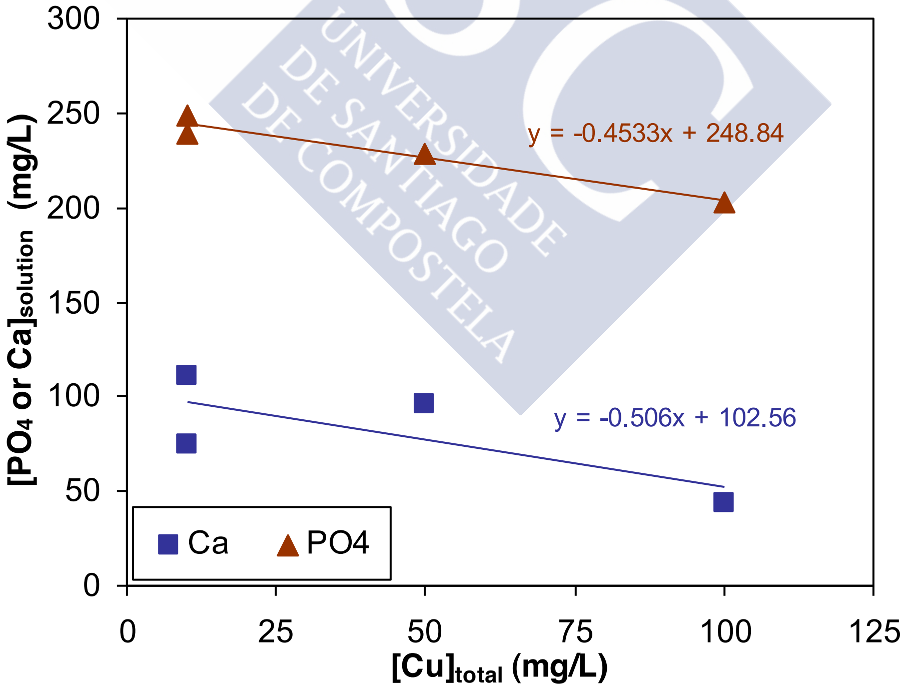

Figure S6. Variation in the contents of calcium and phosphate with increasing amounts of copper added to the BC.

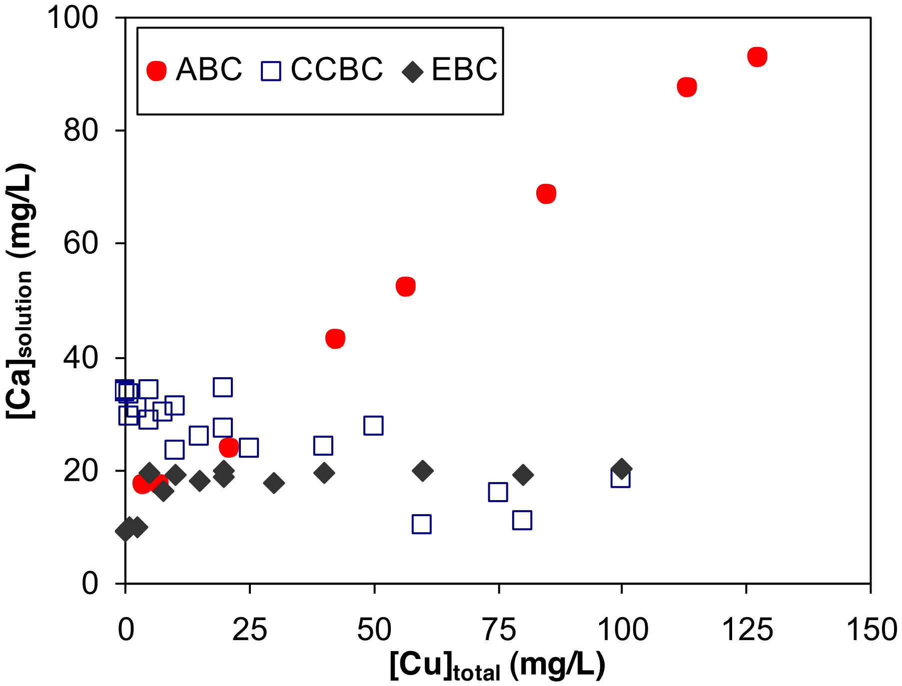

Figure S7. Variation in the content of calcium in solution with increasing amounts of copper added to the second group of BC samples.

Table S1. Capacity of the different types of biochar to remove copper from solution.

Biochars	T pyrolisis (°C)	Q_{max} (mg g^{-1})	References
Peanut straw	400	88.90	Tong et al., 2011
Soybean straw	400	52.71	Tong et al., 2011
RBC	*300-400*	*44.57*	This study
Canola straw	400	37.47	Tong et al., 2011
Dairy manure	350	35.24	Xu et al., 2013
CMBC	*300-400*	*32.23*	This study
Corn stover	500	30.22	Lima et al., 2010
Broiler litter	500	24.32	Lima et al., 2010
OBC	*300-400*	*24.1*	This study
Soybean straw	500	14.41	Lima et al., 2010
Alfalfa stems	500	14.16	Lima et al., 2010
Guayule bagasse	500	12.83	Lima et al., 2010
Corn straw	600	12.52	Chen et al., 2011
Activated carbon	400	11.43	Tong et al., 2011
ABC	*300-400*	*9.7*	This study
Corncob	500	8.45	Lima et al., 2010
Compost	300	7.94	Pellera et al., 2012
Hardwood	450	6.79	Chen et al., 2011
Softwood	500	6.35	Han et al., 2013
Switchgrass	500	5.21	Han et al., 2013
Olive pomace	300	5.12	Pellera et al., 2012
Orange waste	300	4.92	Pellera et al., 2012
Rice husk	300	4.57	Pellera et al., 2012
Rice husk	350	4.16	Xu et al., 2013
EBC	*300-400*	*3.48*	This study
CCBC	*300-400*	*2.7*	This study
Guayule shrub	500	2.48	Lima et al., 2010
Switchgrass	500	0.44	Lima et al., 2010
Hardwood	500	0.38	Han et al., 2013

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USE OF WASTE-DERIVED BIOCHAR TO REMOVE COPPER FROM AQUEOUS SOLUTION IN A CONTINUOUS-FLOW SYSTEM

ABSTRACT

The discharges from industrial processes constitute the main source of copper contamination in aqueous ecosystems. In this study we investigated the capacity of different types of biochar (derived from chicken manure, eucalyptus, corncob, olive mill and pine sawdust) to remove copper from aqueous solution in a continuous-flow system. The flow rate of the system strongly influenced the amount of copper retained. A reduction of 2.03 mg Cu g^{-1} was produced by the corncob biochar as the flux decreased from 13 to 2.5 mL min^{-1}. The physicochemical characteristics of biochar determine the copper retention capacity and the underlying immobilization mechanisms. Biochars with high inorganic contents retain the largest amounts of copper and may be suitable for using in water treatment systems to remove heavy metals. The copper retention capacity of the biochars ranged between ~1.3 and 26 mg g^{-1} and varied in the following order: chicken manure > olive mill >> corncob > eucalyptus > sawdust pine.

1. INTRODUCTION

Increased industrialization during the last century has had a substantial impact on the environment due to the accumulation of heavy metals. Copper is one of the most widely used metals as it is required in many industrial processes (metallurgy, power generation and transmission, electronic manufacturing, mining and agriculture). The waste produced during these processes constitutes the main source of copper and other metals in soils and water (Bogusz et al., 2015). The harmful effects of such contaminants have driven the development of remediation methods based on chemical precipitation, adsorption/co-precipitation on metal oxides, ionic exchange and filtration. However, some treatments require expensive reagents and/or equipment and may also generate huge amounts of waste (Regmi et al., 2012).

The increasing use of inexpensive materials to remove pollutants from the environment has prompted an interest in carrying out adsorption studies aimed at testing different types of material with a view to extrapolating the results to larger scale application. Among the different types of biomass tested for their capacity to scavenge heavy metals, algae and fungi have gained attention because of their elevated retention capacities as well as their wide availability and affordability (Zulfadhly et al., 2001; Lodeiro et al., 2006). The use of biochar (BC) as an adsorbent material also represents an inexpensive option for the efficient removal of contaminants from waste water. Biochar is a low-density carbonized material obtained by the combustion of biomass under conditions of low oxygen atmosphere and low temperature (Beesley and Marmolli, 2011). Various types of plant and animal-derived waste have been used to produce BCs in recent years (Bird et al., 2011; Xu et al., 2013). Different studies have demonstrated the ability of BCs to remove Pb, Cu, Zn, Ni and Cr from aqueous solutions (Quin et al., 2008; Gupta et al., 2013; Arán et al., 2016). Biochar is considered suitable for restoring heavily contaminated environments, such as areas affected by acid mine drainage, because of its high capacity to retain metals (Garrido-Rodriguez et al., 2014). The high retention capacity is due to the affinity of BC for metal species and to changes in the chemical and physical properties of soil in relation to pH, electric conductivity and cationic exchange capacity. The retention capacity of BC can be due to (i) electrostatic interactions, (ii) ionic exchange, and (iii) sorption by p electrons delocalized from carbon (Sohi et al., 2010). Most studies that assess the ability of adsorbent materials to retain contaminants are based on batch experiments. However, the performance of these bioadsorbents should also be assessed in continuous systems to provide a more accurate picture of how they act in real situations, e.g. for decontaminating water (Sadaf and Bhatti, 2014; Callery et al., 2016).

Continuous-flow experiments carried out using adsorption columns have provided useful information in addition to that obtained in batch adsorption experiments (Patrón-Prado et al., 2013; Park et al., 2015). Ramírez-Pérez et al., 2013, performed column experiments to assess the ability of mussel shell amendments to retain heavy metals from a mine soil. These authors concluded that the addition of this waste material to the soil increased the retention capacity and the pH of the soil and decreased the potential desorption of heavy metals. The effects of the physical and chemical properties of the column influent must be established in addition to the optimal operational parameters in order to increase the efficiency of the adsorbent materials. For example, an increase in the ionic concentration and pH of the influent solution led to the removal of more copper from solution when activated carbon was used in fixed-bed columns (Chen et al., 2003). Fixed-bed column experiments with an alkali-modified biochar derived from hickory wood showed good immobilization of heavy metals (Pb, Cd, Cu, Zn, Ni) from aqueous solution, and regeneration of the column was possible after washing with acid solution (Ding et al., 2016).

The main objective of the present study was to assess the performance of different types of BC to remove copper from an aqueous solution in continuous-flow adsorption columns. For this purpose, BCs were produced by pyrolysis of different types of feedstock material at low temperature. The specific objectives of the study were (i) to determine the influence of the flow rate on the efficiency of the biochar to remove copper in a continuous flow system, (ii) to determine and compare the capacity of the different types of biochar to retain copper from aqueous solution, and (iii) to determine the relationships between the characteristics of the different types of BC and their copper retention capacity.

2. MATERIALS AND METHODS

2.1. Preparation and characterization of the biochar samples

Biochars were produced from different types of waste material: chicken manure (CMBC), eucalyptus (EBC), corncob (CCBC), olive mill waste (OBC) and pine sawdust (SBC). The details of the pyrolysis process for CMBC, EBC, CCBC and OBC, as well as the physical treatments applied to the different BCs are described in a previously published paper (Arán et al., 2016). Briefly, the BCs were produced by slow pyrolysis at 300ºC for 4 h under oxygen–limited conditions.

Total C, H, N and S contents were determined in an element analyzer (TruSpec CHN-1000, LecoSC-144DR). The ash content was determined by combustion of samples at 1000 ºC for 6 h in muffle furnace (C.H.E. S.A. HT BT S7 RP 1200 ^{0}C). The O content was determined as follows: O (%) = 100 – (C% + H% + N% + S% + Ash%). The surface area (S_{BET}) was determined by N_2 adsorption with a Micromeritics Gemini 2360 V2.01 instrument. The physicochemical characteristics of the different types of BC are summarized in Table 1.

2.2. Fixed–bed column experiments

The continuous flow adsorption experiments were conducted in a glass column, of 15 mm internal diameter and 40 cm length, filled with 5 g of BC. The BC samples were packed in the columns as follows (Figure 1). First, a layer of glass wool was packed in the bottom of the column, to support the fixed bed. A 5 cm layer of acid–cleaned quartz sand (0.5–0.6 mm average particle size) was then placed on top of the glass wool. The central part of the column was packed with the BC samples to form a layer of thickness 9 cm. Finally, a layer (10 cm thick) of acid-cleaned quartz sand was packed in the top of the column to prevent loss of biomass and to ensure that all of the material was tightly packed. The column was washed with double distilled water for 0.5 h, and a copper solution (5 mg·L^{-1}) (prepared from a $Cu(NO_3)_2 \cdot 3H_2O$ salt, Merck) was then fed through the column at different flow rates by a peristaltic pump (Masterflex) connected to the bottom end of the column and operating in up-flow mode. The pH of the copper solution was adjusted to 5.0 ± 0.1 in all experiments by addition of small aliquots of 0.1 M NaOH or HNO_3 solutions.

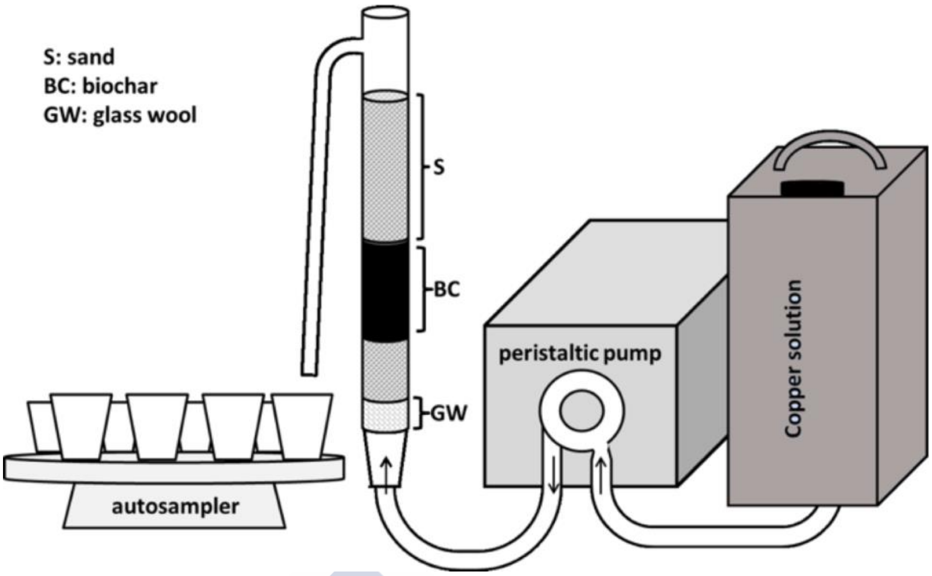

Figure 1. Experimental set-up of adsorption columns

Several experiments were conducted at different flow rates (2.5, 5.0, 7.0 and 13.0 mL min^{-1}), with CCBC as the sorbent material, to evaluate the effect of the flow rate on the removal of copper from aqueous solution. Subsequent continuous-flow experiments were then carried out at a constant flow rate of 7.0 mL min^{-1}, to compare the capacity of the different types of BC to remove copper from the solution. Aliquots of the effluent were collected periodically with an autosampler, and the concentration of copper was determined by atomic absorption spectroscopy (AAS, Perkin Elmer 1100B). All experiments were performed in duplicate, at room temperature.

2.3. Analysis of column data

2.3.1. Mathematical analysis

Copper retention in BC columns was assessed by examination of breakthrough curves, which show the shape of the concentration profile, expressed as the ratio between the concentration of copper in the effluent and in the influent (C/C_0) over time. Numerical integration of the breakthrough curves provides several useful parameters, including the total amount of copper retained by the column, q_{total} (mg), which is expressed by the following equation:

$$q_{total} = \left(\frac{F}{1000}\right)\int_{t=0}^{t=t} C_{ads}\, dt \tag{1}$$

where C_{ads} (mg L^{-1}) is the difference between the initial concentration of copper in the influent (C_0) and the concentration in the effluent (C) at any time; t (min) is the time during which the solution sample circulates through the column, and F (mL min^{-1}) is the flow rate. The amount of copper retained in equilibrium (q_e), expressed in mg g^{-1}, can be calculated as $q_e = q_{total}/M$, where M (g) is the amount of adsorbent material in the column. Other important parameters used to describe the breakthrough curves include the breakthrough point (t_b), which is usually defined as the time needed for the C/C_0 ratio in the effluent to decrease to a value of 0.5 (i.e. so that only 50% of the sorbate remains in the outflowing solution). However, the limiting value of C/C_0 can be established at different values, depending on the purpose and aims of the study and any further applications intended for the effluent. Thus, reductions in the initial concentration of between 3 and 5% have been used by Chen et al., (2003) to study copper retention by activated carbon. On the other hand, Lodeiro et al., (2006) established an even lower value for this ratio, based on European directives, and recommended specific limits for dissolved Cd in water from industrial effluents. In the present study, the C/C_0 ratio was established as 0.05, which is equivalent to 0.25 mg L^{-1} of copper in the effluent. This value corresponds to the limit for wastewater discharges established by the BSR Water Quality Guidelines (2017). This limit is quite strict in view of the range of existing limits in international legislation, which vary from 0.5 to 3 mg L^{-1} for waste water discharges (EC, 2010; BIS IS 2490-1, 1981), and from 0.05 to 2 mg L^{-1} for water destined for human consumption or for irrigation (USEPA, 1991; EC, 1998; WHO, 2004). Additional parameters include the exhaustion time (t_e), defined as the time when the ratio C/C_0 reaches a value of 0.95, and the length of the mass transference front (Z_m), which can be derived from the following equation:

$$Z_m = Z\,(1 - \frac{t_b}{t_e}) \tag{2}$$

where Z is the length of the column, in cm, and the time interval between t_b and t_e (Δt), known as adsorption zone, is indicative of the rate of mass transfer.

2.3.2. Modelling the breakthrough curves

A non-linear equation based on the Bohart-Adams model (Yan et al., 2001) was used to fit the breakthrough curves obtained from the column experiments. Despite the premises of its derivation and of its simplicity, the Bohart-Adams model is able to reproduce the experimental breakthrough curves and has been widely used to describe fixed bed continuous-flow systems and to calculate the maximum adsorption capacity of adsorbents (Kiran and Kaushik, 2008; Chu, 2010). Moreover, fitting data to the Bohart-Adams model generally results in lower errors than in other kinetic models such as the Thomas model (Han et al., 2009), especially for times far from the breakthrough point. The expression proposed by Yan et al., (2001) for the modified Bohart-Adams model, which is based on statistical analysis of experimental data, was used in the present study and is expressed as follows:

$$C/C_0 = 1 - \frac{1}{1 + \left(\frac{C_0 * F}{q_{max} * M} * t\right)^a} \qquad (3)$$

where a is an empirical parameter related to the slope of the regression function and q_{max} is the maximum adsorption capacity of the BC (mg g^{-1}). Both parameters, q_{max} and a, were used as fitting parameters. The models derived from the Bohart-Adams model were only used to describe the experimental breakthrough curves, regardless of theoretical considerations, and to detect any correlations between the model parameters and the experimental variables.

3. RESULTS AND DISCUSSION

3.1. Characterization of the biochar samples

The different BC samples were classified according to their C contents, as follows: high C content (85.2 %), CCBC; intermediate C content (69.3 and 62.6 %), EBC and SBC, and low C content (32.6 and 31.1 %), CMBC and OB. The C content was lowest in the BCs with the highest inorganic contents, i.e. with more than 45 % ash (Table 1). The N content varied between 0.41 % and 3.02 %, and the S content between 0.01 % and 0.32 %. The N contents were much higher in the BCs with the lowest C contents, as reported by Ahmad et al., (2014), who attributed this finding (which is also applicable to S) to the type of feedstock material used to produce the BC rather than to the pyrolysis conditions.

Table 1. Physico-chemical characteristics of the different types of biochar.

	CMBC	OBC	EBC	CCBC	SBC
%C	32.6	31.1	69.3	85.2	62.6
%N	3.02	2.10	0.41	0.80	0.67
%H	3.90	2.40	5.10	2.10	3.67
%S	0.32	0.08	0.01	0.10	0.04
%Ash	46.4	49.5	1.90	3.90	2.13
%O	13.7	14.8	23.2	7.90	30.8
O/C	0.32	0.35	0.25	0.07	0.37
H/C	1.45	0.94	0.88	0.29	0.70
S_{BET} (m^2 g^{-1})	1.79	3.80	1.60	173.0	43.28

The degree of carbonization and condensation of aromatic rings can be described on the basis of the H/C molar ratio. Low H/C ratios indicate a high degree of aromatization and good stability. Conversely, high H/C ratios are indicative of materials that are scarcely transformed by pyrolysis or that have low contents of lignocellulosic compounds. The H/C ratio of the BCs studied here varied between 0.29 and 1.45 (Table 1). These values are within the range reported for BC and other similar materials. H/C ratios of 0.12-0.26 have been reported for activated carbon (Chun et al., 2004; Chen et al., 2008; Qin et al., 2008) (i.e. on the lower side of the range) and also of 0.26 for BC derived from hickory wood (Ding et al., 2016). Intermediate values have been reported for different types of BC, e.g. H/C values of 0.67 for BCs derived from peanut shells (Ahmad et al., 2012), and values of 0.52 and 0.55 for BC derived from respectively hardwood and corn straw (Chen et al., 2011). At the higher end of the range, values of between 1 and 1.4 have been reported for BC derived from pine needles (Chen et al., 2008) or wood pyrolyzed at low temperature (100-200 ºC) (Ahmad et al., 2014). Relative to these previously reported H/C ratios, the values for CCBC are at the lower end of the range, those for SBC are intermediate, and those for EBC, OBC and CMBC are at the upper end of the range.

The O/C molar ratio of the BCs varied between 0.07 and 0.37 (Table 1). High polarity (due to the presence of abundant oxygenated functional groups) leads to high O/C ratios

(>0.25), such as those obtained for SBC, CMBC and OBC. On the other hand, O/C ratios ≤0.25, such as those obtained for CCBC and EBC, are indicative of low polarity. O/C values in the range 0.1-0.63 have been reported for BCs elaborated from pine needles, the lowest value corresponding to BC produced by pyrolysis of the material at high temperature (600 ºC) and the highest value for the BC produced by pyrolysis at a lower temperature (100 ºC) (Chen et al., 2008). Lower O/C values, in the range 0.06-0.11, have been reported for BC derived from wheat residue combusted at different pyrolysis temperatures (Chun et al., 2004). The Van Krevelen diagram for the different types of BC in the present study showed that the values of both ratios (H/C and O/C) were within the range of values reported for different types of biochar, derived from plants, animal material or residues such as sewage sludge (Figure S1).

The specific surface area (S_{BET}) data provided a very heterogeneous set of values for the different types of BC (Table 1), ranging from 1.60 m^2 g^{-1} for EBC to 173 m^2 g^{-1} for CCBC. The surface area of BC is affected by the nature of the feedstock material and also by pyrolysis conditions, with higher temperatures yielding larger surface areas. Moreover, pre-treatment with NaOH or KOH facilitates opening and cleaning of the pores, thus also producing a larger surface area (Chun et al., 2004; Ding et al., 2016).

3.2. Effect of flow rate on the optimization of working conditions of the columns

The copper breakthrough curves obtained for the CBCC fixed-bed column at the different flow rates are shown in Fig. 2. An increase in the inflow rate caused a decrease in the saturation time. The parameters derived from the experimental data plotted in the breakthrough curves (Table 2) revealed different relationships with the operational flow rate. Integration of the breakthrough curves for copper adsorption on CCBC led to an increase in q_{total} and Z_m as the flow rate was increased up to 7.0 mL min^{-1}. Nevertheless, no further increase was observed in q_{total} between 7.0 and 13.0 mL min^{-1}, which is consistent with the almost coincident breakthrough curves obtained at both flow rates (Figure 2).

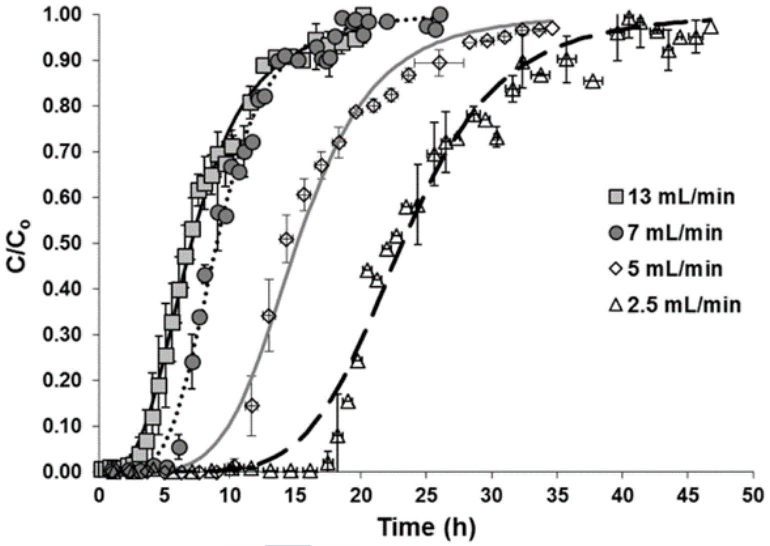

Figure 2. Breakthrough curves for Cu removal by CCBC at different flow rates. Symbols represent the experimental data points and lines represent the modified Bohart-Adams model fit

Analysis of breakthrough time, t_b, and saturation time, t_e, plotted against the flow rate revealed inverse linear correlations within the interval 2.5-7.0 mL min^{-1}. Less variation was observed in these two parameters for the interval 7.0 - 13 mL min^{-1} (Figure 3). This finding can be explained by considering that an increase in the flow rate beyond a certain value will reduce the residence time of the solution in the column, thus preventing the solution from reaching the interior of the pores and causing the appearance of the solute in the effluent before the adsorption equilibrium is reached. This effect has been reported for copper and other contaminants at high flow rates (Saĝ et al., 1995; Ahmad and Hameed, 2010). The reduction in the flow rate resulted in less steep breakthrough curves (Figure 2) as a consequence of the longer breakthrough and saturation times required for complete exhaustion of the column (Table 2).

Table 2. Parameters obtained from the breakthrough curves of copper adsorption by CCBC at different flow rates.

Flow (mL min^{-1})	13.0	7.0	5.0	2.5
q_t (mg)	32.16	32.14	24.46	18.22
q_e (mg g^{-1})	6.43	6.64	4.89	3.64
t_b (h)	3.08	5.17	11.66	18.25
t_e (h)	19.54	24.0	31.00	39.63
Z_m (cm)	7.58	7.06	5.61	4.83
Δt (h)	15.96	18.83	20.00	21.38

Parameter *Δt* was strongly and negatively correlated (R=-0.999) with the flow rate, leading to an increase in the transference zone as the flow rate increases. Taking these results into account, the optimal operational flow rate of the fixed-bed columns was 7.0 mL min^{-1}, and this rate was used in subsequent experiments carried out to investigate the capacity of the different types of BC to remove copper from aqueous solution.

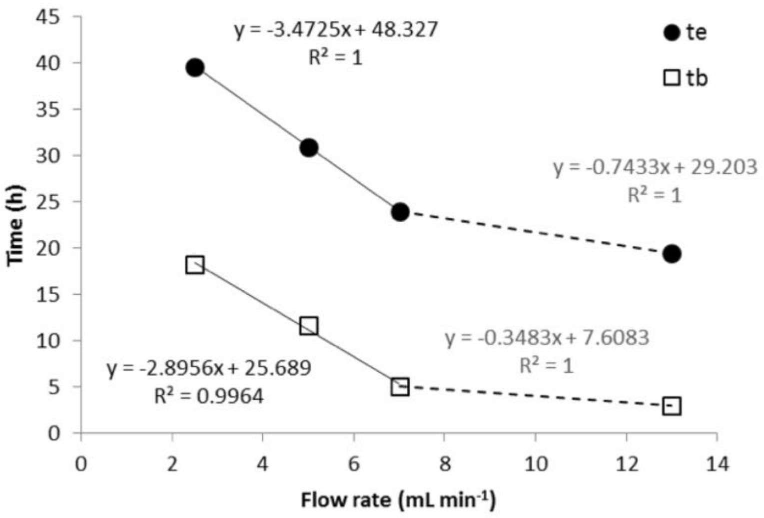

Figure 3. Variation in breakthrough, t_b, and exhaustion, t_e, times in relation to the flow rate

The modified Bohart-Adams model provided acceptable fits for the experimental data obtained at the different flow rates, with correlations > 0.980 and squared sum of residuals < 0.11 (Figure 2). The fitting parameters are listed in Table 3. The q_{max} value increased linearly with the flow rate ($R^2 > 0.737$). The highest q_{max} value, 5.51 mg g^{-1}, was obtained for a flow rate of 13 mL min^{-1}, and the lowest value, 3.48 mg g^{-1}, corresponded to a flow rate of 2.5 mL min^{-1}. The fitting parameter *a*, which is related to the slope of the regression, varied between 3.2 and 6.7. The decrease in parameter *a* with the increase in flow rate was also linear ($R^2 = 0.978$).

Table 3. Parameters obtained from the non-linear fit of the modified Bohart-Adams model to the breakthrough curve for CCBC.

Flow rate (mL min^{-1})	q_{max} (mg g^{-1})	a	R^2	RRS
13	5.51 ± 0.06	3.2 ± 0.1	0.995	0.023
7.0	3.78 ± 0.03	4.6 ± 0.2	0.992	0.036
5.0	4.55 ± 0.06	5.6 ± 0.3	0.988	0.045
2.5	3.48 ± 0.04	6.7 ± 0.4	0.984	0.102

3.3. Comparison of copper sorption on different types of biochar

The copper breakthrough curves obtained with the BC samples under study are shown in Figure 4, and the parameters derived from these curves are shown in Table 4. All experiments were conducted at the same flow rate (7.0 mL min^{-1}) and with a fixed bed height of the adsorbent layer (9 cm). The breakthrough curves show that the BCs can be classified in two groups, with respectively a high and low capacity to remove copper from solution. The BCs with the highest copper retention capacities (CMBC and OBC) corresponded to those with the highest q_e and t_b values, and the BCs with the lowest copper retention capacities (CCBC, EBC, SBC) were those with low q_e and t_b values (Table 4). There was no significant difference in the breakthrough time, t_b, obtained for CMBC and OBC, approximately 45 h. The breakthrough times for the other three samples were all below 10 h. The difference between breakthrough and saturation time, Δt, which is related to the rate of mass transfer, is consistent with the previous classification. The samples with the longest transfer intervals, CMBC and OBC, produced breakthrough curves with smoother slopes, whereas the slopes for CCBC, EBC and SBC, with shorter transfer intervals, were steeper. Smoother slopes indicate that saturation of the biochar material in the column takes longer. Curves with steeper slopes and short breakthrough times indicate that the retention capacity of the material is relatively low.

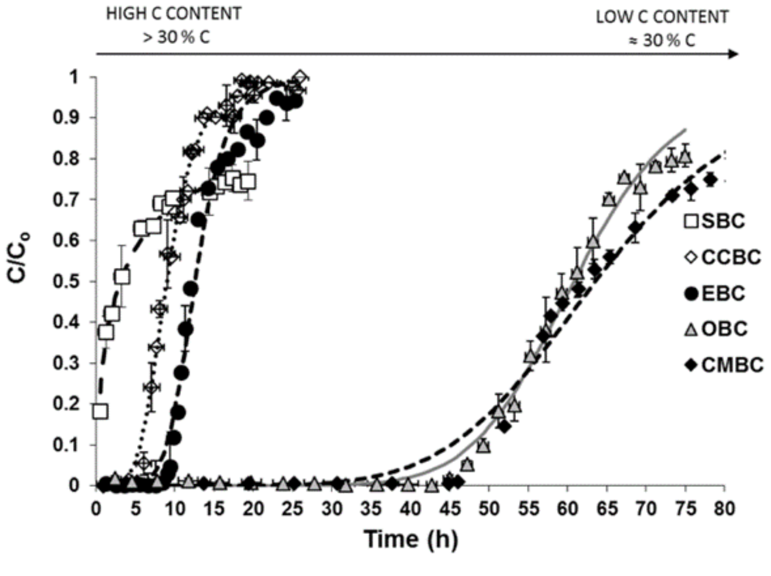

Figure 4. Breakthrough curves for Cu removal by different types of BC at a constant flow rate 7 mL min^{-1}. Symbols represent the experimental data points and lines represent the modified Bohart-Adams model

Some of the parameters defined by the breakthrough curves were correlated with the physicochemical characteristics of the BCs. In previous batch studies of copper retention on BC, some physicochemical characteristics were found to affect the amount of copper retained (Arán et al., 2016). In the present study, copper retention was highest in samples with an O/C molar ratio higher than 0.3 and high ash and phosphorus contents. The mechanism of retention was also found to differ depending on the amount of the inorganic and organic fractions, e.g. the predominance of the mineral fraction over the organic fraction resulted in higher retention capacities due to the combination of adsorption and precipitation processes. Similar correlations between physicochemical properties and retention capacity were observed for other metals such as lead, zinc and cadmium, and the retention capacity was highest in BCs with the highest ash contents, i.e. in which the mineral fraction predominates (Xu et al., 2013). In the present study, the physicochemical properties that were most closely correlated with the parameters of the breakthrough curves (q_e, t_b, t_e) were %C, %N and %ash (Table S1). The highest positive correlation was found with the %ash, e.g. copper retention was favourable in the BCs with the highest inorganic contents, which is consistent with the results of batch experiments (Arán et al., 2016). As expected, the parameters of the breakthrough curves were negatively correlated with the %C.

Table 4. Parameters obtained from the breakthrough curves of copper adsorption by different types of BC at a constant flow rate of 7.0 mL min^{-1}.

Type of BC	CCBC	CMBC	OBC	EBC	SBC
q_{total} (mg)	32.14	136.98	124.35	26.79	14.87
q_e (mg g $^{-1}$)	6.64	27.40	24.87	5.36	2.97
t_b (h)	5.17	47.00	47.25	9.50	0.25
t_e (h)	24.0	86.00	82.00	25.30	16.00
Z_m (cm)	7.06	4.08	3.81	5.62	8.86
Δt (h)	18.83	39.00	34.75	15.80	17.75

The modified Bohart-Adams model fitted well to the experimental data (Figure 4), yielding R^2 values higher than 0.970 and RRSE lower than 0.10 (Table 5). The q_{max} values obtained for the different BC materials, i.e. the maximum retention capacity, varied as follow: CMBC > OBC > EBC > CCBC > SBC. The samples with the highest inorganic content, CMBC and OBC, retained more copper: 26.63 and 25.30 mg g^{-1}, respectively. As expected, this parameter was closely correlated with the ash content (R^2 = 0.980). The BC with high organic content, reflected in higher %C and lower ash content, retained less copper, with a decrease in the q_{max} values ranging from 79 to 95 % (Table 5). Parameter a, obtained by fitting the modified Bohart-Adams model to the data, was not correlated with the physicochemical properties of the BCs. The values of this parameter ranged between 0.66 for SBC and 9.12 for OBC (Table 5).

Table 5. Parameters obtained by fitting the modified Bohart-Adams model to the breakthrough curves for the different BCs.

	q_{max} (mg g^{-1})	a	R^2	RRSE
CMBC	26.6 ± 0.26	6.43 ± 0.46	0.978	0.042
OBC	25.3 ± 0.11	9.12 ± 0.36	0.992	0.022
EBC	5.28 ± 0.08	6.40 ± 0.52	0.978	0.008
CCBC	3.78 ± 0.03	4.62 ± 0.19	0.992	0.036
SBC	1.28 ± 0.07	0.66 ± 0.03	0.980	0.007

The affinity sequence is consistent with the maximum adsorption capacity obtained in batch experiments conducted with the same BCs (Arán et al., 2016). A good correlation was observed between the maximum adsorption capacities obtained with the Langmuir-Freundlich model (batch experiments) and those obtained with the modified Bohart-Adams model (continuous experiments) (Figure 5).

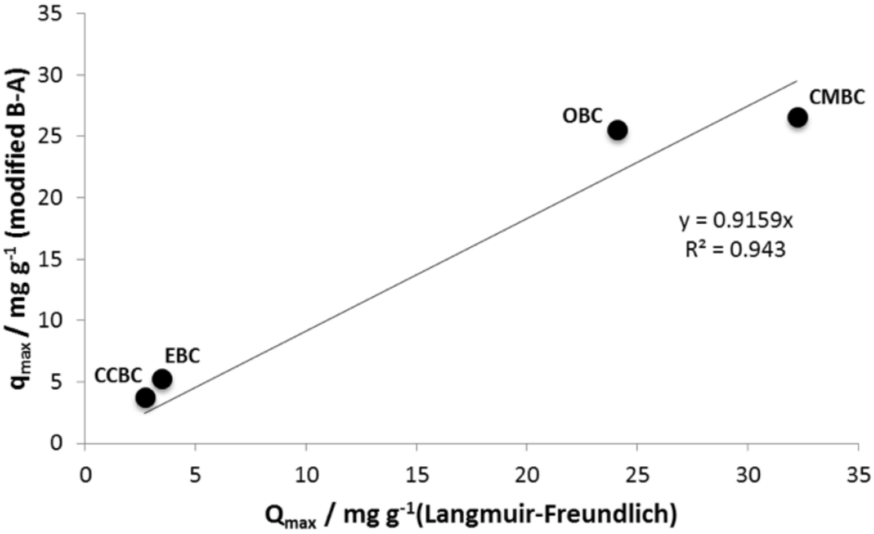

Figure 5. Correlation between the maximum retention capacities predicted by the empirical models for batch and continuous flow experiments. Q_{max} values obtained with the Lagmuir-Freundlich model are taken from Arán et al. (2016)

The maximum retention capacity predicted by the modified Bohart-Adams model was also closely correlated with the breakthrough time (t_b) (R^2=0.991) (Figure S2). The good correlations between parameters enable direct prediction of the behavior of a given biochar in continuous systems and also enable the operational conditions of the columns to be established using the available information obtained in batch experiments.

The copper retention capacity of the BCs were similar to or higher than observed for other BCs. Biochar or activated carbon derived from different types of waste such as pine, pomegranate wood, silver birch, jarrah and wheat straw had similar Cu retention capacities, of between 0.129 mg g^{-1} and 17.83 mg g^{-1} (Chen et al., 2003; Muhamad et al., 2010; Alslaibi et al., 2014; Ghaedi et al., 2015; Komkiene and Baltrenaite, 2016). CMBC and OBC appear to be the most suitable types of BC for copper retention, because they can remove higher amounts of Cu from aqueous solution and also because the removal mechanism involves co-precipitation and adsorption, thus producing more stable forms.

4. CONCLUSIONS

Flow rate is a key parameter in continuous flow systems with a high adsorption capacity. In the present study, high flow rates (> 7 mL min^{-1}) yielded short breakthrough and saturation times, whereas intermediate to low flow rates provided optimal conditions for retention of copper by BC. Columns filled with CCBC and operating at flow rates of 7 and 5 mL min^{-1} yielded breakthrough times of 5 and 12 hours and maximum copper retention capacities of 3.78 and 4.55 mg g^{-1}, respectively.

The copper retention capacities of the different types of BC tested in the present study were high, with values ranging from 1.28 mg g^{-1} for SBC to 26.63 mg g^{-1} for CMBC. Biochars may therefore be effective and economic alternatives to other sorbent materials for removing heavy metals from aqueous systems. The physicochemical characteristics of the materials used to produce the BCs determine the copper retention capacity and the underlying immobilization mechanisms. The biochars with the highest retention capacity, CMBC and OBC, were also those containing the highest amounts of inorganic compounds. These biochars may be suitable for use in water treatment systems to remove copper or other heavy metals. Finally, a good correlation was observed between the sorption parameters in continuous flow systems and in discontinuous systems. This enables prediction of the behaviour of BC materials and optimization of the operational conditions with very few sorption experiments.

5. ACKNOWLEDGEMENTS

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Supplementary materials

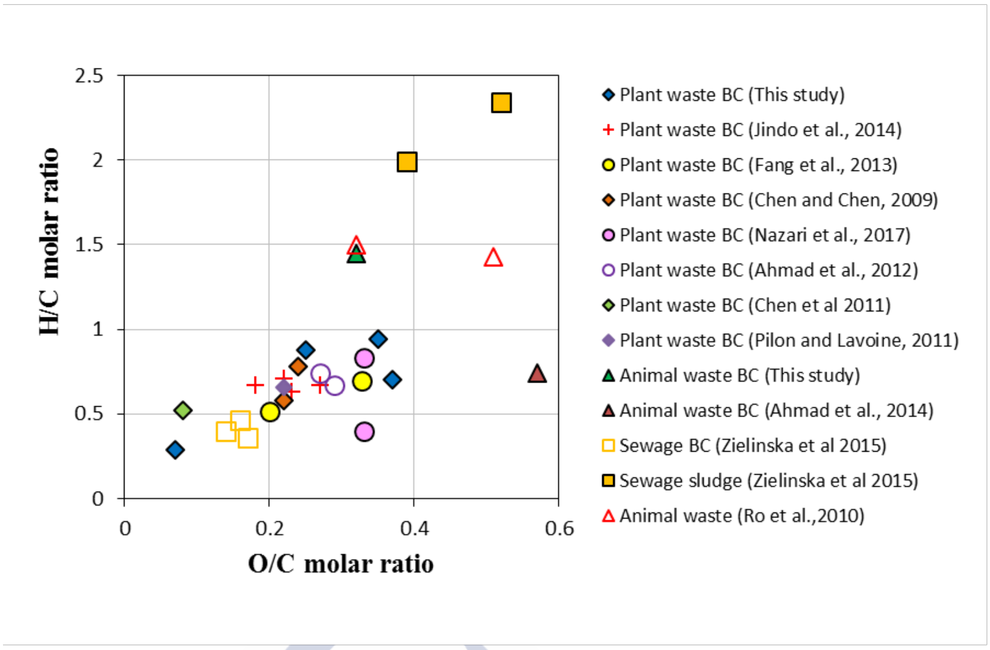

Figure S1.-The Van Krevelen diagram for BCs of this study in relation to other materials present in different studies

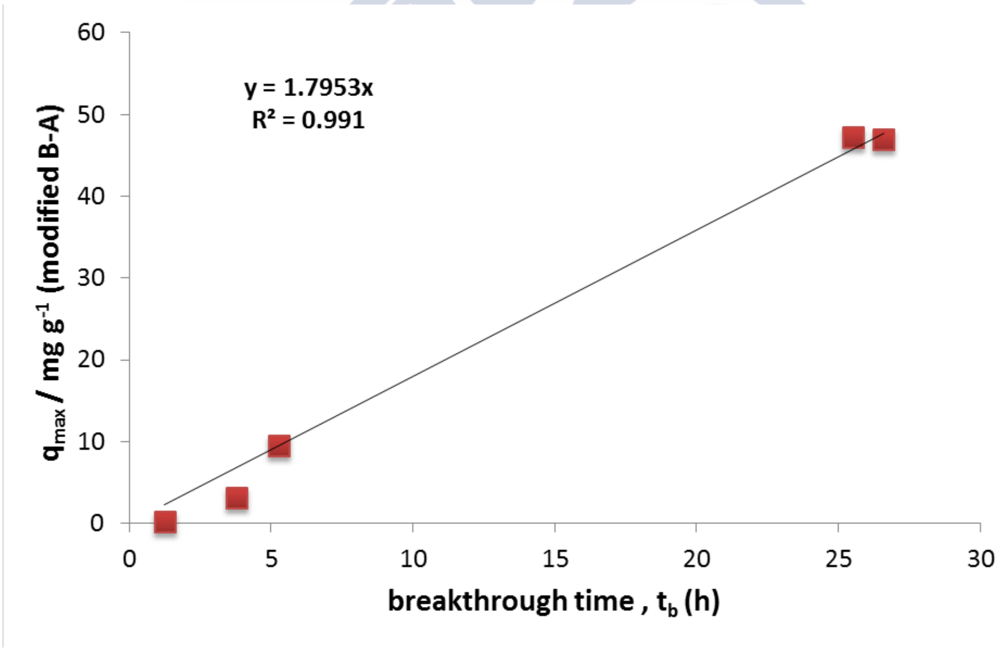

Figure S2. Correlation between maximum adsorption predicted by continuous flow experiments and breakthrough times

Table 5. Pearson correlation coefficients between parameters derived from the breakthrough curves and the physico-chemical properties of the BC samples.

	q_e	t_b	t_e
pH	0.3079	0.3470	0.3131
% C	-0.9237	-0.9075	-0.9243
% N	0.9597	0.9283	0.9473
% H	-0.1522	-0.1695	-0.1513
%S	0.7129	0.6541	0.6858
% Ash	0.9899	0.9887	0.9910
% O	-0.4139	-0.4462	-0.4137
O/C	0.4381	0.4028	0.4381
H/C	0.7835	0.7483	0.7762
S_{BET}	-0.5284	-0.5240	-0.5388

IMMOBILIZATION OF PHOSPHATE BY A SPOLIC SILANDIC TECHNOSOL: BATCH AND CONTINUOUS TESTS

ABSTRACT

Phosphorus is an essential element that at high concentrations generates eutrophication of aquatic systems. In this study, we used batch and continuous tests to evaluate the efficiency of a Technosol to retain the phosphorus present (as phosphate) in water samples. In the batch tests, we determined how pH and the presence of different anions (HCO_3^-, SO_4^{2-}, Cl^-, CrO_4^{2-}, MoO_4^{2-}) affected phosphate retention. The main mechanisms involved in the sorption process were precipitation (as Ca-P minerals) and surface adsorption. In the column experiments, we determined the effect of flow rate and observed a reduction of approximately 60 % in the retention capacity, from 6.19 ± 0.06 to 2.37 ± 0.06 mg g^{-1}, as the flow rate increased from 1.5 to 5.0 mL min^{-1}. In addition, the retention capacity decreased by 14% when the thickness of the reactive layer was halved. Phosphate retention was higher in the samples in which the influent solution was acidic. Finally, the retention capacity of the spolic silandic Technosol recovered well after several adsorption-desorption cycles. After one cycle, the retention capacity reached 40 % of the original value and the same rate of recovery was observed after the second cycle.

1. INTRODUCTION

Phosphorus (P) is essential for biomass growth and is a basic component of fertilizers applied to crop and fields. Stocks of P are declining due to the high rate of consumption and uncontrolled use in agriculture, which has become dependent on phosphorus derived from phosphate rock. World reserves of phosphate rock are limited and are being exhausted (FAO and ITPS, 2015; Xie et al., 2015). Application of phosphate to agricultural land at high concentrations also leads to increased concentrations of the element in rivers, lakes and reservoirs. This favours abnormal growth of algae and aquatic plants, leading to degradation of water quality through eutrophication (Barca et al., 2012, Belelli et al., 2014; Xi et al., 2014). Excessive concentrations of N and P are the main cause of growth of cyanobacteria in water bodies (Smith et al., 2006), and removal of both of these nutrients becomes essential to minimize the environmental risks associated with uncontrolled blooms. European legislation establishes a maximum limit for waste water discharge of 1 mg P L^{-1} (EC, 1991).

Different materials, including sand, gravel, rocks, soils, iron oxide, nanocomposites and fly ash, have been tested for their ability to remove phosphate from water. These materials display a high affinity for phosphate due to the high amounts of Ca, Al and/or Fe that they contain (Perassi and Borgnino, 2014; Vohla et al., 2011; Westholm, 2006). The different adsorbent materials are generally evaluated in batch and continuous (column) tests that enable analysis of their behaviour under different physico-chemical conditions. Batch tests are used to evaluate the retention capacities of different adsorbent materials and to compare the efficacy of the materials as filtration or retention systems in slow-moving bodies of water such as lakes, ponds and reservoirs. By contrast, continuous tests allow more realistic evaluation of the efficacy of the materials under dynamic conditions, by simulating water flow rates similar to those observed in rivers, canals and reservoir influents.

Technosols, defined as soils whose formation and properties are influenced by human activity, include soils derived from anthropogenic waste (IUSS Working Group WRB, 2015). They are often derived from waste material such as mine spoils, landfill, cinder and sludge, and their formation and properties depend on their technical origin (IUSS Working Group WRB, 2015). Thus, unconsolidated waste material can be used to elaborate Technosols with desired characteristics, by using different natural soils as models (Camps et al., 2008). The usefulness of artificially-generated soils for restoring soils, water bodies and degraded or polluted areas has been investigated in numerous studies in which microcosm tests have been conducted under controlled conditions (Novo et al., 2013; Rodríguez-Vila et al., 2016; Santos et al., 2014, 2016) and in field trials (Monterroso et al., 1998).

Technosols with andic properties can be generated from residues by using Andic soils as a model. Andic properties are associated with the nature of the amorphous clay fraction and Al and Fe organomineral complexes (Arnalds, 2008). Andic soils are characterized by high contents of amorphous Fe and Al, low bulk density and high P retention capacity (IUSS Working Group WRB, 2015). The main objective of the present study was to evaluate the efficacy of a Technosol with andic properties to retain phosphate from aqueous solution. For this purpose, the specific objectives of the study were as follows: i) to determine the maximum adsorption capacity of the Technosol; ii) to evaluate the influence of the phosphate concentration and solution pH; iii) to analyse the possible competition between phosphate and other major or minor ions under different reaction conditions; iv) to determine the phosphate retention capacity under different dynamic conditions (effect of flow rate); v) to determine the effect of the pH of the influent solution on the efficacy of phosphate retention by the Technosol, vi) to determine the influence of the contact time on the phosphate retention; and vii) to evaluate the capacity of reusing the Technosol.

2. MATERIAL AND METHODS

2.1. Technosol

The Technosol used in the tests was elaborated from industrial and agro-industrial waste and was supplied by CVAN (Centro de Valorización Ambiental del Norte, Touro, Spain). The main physico-chemical characteristics of the material were determined following standard methods for soil analysis (Sparks, 1996). The results obtained (Table 1) enabled classification of the material as a spolic silandic Technosol (IUSS Working Group WRB, 2015).

Table 1. Physico-chemical properties of the spolic silandic Technosol.

Technosol characteristics	
pH$_{H_2O}$	7.96
pH$_{KCl}$	7.73
pH$_{NaF}$	11.50
C (g kg^{-1})	80.40
N (g kg^{-1})	4.70
Andic properties	
Al_{ox} (g kg^{-1})	40.4
Al_{py} (g kg^{-1})	14.5
Fe_{ox} (g kg^{-1})	4.1
Fe_{py} (g kg^{-1})	1.6
Al_{ox} + ½ Fe_{ox} (%)	4.25
Al_{py} / Al_{ox}	0.35
Phosphate retention (%)	100
Equilibrium solution (1:20)	
pH$_{H_2O}$	7.92
Ca (mg L^{-1})	194
Mg (mg L^{-1})	26.0
PO_4 (mg L^{-1})	0.20

2.2. Adsorption kinetics

Technosol suspensions at a solid:solution ratio of 1:50 kg L^{-1} were prepared in 0.1 M KNO_3 at four initial phosphate concentrations: 0.5, 1.6, 3.2 and 6.4 mM (47.5, 152, 304, and 608 mg PO_4 L^{-1}). The suspensions were shaken at 150-200 rpm in a reciprocal shaker (IKA-HS501 digital) at room temperature. A blank was prepared by just suspending the Technosol in 0.1 M KNO_3 without further addition of phosphate. The amount of phosphate was measured in the filtered (0.45 µm, MF-Millipore, Millex) supernatants of the independent batch experiments (samples and blanks) at different time intervals during a 4 h period. The concentration of PO_4 in solution was determined by the molybdenum blue method (Murphy and Riley, 1962) and was corrected for the corresponding blank concentration.

2.3. Sorption isotherms and pH effect

Phosphate (PO_4) retention was studied by batch tests in which the initial concentration of PO_4 varied between 0.5 and 5 mM (47.5 and 475 mg PO_4 L^{-1}). These concentrations were prepared by dilution of a stock solution of 80 mM (7600 mg PO_4 L^{-1}) prepared from the PO_4 salt $NaH_2PO_4·7H_2O$. Suspensions of the Technosol were prepared in 0.1 M KNO_3 solution (inert electrolyte) at a solid:solution ratio of 1:50 (kg L^{-1}). The pH of the suspensions was adjusted to 4, 6, 7.5 and 9 by addition of 0.1 or 1.0 M HNO_3 or NaOH. The samples were then shaken for 24 h to ensure that the adsorption equilibrium was reached. The suspensions were then filtered through 0.45 µm filters (MF-Millipore, Millex). Finally, the concentration of PO_4 in solution was determined as previously indicated.

An adsorption assay was carried out with a constant PO_4 concentration of 1.5 mM (142.5 mg PO_4 L^{-1}) and variable concentrations of K_2SO_4, $NaHCO_3$, KCl, K_2CrO_4 and $Na_2MoO_4·2H_2O$ in order to evaluate the effect of the different ions (sulphate, bicarbonate, chloride, chromate and molybdate) on PO_4 retention. The concentration of these compounds varied between 0 and 0.5 M. The procedure used was as previously described, although the tests were only carried out at pH 4 and 9. The competition effect was determined as the variation in the percentage retention of PO_4 in the presence and the absence of the competing ions.

2.4. Continuous (column) experiments

The continuous tests were carried out in columns of internal diameter 15 mm and length 40 cm, which were filled with adsorbent material. The fixed bed columns were filled with a layer of active material composed by 11.20 g of the Technosol, which was sandwiched between two layers (each of 5 cm) of acid-washed quartz sand (particle size 0.5-0.6 mm). Different factors were evaluated in the continuous systems: influent flow rate, thickness of the adsorbent layer, pH of the influent and regeneration capacity of the Technosol adsorbent. In all column tests, the concentration of PO_4 in the influent solution was 20 mg L^{-1} (C_0), the ionic strength was 0.1 M in KNO_3, and the pH was 5.5 ± 0.1 (except in those assays in which the effect of pH was studied). The concentration of PO_4 used was 20 times higher than the maximum concentration permitted for discharge in waste water (EC, 1991). The influent solution was pumped upwards through the fixed bed column at different rates with a peristaltic pump (Masterflex).

Phosphate retention assays were carried out at three different flow rates (1.5, 2.1 and 5 mL min^{-1}) to evaluate the effect of this factor. Further assays were carried out at a constant influent flow rate of 5 mL min^{-1} with 11.20 and 5.60 g of Technosol and with the column filled with adsorbent material to heights of 19 and 10 cm respectively, to determine the effect of the thickness of the adsorbent layer in the column on phosphate retention. Assays were also carried out at pH 5.5 ± 0.1 and 3.0 ± 0.1 to evaluate the effect of the pH of the influent solution on PO_4 retention. In this assay, 11.20 g of Technosol were used and the pumping rate was 5 mL min^{-1}. Finally, sorption-desorption assays were carried out to evaluate the reuse capacity of the Technosol. For the desorption assays, a solution of KNO_3 of the same pH and ionic strength as the phosphate solution was used. Thus, sorption was first carried out under the standard conditions established (in relation to [PO_4], flow rate, pH, amount of Technosol) and once the column was saturated, the desorption stage began. When the concentration of PO_4 in the effluent was lower than 1 mg L^{-1}, the sorption-desorption cycle was repeated. All experiments were carried out in duplicate at room temperature.

During all the experiments, aliquots were periodically collected with an autosampler. The PO_4 concentration in the aliquots (C) was determined by the molybdenum blue colorimetric method (Murphy and Riley, 1962). The breakthrough point was established at $C/C_0 = 0.05$, corresponding to a PO_4 concentration of 1 mg L^{-1}, which is the maximum concentration permitted for discharge in waste water (EC, 1991).

2.5. Modelling

2.5.1. Kinetics

Kinetic experiment data were analysed by the pseudo-first- and pseudo-second-order kinetic models, and the Weber and Morris intra-particle diffusion model:

- Pseudo-first-order kinetic model

$$ln(q_e - q_t) = lnq_e - k_1 t$$

- Pseudo-second-order kinetic model

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

- Intra-particle diffusion model

$$q_t = k_d t^{1/2} + C$$

where t (min) is the reaction time, k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the adsorption rate constants, and q_e and q_t (mg g^{-1}) are the phosphate sorbed on the Technosol at equilibrium and time t (min), respectively. K_d (mg g^{-1} $\mathrm{min}^{-1/2}$) is the intra-particle diffusion constant and C is an empirical parameter.

2.5.2. Sorption isotherms

Empirical isotherm models are commonly used to describe sorption of ions from aqueous solutions to solid sorbents at equilibrium. The parameters obtained from these empirical models can provide useful comparative information, such as adsorption capacities or affinity constants. Isotherm parameters were obtained from the measured data using nonlinear least squares regression. In this study, Langmuir and Freundlich isotherm models were used to describe phosphate sorption:

- Langmuir model

$$q_e = \frac{K_L\, Q_{max} C_e}{(1 + K_L C_e)}$$

- Freundlich model

$$q_e = K_F * C_e^{1/n}$$

where q_e is the concentration of phosphate sorbed on the Technosol (mg g^{-1}) and C_e is the concentration of phosphate in solution (mg L^{-1}). K_L is the Langmuir sorption constant related to the affinity and Q_{max} is the maximum adsorption capacity of the technosol (mg g^{-1}). K_F is the Freunlich constant related to the adsorption capacity (mg g^{-1}) (L mg^{-1})$^{1/n}$, and n is a constant related to the intensity of adsorption and the heterogeneity of the binding sites.

2.5.3. Breakthrough curves modelling

The breakthrough curves obtained in the continuous tests were interpreted using a non-linear equation based on the Bohart-Adams model (Yan et al., 2001). The modified model of the Bohart-Adams model used is expressed as follows:

$$C/C_0 = 1 - \frac{1}{1 + \left(\frac{C_0 * F}{Q_{max} * m_s} * t\right)^a}$$

where C is the concentration of PO_4 in the effluent solution (mg L^{-1}), C_0 is the concentration of PO_4 in the influent solution (mg L^{-1}), F is the flow rate (L h^{-1}), a is an empirical parameter inversely related to the slope of the regression function, Q_{max} is the maximum adsorption capacity of the Technosol (mg g^{-1}), m_s is the sorbent mass (g) and t is the run time (h).

3. RESULTS AND DISCUSSION

3.1. Adsorption kinetics

The kinetics of phosphate sorption onto the Technosol is shown in Fig S1 for the different PO_4 loadings. The analysis of the reaction time of phosphate adsorption on the Technosol revealed that an apparent equilibrium is reached within four hours. This is in agreement with previous data for other sorbent materials, ie. goethite (Luengo et al. 2006), iron hydroxide-eggshell waste (Mezenner and Bensmaili, 2009), chitosan (Liu and Zhang, 2015) or laterite and sandstone (Coulibaly et al., 2016). Although sorption seems to reach completion rapidly, the following sorption experiments were conducted with an equilibrium time of 24 hours in order to ensure that diffusion processes, or other kinetically slow-sorption process that may control phosphate mobility, occur.

Phosphate sorption process follows the pseudo-second-order kinetic model (Fig. 1), rather than the other kinetics models considered (Fig. S2, Table S1). The fitting parameters obtained with the pseudo-second-order kinetic model for the different phosphate loadings are shown in Table 2.

There is a good correlation between the experimental and the calculated q_e, which increases as the PO_4 loading increases. k_2 values remain invariable at intermediate to high loadings. The good agreement of the experimental data with the pseudo-second-order kinetic model suggests that chemisorption could be the dominant sorption mechanism controlling phosphate sorption on the Technosol. The intra-particle diffusion model also adequately describes the kinetic behaviour, although the R^2 values obtained were lower for all phosphate loadings (Table S1). The linear plots, q_t vs $t^{1/2}$, at each loading did not pass through the origin, indicating that diffusion is not the only controlling mechanism. Diffusion may simultaneously operate with the surface sorption to immobilize phosphate on the Technosol.

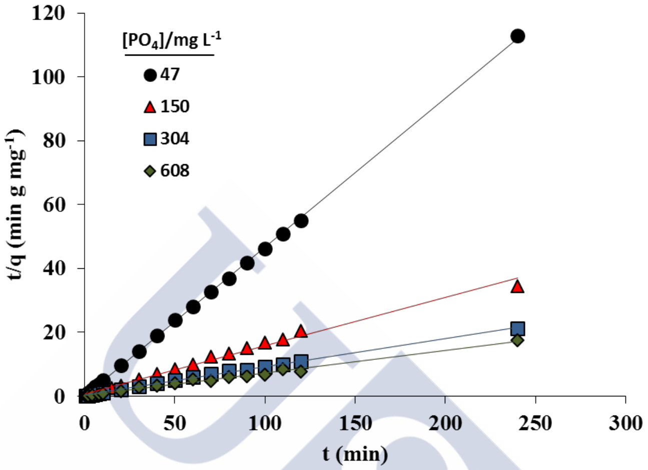

Figure 1. Adsorption kinetics of phosphate on the Technosol at four different phosphate loadings using the pseudo-second-order kinetic model. Symbols correspond to the experimental data and lines to the model fit.

Table 2. Fitting parameters for the pseudo-second order kinetics of phosphate adsorption on the Technosol.

$[PO_4]$ (mg L^{-1})	q_e (mg g^{-1})	k_2 (g min^{-1} mg^{-1})	R^2	RSS
47.5	2.14	4.04	0.999	2.84
152	6.62	0.030	0.99	14.58
304	11.24	0.025	0.997	1.57
608	14.08	0.037	0.997	3.04

3.2. Batch tests

3.2.1. Effect of pH on phosphate retention

The sorption isotherms of phosphate at the different pH values are shown in Fig. 2. The concentration of the phosphate sorbed onto the Technosol increases with the increase of the initial phosphate concentration until saturation is reached. The isotherm model that provided the best fit to the experimental data was the Langmuir model, with

R^2 values between 0.86 and 0.97 (Table 3). Only at the lowest pH, the adsorption process behaves as the Freundlich model. The good agreement between the adsorption data and the Langmuir model indicates that the adsorption process is homogenous and a monolayer is formed. Q_{max} values ranged from 7.1 to 18.5 mg g^{-1}, which are close to the values determined experimentally. The retention values are comparable with those obtained for other materials, i.e. andosol-bagasse mixtures (2.82–4.18 mg g^{-1}), ground burnt patties-red soil mixtures (0.86–2.12 mg g^{-1}), dolochar (2.87–8.56 mg g^{-1}), activated carbon (0.8-6.0 mg g^{-1}), iron oxide tailings (8.2 mg g^{-1}) or goethite (6.4 mg g^{-1}) (Boorgard et al., 2005; Rout et al., 2014, 2017; Wang et al., 2014; Woumfo et al., 2015; Zeng et al., 2004).

Table 3. Fitting parameters to the Langmuir and Freundlich models for the adsorption of phosphate on the Technosol as a function of pH.

pH	Langmuir equation			
	Q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	RSS
4	7.18	0.043	0.86	3.13
6	7.86	0.028	0.97	1.87
7.5	12.64	0.027	0.96	3.46
9	18.51	0.059	0.95	35.54

pH	Freundlich equation			
	K_F (mg g^{-1})/(L mg^{-1})$^{1/n}$	n	R^2	RSS
4	1.42	3.32	0.94	1.37
6	1.16	2.82	0.92	5.59
7.5	1.61	2.16	0.90	8.70
9	3.28	1.78	0.86	100

The results obtained indicate that phosphate retention on the Technosol was dependent on the pH of the solution (Fig. 2 and Fig. S3). At pH < 6, an increase in the concentration of PO_4 from 0.5 to 4 mM (47.5 to 380 mg PO_4 L^{-1}) produced a reduction of more than 50% in the PO_4 retention (Fig. S2). At pH > 6, adsorption of the PO_4 increased on increasing pH and the retention capacity became doubled as the pH increased from 6 to 9. Phosphate retention may be modified by changes in the surface charge and/or in the speciation of phosphate induced by variations in pH (Del Nero et al., 2010). Different authors have shown that the adsorption of PO_4 on clays and mineral oxides decreases as the solution changes from acid to neutral or alkaline (Antelo et al., 2005; Liu et al., 2012; Perassi and Borgnino, 2014). However, this trend is not observed with all types of adsorbents, and e.g. PO_4 retention on calcite increases with pH (Karageogin et al., 2007; Millero et al., 2001). Precipitation of Ca-P compounds is favoured at pH close to or higher than 8, due to the formation of different species of calcium phosphate ($Ca_3(PO_4)_2$, $Ca_4H(PO_4)_3{\cdot}3H_2O$ and $Ca_5(PO_4)_3OH$). The PO_4 retention mechanism may thus involve surface adsorption with a ligand exchange reaction or precipitation processes. Formation of these solid phases was analysed in the present study by using PHREEQC speciation software (Parkhurst and Appelo, 2013). Saturation indices were calculated for Ca-P minerals, i.e. hydroxyapatite, $Ca_3(PO_4)_2$ (beta), $Ca_4H(PO_4)_3{\cdot}3H_2O$, $CaHPO_4$ and $CaHPO_4{\cdot}2H_2O$, and the results indicated that precipitation may occur at pH > 6. Surface precipitation cannot be discarded at lower pH values, since the concentration of phosphate ions near the surface might be larger than the concentration in the bulk solution. Therefore, in the surface region oversaturation with respect to the solid phases considered may be achieved with lower concentrations (Loganathan et al., 2014). In other words, at pH 4 - 6, the presence of PO_4 is mainly controlled by surface adsorption on the Technosol, although surface precipitation may also occur, whereas at pH > 6 the main mechanism involved in PO_4 retention is surface precipitation, in which formation of hydroxyapatite is favoured (Fig. S4).

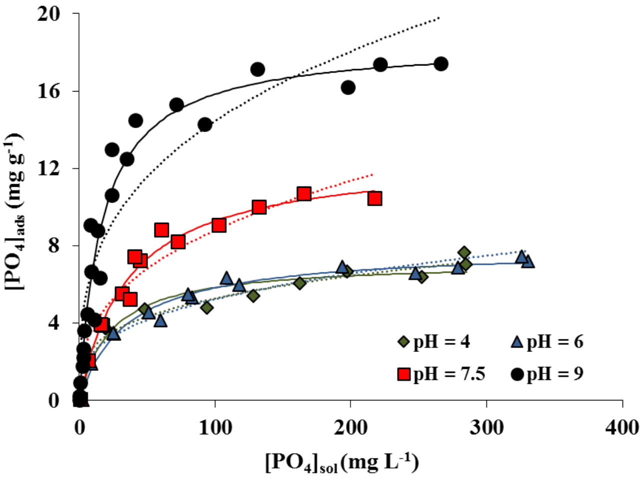

Figure 2. Phosphate adsorption isotherms for the Technosol at different pH values, 4.0–9.0. The solid and dashed lines represent the fit of the Langmuir and Freundlich isotherm to the experimental data, respectively.

3.2.2. Effect of the presence of different anions on PO_4 retention

The PO_4 retention capacity of the Technosol varied in relation to the anion present and the pH of the system (Fig. 3 and 4). At pH 4, the PO_4 retention on the Technosol was 33%. Under these working conditions, the presence of HCO_3, SO_4 and Cl did not modify the retention capacity (Fig. 3). The presence of chromate yielded an increase in PO_4 retention of more than 50% (Fig. 3). We expected that the opposite would occur in the presence of this anion, i.e. a decrease in retention due to competition between PO_4 and CrO_4 (Gu et al., 2017). Finally, the presence of the molybdate anion (MoO_4) produced a decrease in PO_4 retention. Higher concentrations, [MoO_4] = 0.1 M, reduced the PO_4 retention by up to 239 % (Fig. 3). Previous studies have indicated that iron and aluminium oxides show a high affinity for MoO_4 thus favouring competition involving other ions (Manning and Goldberg, 1996; Pérez et al., 2014)

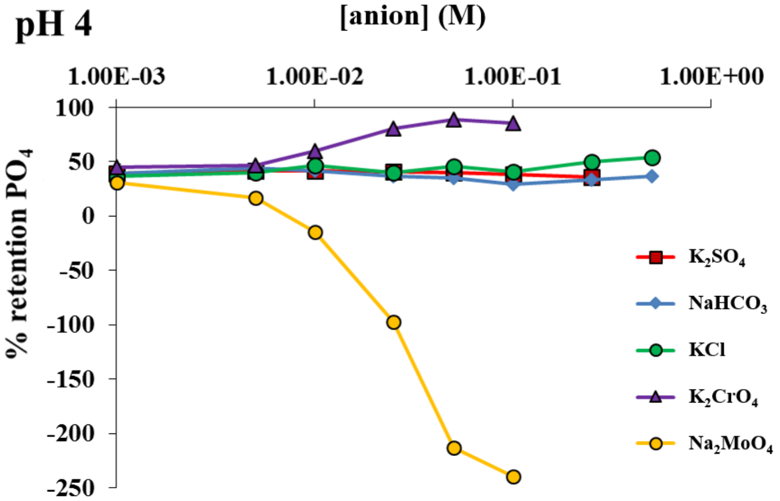

Figure 3. Effect of different anions on the retention of phosphate by the Technosol at pH 4. Negative values correspond to the release of phosphate.

The retention of PO_4 at pH 9 was 89.9 %. The presence of SO_4, Cl and CrO_4 did not affect PO_4 retention by the Technosol (Fig. 4). The addition of small amounts of MoO_4 also did not affect the PO_4 retention. However, PO_4 retention was lower at [MoO_4] > 0.1 M. The competition is less intense than at pH 4, as the retention of MoO_4 is not favoured at high pH (Pérez et al., 2014; Xu et al., 2006). On the other hand, the presence of HCO_3 caused a considerable decrease in the PO_4 retention, due to bicarbonate-phosphate competition at high pH and high concentrations of HCO_3 in the medium.

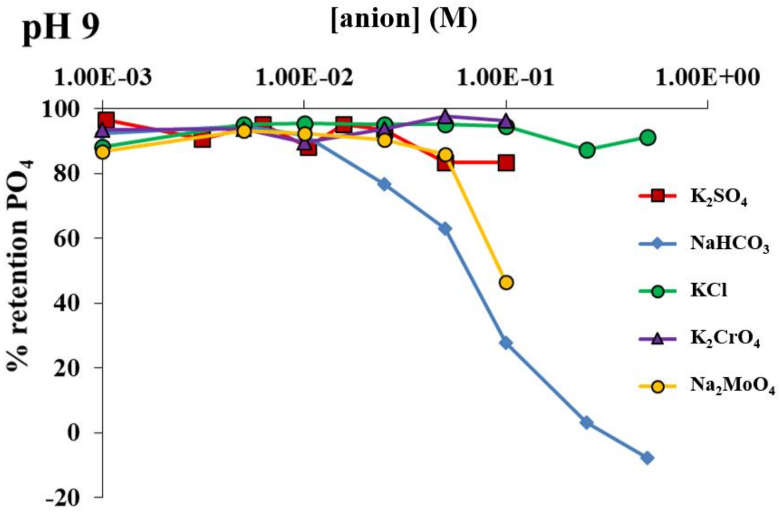

Figure 4. Effect of different anions on the retention of phosphate by the Technosol at pH 9. Negative values correspond to the release of phosphate.

3.3. Continuous flow experiments using fixed bed columns.

3.3.1. Effect of flow rate on PO_4 retention

As can be observed in the breakthrough curves determined at different flow rates, the increase in the influent flow rate in the fixed bed column caused a decrease in the saturation time and in the amount of PO_4 retained by the Technosol (Fig. 5). The breakthrough time, defined as the time at which the concentration of PO_4 in the effluent reached 1 mg L^{-1}, also decreased as the flow rate increased. Thus, for a flow rate of 1.5 mL min^{-1} the breakthrough time was 16 h, while for a flow rate of 2.1 mL min^{-1} the breakthrough time was halved, to 8 h, and an increase in the flow rate to 5.0 mL min^{-1} led to a reduction of 91% in the breakthrough time of the fixed bed column, from 16 h to 1.44 h (Fig. 5). The decrease in the breakthrough time (t_b) in relation to the flow rate (F) was described by a non-lineal equation (Fig. S5).

The amount of PO_4 retained by the Technosol was calculated by fitting the modified Bohart-Adams model to the experimental breakthrough curves. The values of the parameters obtained in the model fit are shown in Table 4. The amount of PO_4 retained (Q_{max}) decreased as the rate of inflow increased, from 6.19 mg g^{-1} at a flow rate of 1.5 mL min^{-1} to 2.37 mg g^{-1} at a flow rate of 5 mL min^{-1}. The decrease in flow rate led to longer times of interaction between the PO_4 and the Technosol, thus favouring the sorption processes (surface adsorption, precipitation) and increasing the retention capacity of the Technosol.

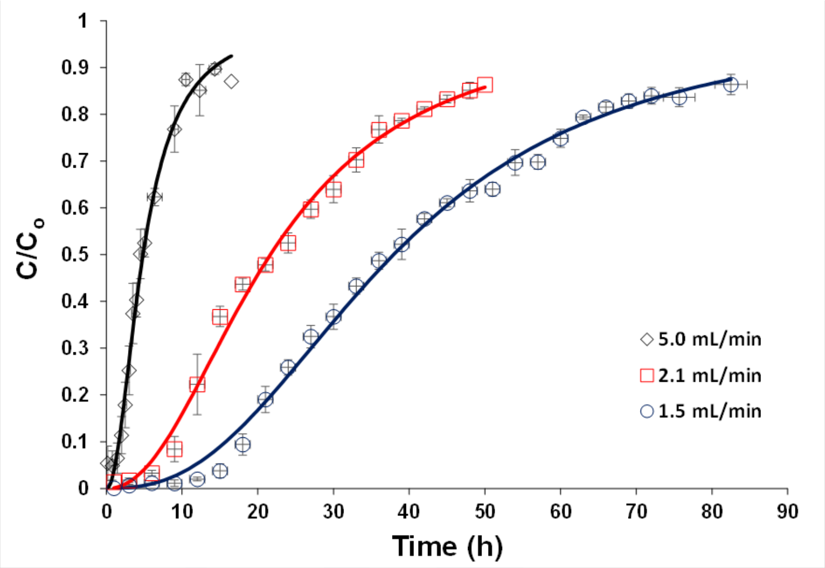

Figure 5. Effect of the flow rate on the phosphate retention by the Technosol. Symbols are experimental data points and lines correspond to the modified Bohart-Adams model

Table 4. Fitting parameters to the modified Bohart-Adams model for phosphate retention by the Technosol at different column working conditions. In all cases [PO_4] = 20 mg L^{-1} in 0.1 M KNO_3

Reactive layer		pH	Flow	Q_{max} (mg g^{-1})	a	R^2	RRS
m/g	h/cm		(mL min^{-1})				
11.20	20	5.5	5.0	2.37 ± 0.06	1.97 ± 0.10	0.983	0.054
11.20	20	5.5	2.1	4.85 ± 0.08	2.15 ± 0.08	0.993	0.010
11.20	20	5.5	1.5	6.19 ± 0.06	2.50 ± 0.06	0.995	0.011
5.60	10	5.5	5.0	2.04 ± 0.07	1.44 ± 0.06	0.989	0.023
11.20	20	3.0	5.0	6.21 ± 0.12	1.14 ± 0.04	0.986	0.013

3.3.2. Effect of the thickness of the reactive layer on PO_4 retention

The thickness of the reactive layer inside the fixed bed column strongly influenced the amount of PO_4 retained. Halving the thickness of the layer led to a considerable reduction in the efficacy of the column, shortening the breakthrough time by 65 %, from 1.44 to 0.5 h (Fig. 6). The results of the modified Bohart-Adams model fits showed a reduction of a 14 % in the retention capacity on reducing the thickness of the reactive layer, from 2.37 to 2.04 mg g^{-1} (Table 4). Likewise, parameter *a* was reduced from 1.97 to 1.44, i.e. the fixed-bed column with the thinner reactive layer displayed a greater speed of saturation and a lower PO_4 retention capacity.

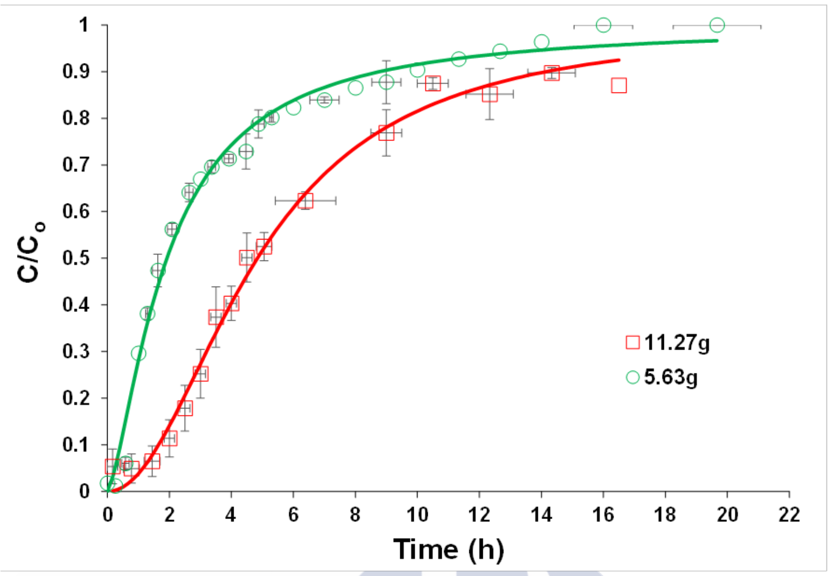

Figure 6. Effect of the thickness of the layer bed on the phosphate retention by the Technosol. Symbols are experimental data points and lines correspond to the modified Bohart-Adams model. The flow rate was 5 mL min-1 and the pH of the influent was 5.5.

3.3.3. Effect of pH on PO_4 retention

The pH of the influent solution in the fixed bed column had an important effect on PO_4 retention, as it modified the predominant retention mechanisms (Fig. 7). Initially, as the influent flows through the column at pH 3, surface adsorption will be the preferred mechanism of retention. This mechanism will be particularly favoured at pH 3 (relative to that at pH 5.5) as an increase in the pH is known to decrease the surface adsorption process (Antelo et al., 2005; Pérez et al., 2014). However, as the pH of the influent increased due to the buffering effect of the Technosol, precipitation will become important due to the formation of Ca-P precipitates. The parameters of the modified Bohart-Adams model (Table 4) show that the sorption capacity of the Technosol was increased from 2.37 mg g^{-1} to 6.21 mg g^{-1} when the pH of the influent was decreased from 5.5 to 3.

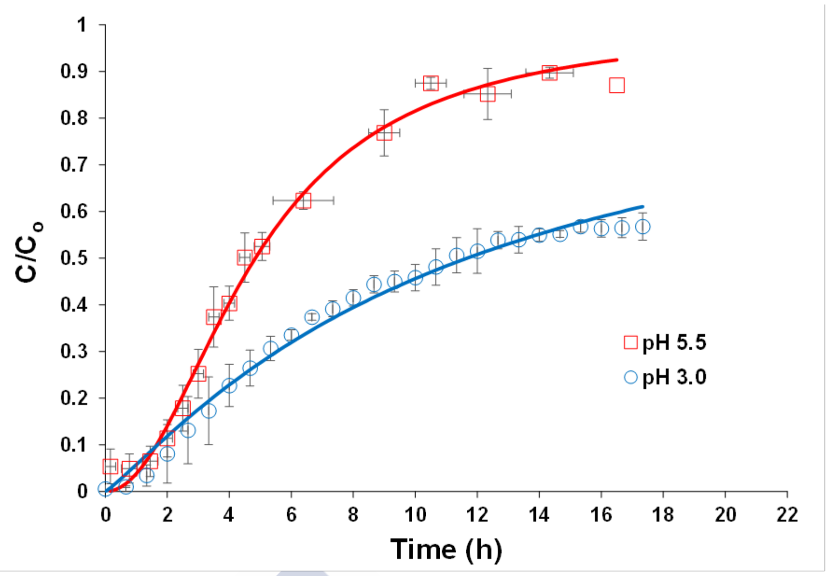

Figure 7. Effect of pH on the phosphate retention by the Technosol. Symbols are experimental data points and lines correspond to the modified Bohart-Adams model.

3.4. Repeated use of the Technosol

The data for the sorption-desorption cycles are shown in Fig. 8. Saturation times of between 8 and 10 h were obtained for all stages of sorption, whereas the corresponding desorption stages were shorter, < 1 h. The breakthrough curves (Fig. 9) show a reduction in the capacity of the Technosol to retain PO_4 after the first cycle. The efficacy of the column decreased and the breakthrough time varied from 1 h to less than 15 minutes, although the variation in the saturation time was not significant. The experimental data on the three stages of sorption were fitted to the modified Bohart-Adams model, the parameters of which are shown in Table 5. The values of these parameters corroborate the decrease in the retention capacity in successive stages (Table 5).

Although the retention capacity of the Technosol was reduced after the first sorption-desorption cycle, from 2.37 mg g^{-1} to 0.87 mg g^{-1}, the system still displayed an optimal capacity to immobilize PO_4. The initial decrease was due to surface changes in the material that occurred after the first sorption-desorption cycle. After two sorption-desorption cycles, the Technosol exhibited a constant retention capacity. These results indicate that the Technosol used as an adsorbent material in water filtration systems can be reused after washing.

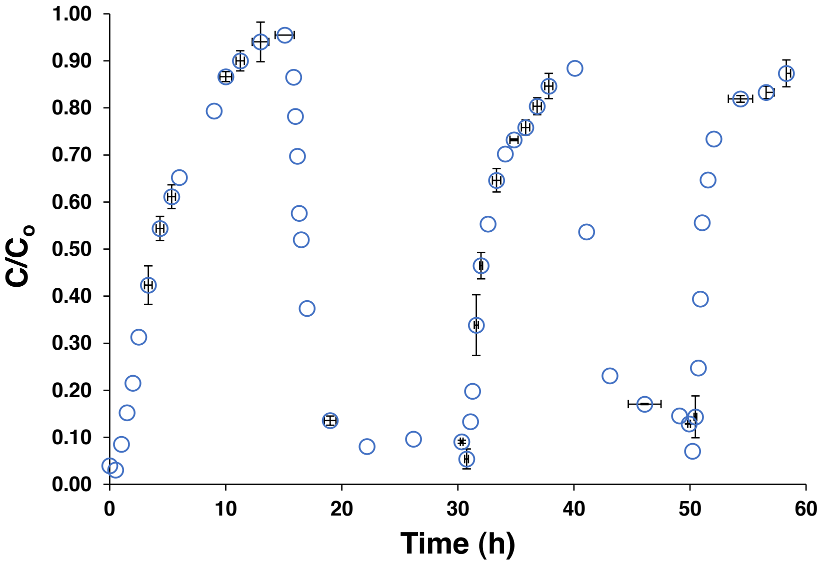

Figure 8. Phosphate sorption-desorption cycles on Technosol. The conditions of the experiments were: [PO$_4$] = 20 mg L^{-1} in 0.1 M KNO$_3$, pH = 5.5 and 10.2 g Technosol.

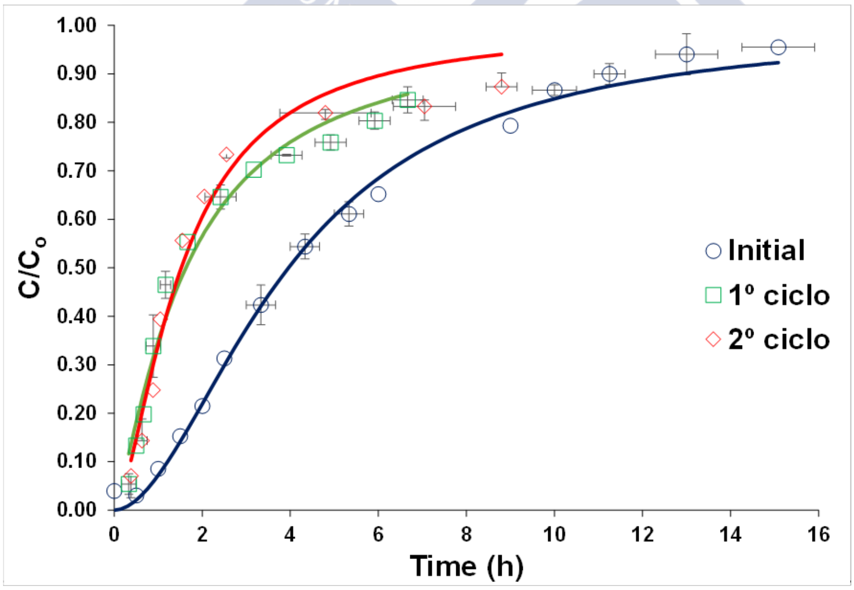

Figure 9. Effect of successive phosphate sorption-desorption cycles on the performance of the fixed bed column. Symbols are the experimental data points and lines correspond to the modified Bohart-Adams model. The conditions of the experiments were: [PO4] = 20 mg L-1 in 0.1 M KNO3, pH = 5.5 and 10.2 g Technosol.

Table 5. Fitting parameters to the modified Bohart-Adams model for phosphate retention on the Technosol for some consecutive phosphate adsorption/desorption cycles. The experimental conditions were: [PO_4] = 20 mg L^{-1} in 0.1 M KNO_3, pH = 5.5 and 11.2 g Technosol.

Cycle	Q_{max} (mg g^{-1})	a	R^2	RRS
Initial	2.37 ± 0.06	1.97 ± 0.10	0.983	0.054
1st	0.87 ± 0.05	1.28 ± 0.09	0.974	0.021
2nd	0.81 ± 0.05	1.57 ± 0.17	0.963	0.026

4. CONCLUSIONS

The experiments carried out to study PO_4 retention by an andic Technosol allowed us to identify two possible retention mechanisms: surface adsorption and precipitation. The latter was favoured at high pH by the high concentrations of calcium in the Technosol. The material effectively retained PO_4 in both static and dynamic systems, with much higher retention capacities than displayed by other types of material commonly used to remove PO_4 from natural systems. The Technosol therefore proved an efficient adsorbent able to mitigate the effects of phosphate pollution. Use of the andic Technosol to remove excess PO_4 from polluted waters thus represents an effective, inexpensive method of resolving two important problems: eutrophication of aquatic systems and the scarcity of natural sources of phosphate for agricultural use. The Technosol can be used several times and once totally saturated, it could be recycled as a phosphate-rich amendment and the leachates could be used to produce liquid fertilizer.

5. ACKNOWLEDGMENTS

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Supplementary materials

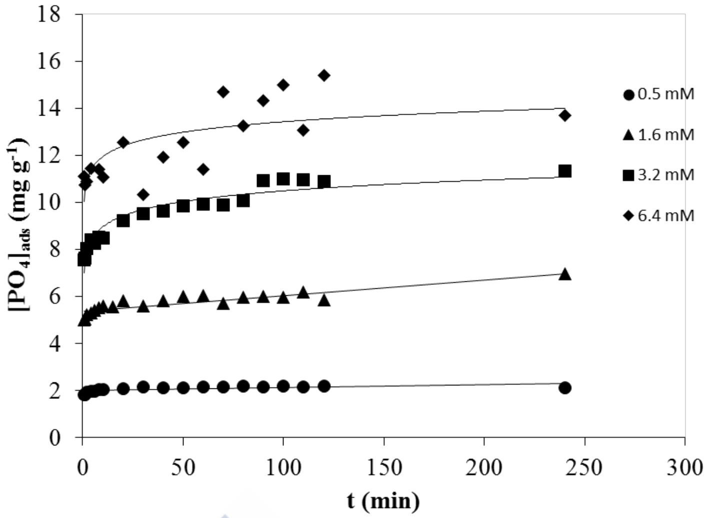

Fig. S1. Phosphate adsorption on the Technosol as a function of time and initial phosphate concentration.

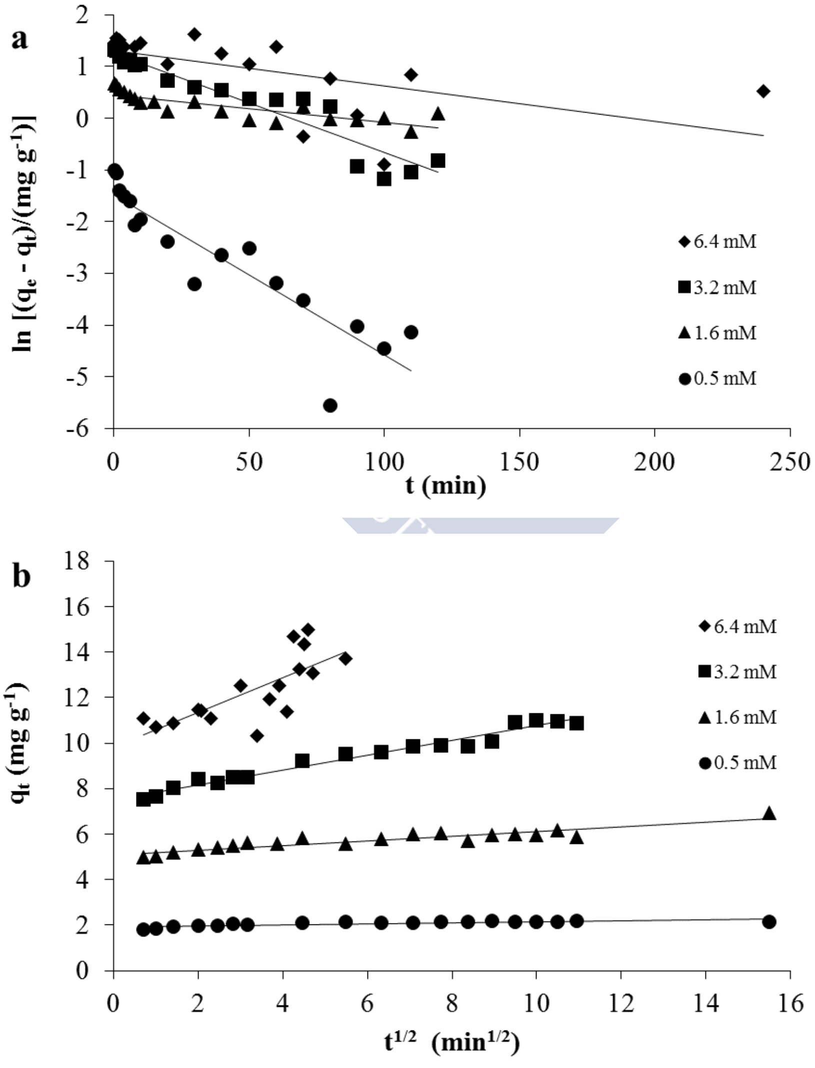

Fig. S2. (a) Pseudo-first-order and (b) intra-particle diffusion kinetic models of phosphate adsorption on the Technosol at different initial concentrations.

Table S1. Fitting parameters for the pseudo-first order, pseudo-second order and intra-particle diffusion kinetic models of phosphate adsorption on the Technosol.

	Pseudo-first order model		
[PO$_4$] (mg L^{-1})	q$_e$ (mg g^{-1})	k$_1$ (min^{-1})	R^2
47.7	4.39	-0.030	0.82
152	1.57	0.005	0.68
304	3.46	0.019	0.84
608	3.71	0.007	0.32
	Pseudo-second order model		
	q$_e$ (mg g^{-1})	k$_2$ (g min^{-1} mg^{-1})	R^2
47.7	2.14	4.04	0.99
152	6.62	0.030	0.99
304	11.24	0.025	0.99
608	14.08	0.037	0.99
	Intra-particle diffusion model		
	C (mg g^{-1})	K$_{ID}$ (mg g^{-1} min^{-1})	R^2
47.7	1.92	0.02	0.67
152	5.09	0.10	0.85
304	7.52	0.32	0.97
608	9.81	0.77	0.56

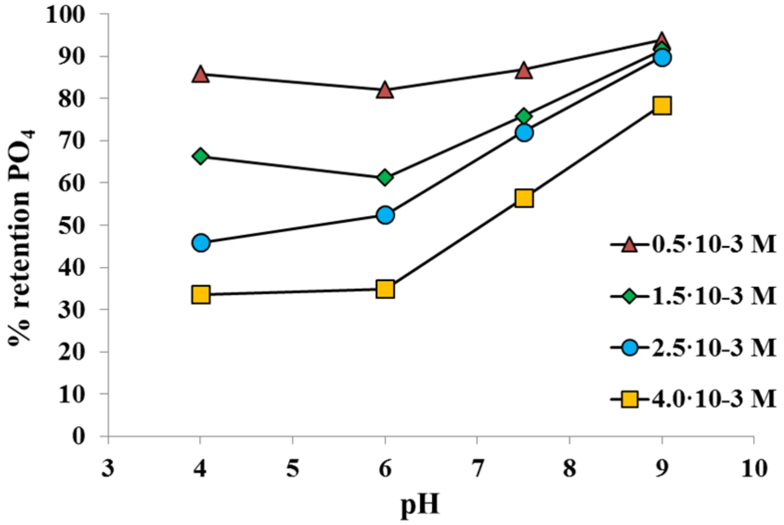

Fig. S3. Effect of pH and concentration of the solution on the phosphate retention by the Technosol.

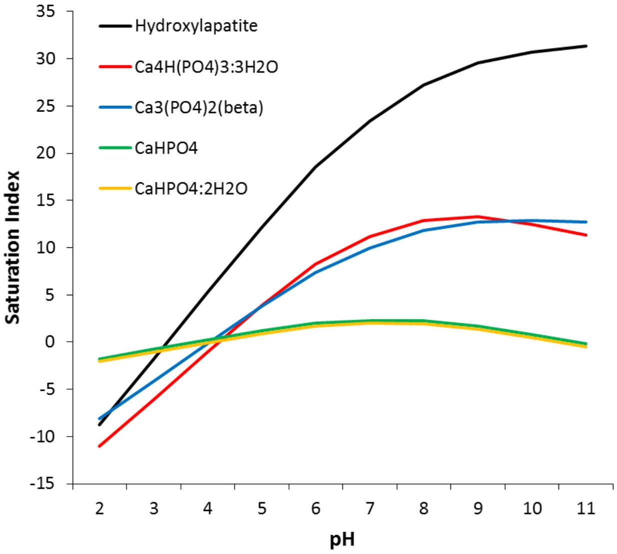

Fig. S4. Saturation indices calculated for phosphate–calcium minerals as a function of pH. Phosphate concentration was 0.5•10-3 M.

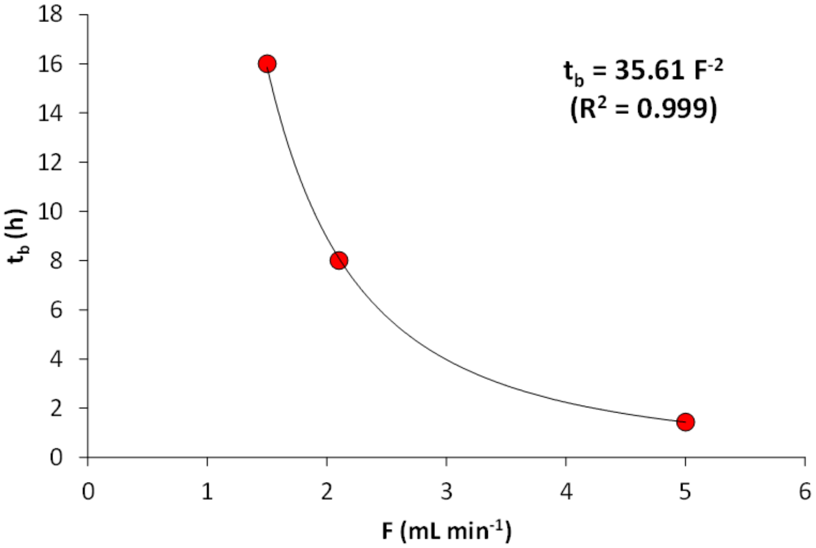

Fig. S5. Variation of the breakthrough point as a function of the flow rate

COMBINATION OF CHEMICAL, BIOLOGICAL AND ECOTOXICOLOGICAL TOOLS FOR THE EVALUATION OF TAILINGS REHABILITATED WITH TECHNOSOL

ABSTRACT

Mine spoils are important pollution sources for the surrounding soil and water systems. Soil and water characteristics and biogeochemical processes can be improved by an integrated technology based on circular economy: Technosol application. The efficiency of the application of a superficial layer of a Technosol with andic and eutrophic properties on the rehabilitation of sulfide-rich tailings of the Fé mining area (Spain) was tested. After 20 months of the Technosol application, the tailing rehabilitation status (Recovered tailing) was evaluated and compared to a non-rehabilitated tailing (Tailing). To assess the recovery of these systems, several properties were analysed: chemical characteristics of the materials and their leachates, soil enzymatic activities (dehydrogenase, β-glucosidase, acid phosphatase and urease), basal respiration and several plant endpoints from direct and indirect bioassays and pot experiment using *Lollium perennse* and *Trifolium pratense*.

Toxic concentrations of Co, Mg, Mn and Ni were identified in both the available fraction and leachates, pointing out the serious environmental risk posed by the tailing. The improvement of the overall physico-chemical properties in the recovered tailing materials (e.g. the decrease of the concentrations of hazardous elements in leachates and available fraction, and the improvement of the fertility and structure) allowed a quick plant cover with pasture species and provided a suitable habitat for the active microbial community (evaluated by the increase of dehydrogenase activity and basal respiration). This improvement in the recovered tailing contributed to a significant decrease of the ecotoxicological risk and the spread of hazardous chemical elements. The field application of this specific Technosol was a promising solution for long-term rehabilitation of this type of tailings.

1. INTRODUCTION

Both abandoned and active mines have several environmental problems associated with the physico-chemical characteristics of mine wastes and their leachates (FAO and ITPS, 2015; Santos et al., 2017a; Wong, 2003). Mining areas associated with coal, metals and radionuclides extraction have additional environmental problems because their mineralization is associated with reactive solid phases such as sulfides. Sulfide minerals are easily weathered by oxidation processes, thus generating acid mine drainage rich in potentially hazardous elements (PHEs; e.g. As, Cu, Pb, and Zn) (Abreu et al., 2010; Arán et al., 2016; Bian et al., 2010; Monterroso and Macías, 1998; Monterroso et al., 1998; Sánchez-España et al., 2005). This fact increases significantly the hazardousness of the mine wastes.

A well-designed environmental rehabilitation strategy is necessary to decrease the environmental and human risks and recover the ecological and geochemical functions of the mining soils and tailings. This would increase the water quality and promote the pedogenesis in mine wastes. In fact, nowadays a recovery plan is already a key component of any mining and processing operation. In general, the environmental rehabilitation strategy should include low-cost technologies based on sustainability and circular economy and, if possible, those which promote environmental services. The negative effects of this environmental problem will remain, or even increase, when the selection of the rehabilitation and management practices is poor (Rivas-Pérez et al., 2016).

The ecological rehabilitation of sulfide-rich mining areas is achieved by minimizing the oxidation processes and improvement of the chemical characteristics in the mine wastes. Consequently, the leaching of potentially hazardous elements to surface and groundwaters will be minimized (Santos et al., 2014a, 2016). Surface coverage of this type of mine wastes with a considerable layer of specific Technosols is considered the most promising and eco-friendly rehabilitation technology (rather than amendments application). The use of Technosols reduces the generation of acid mine drainage and improves the physico-chemical and biological quality of the mine wastes and their leachates (Arán et al., 2016; Asensio et al., 2013a,b,c; Monterroso et al., 1998; Santos et al., 2016). Nevertheless, only some Technosols allow vegetation establishment and sustainability of ecosystem services (Monterroso et al., 1998; Rodríguez-Vila et al., 2016; Santos et al., 2014b, 2016).

Long-term assessment of recovery of the overall systems at field-scale is essential to verify the effectiveness of the rehabilitation technologies applied. Although monitoring and evaluation at short-term is important, the sustainability of the rehabilitation strategy in the recovered area is only confirmed at medium-long time range, especially in sulfide-rich mining areas. Several authors reported negative effects of classical remediation technologies (e.g. application of amendments) at short-term (Macías, 2004; Macías et al., 2011; Santos et al., 2014a, 2017a). Thus, successive applications are needed, (Pérez-de-Mora et al., 2011) increasing the rehabilitation costs.

In general, the soil quality is evaluated by analysis of different physico-chemical, biological and biochemical characteristics (Karlen et al., 1997; Kumar et al., 2013; Martinez-Salgado et al., 2010). However, the functions and services of the soils are the result of the combined interactions among these characteristics. For this reason, the single use of chemical, biological or ecotoxicological analysis is insufficient to evaluate the potential environmental risk of contaminated soils, tailings and/or waters and/or their recovery end materials.

The interaction among PHEs, matrix and organisms and the consequent effects cannot be assessed only with a physico-chemical study (ISO 17402 2006; Leitgib et al., 2007; van Gestel et al., 2001). Moreover, the ecotoxicity tests by itself cannot provide an integrated evaluation of the availability and toxic effects of the PHEs on organisms and ecosystem, since some recommended species does not show sensitiveness to hazardous elements (Abreu et al., 2014; Santos et al., 2013). Therefore, only the combined analysis of chemical, biological and ecotoxicological properties is recommended for the evaluation of the rehabilitation of mine wastes and their leachates following the application of Technosols. This allows an adequate assessment of the potential risks.

The main objective of the present study was to evaluate, at physico-chemical, biological and ecotoxicological level and under field conditions, the efficiency of a Technosol with andic and eutrophic properties on the rehabilitation of the tailings composed of a mixture of sulfide-rich materials and host rocks.

2. MATERIALS AND METHODS

2.1 Site characterization and sampling

Fé mining area is a uranium mine located at Saelicies el Chico (29T 702113 4501299), near Ciudad Rodrigo (Salamanca, Spain). It was the most important U deposit in Spain with a reserve exceeding 16000 Mg of U_3O_8 with a hydrothermal system origin 34.8 ± 1.6 Ma (Both et al., 1994). In this deposit, the U mineralization contains sulfides, mainly pyrite. The mining activity, surface extraction and concentration of U occurred between 1975 and 2000 and was conducted by the company ENUSA. The region is under a hot-summer Mediterranean climate (CSA climate according to Köppen classification) with annual temperatures ranging between 4 and 30 °C and average annual rainfall of ≈ 503 mm, which frequently occurs only in the winter months. The soil moisture and temperature regimes are xeric and mesic, respectively.

The exploitation and extraction processes produced large amounts of different mining wastes, which were selected according to their radioactive risk. After the mining activity cease, a rehabilitation plan was implemented to avoid the risk of radioactivity in the area. A dumping zone was built and radioactive wastes were encapsulated under a layer of arkose material. The remaining mine wastes without radioactive risk, mainly constituted by sulfide-rich materials, and the host rocks were used to recover the previous cover. Although this management practice allowed the isolation of the radioactive mine waste and minimized the radioactive risk, the environmental problems associated with the sulfide-rich materials were not solved. Thus, a pilot assay (total area: 625 m^2) was implemented within the mine area in order to recover a tailing, composed of a mixture of sulfide-rich materials and host rocks, and its leachates. A *green technology* solution was applied here following the application of a Technosol. For this, a 20 cm-layer of Technosol with andic and eutrophic properties was applied over the tailing.

After 20 months of application, composite samples were collected from Technosol (0–20 cm depth), the recovered tailing below the Technosol (20–40 cm depth) and Tailing without recuperation (0–20 cm depth). The later was used as a control. These samples were air-dried and homogenized for physico-chemical, biological and ecotoxicological analysis and to obtain simulated leachates.

2.2 Physico-chemical and biological characterization of the materials

The fraction < 2 mm of the materials (Technosol, Recovered tailing and Tailing) was characterized for: pH in H_2O and KCl (1:2.5 m: *V*); extractable P (Olsen method); total CNS (analysed by combustion with a LECO analyser), organic C (Sauerlandt method), and exchange cation capacity (CEC) (Peech et al., 1947). Pseudototal content of major and trace elements was obtained by microwave-assisted digestion with *aqua regia* (15 minutes to reach 180 °C + 5 minutes at 180 °C + 5 minutes to reach 200 °C + 5 minutes at 200 °C). Also, the available content (water soluble + exchangeable complex) for these elements was obtained following the rhizosphere-based method (Feng et al., 2005). These materials (fraction < 2 mm) were also used to obtain simulated leachates (DIN 38414-S4, 1984). Following the DIN extraction, pH and electrical conductivity (EC) were measured. Simulated leachates and extracts corresponding to the pseudototal and available fractions were filtrated (0.45 µm) and stored at −18 °C until multielemental determination. Chloride, nitrate, and sulfate content was determined by ion chromatography; fluoride concentration by ion selective electrode; metals and metaloids by ICP-MS; and ammonium by continuous flow analyser. Nitrite and phosphate were determined following the Zambelli method (Rodier, 1976) and the molybdenum blue method (Murphy and Riley, 1962), respectively. Particle size distribution was done by sieving and sedimentation in water dispersion, after organic matter destruction with hydrogen peroxide, following Stokes law.

Soil basal respiration and four enzymatic activities in the materials (total fraction) were evaluated as biological indicators. Dehydrogenase (Tabatabai, 1994) was used as an indicator of overall microbial activity, while β-glucosidase (EC 3.2.1.21; Eivazi and Tabatabai, 1988), acid phosphomonoesterase (acid phosphatase EC 3.1.3.2; Eivazi and Tabatabai, 1977) and urease (EC 3.5.1.5; Kandeler and Gerber, 1988) are associated with C, P and N cycling, respectively. Before the determination of enzymatic activities, the materials were incubated in a growth chamber under controlled conditions (25 ± 1 ºC; 16 h light/8 h darkness) at 70 % water-holding soil capacity for 12 days. The quality and metabolic capacity of the different microbial communities were determined with a respirometer with sensors of CO_2 and CH_4 under controlled conditions for 450 h. For this analysis, samples were moistened (≈70 % of the water holding capacity) and pre-incubated under controlled conditions (30 ± 1 ºC and in the darkness) for 24 h.

2.3 Ecotoxicological characterization

Ecotoxicological evaluation of the studied materials and their leachates was performed using two plant species, *Lollium perenne* L. (monocot) and *Trifolium pratense* L. (dicot). The selection of both plant species was based on ISO recommendations (ISO 11269–2, 1995). Moreover, these species present a rapid development under field conditions being used, frequently, in the seeds mixtures from revegetation projects.

Three bioassays were carried out under growth chamber conditions to evaluate the ecotoxicological effect of the whole materials (direct bioassay) and their leachates (indirect bioassays): filter paper test (Salvatore et al., 2008), hydroponic test (Santos et al., 2013), and soil test (ISO 15799, 1999; Martí et al., 2007). Ecotoxicological effect of the materials for the same plant species was also evaluated through a microcosm assay (pot experiment) for a slight longer period and under greenhouse conditions.

For the filter paper test, three layers of filter paper (140 mm Whatman No. 1 filter) were placed at the bottom of a petri-box, which was moistened with 5 mL of simulated leachate from each material. Twenty-five seeds of each plant species were placed per replicate (n = 4 for each material). In the soil test, 15 g of each material (fraction < 2 mm) at 70 % of the water-holding capacity were placed in glass beakers. Seven seeds of *L. perenne* and 10 seeds of *T. pratense* were used per replicate. Deionised water and a sandy soil were used as the negative control. The filter papers and soil test were incubated in a growth chamber under controlled conditions (25 ± 1 ºC; 16 h light/8 h darkness). These samples were also kept moist. The germinated seeds were periodically counted during 10 and 12 days for *L. perenne* and *T. pratense*, respectively. The criterion of germination was the emergence of a radicle through the seed coat.

For the hydroponic test, both species seeds were germinated in the dark at 25 ± 1 ºC for 7 days. Seedlings were measured before their use in the test. Four seedlings of each species were used per replicate to grow in beakers filled with 50 mL of simulated leachates from the different materials. The seedlings were supported by a thin and flexible plastic net placed on the top of each beaker, so only the roots were immersed in the leachate. After 16 days of growth in the same conditions as before, the plant endpoints were evaluated.

The evaluation of the ecotoxicity effects on plants was determined through visual aspects, germination rate, root and shoot elongation and dry biomass after the exposure of the seeds and seedlings to moistened soil or leachates (OECD, 2006; Salvatore et al., 2008). The plants survival was also evaluated in the hydroponic test.

Microcosm assay was carried out in pots containing 500 g of each studied material. One g of *L. perenne* seeds (≈410seeds) or 1.0 g of *T. pratense* seeds (≈520 seeds) was sown in each pot. All materials were incubated at 70 % of water-holding capacity under greenhouse-controlled conditions for one month. In the end of the experiment, visual aspects, plant cover and dry biomass of aerial part of the plants were analysed.

2.4 Data analysis

Statistical analysis was performed using SPSS v18.0. All data were checked for homogeneity of variance (Levene test) and normality (Shapiro–Wilk test). If possible, one-way ANOVA and post-hoc Duncan test ($p < 0.05$) were applied. When the data did not satisfy assumptions for ANOVA, they were analysed non-parametrically using Kruskal–Wallis test. For statistical purposes, the results below the detection limit were assumed as half of the detection limit. The correlations between the characteristics of the materials were determined by Pearson's correlation ($r > 0.8$). Principal component analysis (PCA) was applied to the data set to identify possible relations among the chemical characteristics, biological and ecotoxicological parameters of the materials and/or leachates. Quality control of the analysis was made by replicate samples (n = 3-5), use of certified standard solutions and laboratory standards.

Toxicity indexes [(% $\text{germination}_{\text{sample}}$ – % $\text{germination}_{\text{control}}$)/ % $\text{germination}_{\text{control}}$ and (Root $\text{elongation}_{\text{sample}}$ – Root $\text{elongation}_{\text{control}}$)/ Root $\text{elongation}_{\text{control}}$; Bagur-González et al., 2011] were calculated for both plant species. These indexes were also calculated for the controls, i.e. deionised water and sandy soil. The indexes can vary from −1 (maximum phytotoxicity) to > 0 (no toxicity).

3. RESULTS AND DISCUSSION

3.1 Physico-chemical characterization of the materials

The chemical characteristics of the tailing materials indicate a considerable environmental risk (Tables 1 and 2). These materials are moderately acid, possibly due to small proportion of sulfide-rich materials, with unfavourable physical structure and very low fertility (non-detectable organic C and small concentrations of extractable P and exchangeable Ca, K and Mg). Furthermore, these tailings present high pseudototal concentrations of several PHEs (e.g. Al, As, Mn and Ni) compared to soil guidelines from Galician where similar geological materials and formation exist (DOGA, 2009).

The measured values of pH (in KCl) indicated a slight tendency of the tailing materials to acidification, while CEC (10-20 cmol_+/kg; de Varennes, 2003) indicated their weak capacity to retain the chemical elements. This low CEC is related to the small organic carbon concentration.

The applied Technosol, after 20 months under the negative influence of tailing materials, still present adequate chemical characteristics to stabilize the pH and provide nutrients and organic C (and other C forms as carbonates, which represent between 10-23 % of the total C content) ensuring the biogeochemical processes involved in the rehabilitation process. The Technosol showed the highest values of pH, total and organic C, total N, extractable P, CEC and concentration of exchangeable cations. In general, this material also present high total concentrations of some nutrients (Ca, Cu and P) and low concentrations of PHEs (e.g. As, Co, Cr, Ni).

In general, the application of the Technosol with andic and eutrophic properties over the tailing materials contributed to a significant improvement of their physico-chemical characteristics (Recovered tailing, Tables 1-3). Similar results were obtained in other rehabilitation process with Technosols (Asensio et al., 2013b,c; Santos et al., 2014b, 2016). Values of pH, total and organic C, extractable P and CEC increased significantly compared to those in the tailings without rehabilitation, although no differences were found for the total N content (Table 1). CEC in the Recovered tailing may be considered high (de Varennes, 2003) and is correlated to the increase of organic matter ($r = 0.87$). High CEC values favour higher immobilization of PHEs and, consequently, the decrease of the contamination spreading. The structure was also improved (compared with the non-treated tailing) due to the increase of the sand fractions (coarse and fine) and organic matter. The improvement of several physical characteristics (e.g. porosity and content of sand, silt and clay), as well as the increase of pH and C content, for treated-mine soils was also observed in Touro mining area following the application of a Technosol (Asensio et al., 2013b).

Table 1. Characteristics of the studied samples (mean ± SD; n = 4, except for particle size distribution n = 2)

	Tailing	Recovered tailing	Technosol
pH (H_2O)	4.3 ± 0.01*	4.5 ± 0.02*	7.7 ± 0.01
pH (KCl)	3.4 ± 0.02*	4.1 ± 0.02*	7.6 ± 0.01
Total C (g/kg)	0.8 ± 0.1*	4.3 ± 0.7*	48.2 ± 1.9
Organic C (g/kg)	<DL*	3.3 ± 0.7*	40.4 ± 1.2
Total N (g/kg)	0.4 ± 0.2	0.4 ± 0.2	2.6 ± 1.0
Extractable P (mg/kg)	1.0 ± 0.1*	16.2 ± 0.1*	97.9 ± 1.2
	Effective cations exchange capacity ($cmol_+/kg$)		
pH	3.5 ± 0.1*	3.7 ± 0.1*	7.3 ± 0.2
CEC*	14.2 ± 6.7*	26.1 ± 3.8*	41.0 ± 2.3
H^+	0.3 ± 0.1*	0.1 ± 0.1*	—
Al	1.0 ± 0.02	1.0 ± 0.1	< 0.1
Ca	6.8 ± 1.4*	20.5 ± 3.8*	34.6 ± 2.3
K	0.1 ± 0.02*	0.5 ± 0.02*	1.4 ± 0.1
Mg	5.8 ± 8.1	3.3 ± 0.1	3.8 ± 0.4
Na	0.3 ± 0.1*	0.7 ± 0.2*	1.3 ± 0.4
	Particle size distribution (g/kg)		
Coarse sand	156.2 ± 10.8*	187.1 ± 5.4*	269.2 ± 5.0
Fine sand	357.4 ± 12.2*	396.1 ± 22.3*	384.4 ± 8.0
Silt	436.5 ± 21.7	372.1 ± 11.4	339.9 ± 14.8
Clay	50.0 ± 1.3	44.7 ± 5.8	6.4 ± 4.9

DL: detection limit of the methodology; CEC: Cation exchange capacity. Values in each parameter followed by an asterisk indicate significant differences between Tailing and Recovered Tailing ($p < 0.05$).

Table 2. Pseudototal concentration of the elements (mg/kg) in the collected materials (mean ± SD; n = 3)

Elements	Tailing	Recovered tailing	Technosol
Al	(46.2 ± 10.2) x10^3	(43.3 ± 0.5) x10^3	(46.1 ± 1.3) x10^3
As	23.2 ± 1.0	26.4 ± 3.0	11.6 ± 1.9
Ca	(1.1 ± 0.2) x10^3*	(3.8 ± 0.4) x10^3*	(24.7 ± 0.5) x10^3
Cd	< 0.1	< 0.1	< 0.1
Co	29.8 ± 3.5*	19.5 ± 1.9*	10.6 ± 2.8
Cr	60.5 ± 9.9	50.2 ± 3.8	28.6 ± 1.4
Cu	47.3 ± 3.1*	66.9 ± 8.5*	116.1 ± 1.5
Fe	(63.2 ± 2.0) x10^3	(61.4 ± 2.0) x10^3	(25.4 ± 1.0) x10^3
K	(4.2 ± 2.9) x10^3	(4.6 ± 0.1) x10^3	(2.9 ± 0.2) x10^3
Mg	(17.8 ± 0.3) x10^3*	(13.0 ± 0.3) x10^3*	(6.8 ± 1.2) x10^3
Mo	< 0.5	< 0.5	2.1 ± 0.3
Mn	1349 ± 145*	620 ± 58.2*	663 ± 138
Na	499 ± 284	728 ± 125	893 ± 105
Ni	103 ± 10.5*	59.0 ± 4.3*	33.8 ± 3.6
P	392 ± 13.0*	1063 ± 7.6*	7230 ± 373
Pb	17.0 ± 2.1*	11.7 ± 0.6*	14.0 ± 1.6
S	(3.0 ± 0.1) x10^3	(3.2 ± 0.3) x10^3	(3.0 ± 0.4) x10^3
Sb	< 1.0	< 1.0	< 1.0
Se	< 2.0	< 2.0	< 2.0
Zn	202 ± 9.2*	224 ± 5.3*	280 ± 77.3

Values in each parameter followed by an asterisk indicate significant differences between Tailing and Recovered Tailing (p < 0.05).

Positive effects of the Technosol application were also verified according to the pseudototal concentrations found in the Recovered tailing (Table 2). Thus, eluviation of particles from Technosol to the tailing (located under the Technosol) contributed to the decrease of the pseudototal concentrations of Co, Mg, Mn, Ni and Pb, between 17 and 55 % of the concentration depending on element, while macronutrients and micronutrients, as Ca, Cu and P increased their concentration by 3.5, 1.4 and 2.7-fold, respectively. For the remaining elements, no significant differences were observed between samples Tailing and Recovered tailing.

The available content (water soluble + exchangeable complex) of PHEs in the tailing materials (Table 3) corresponds to <2.5 % of the pseudototal concentrations, except for Co, Mo, Mn and Ni. For these elements, the available concentration corresponded to 10-19 % of their total concentrations. Pb, Sb and Se were in all case below the detection limit. No significant differences were found between Tailing and Recovered tailing for the concentration of As and Cd in the available fraction. On the other hand, the concentration of Co, Mg, Mn and Ni in the treated tailing significantly diminished compared to the non-treated tailing (Table 3). Although the pseudototal concentration of these elements in the Recovered tailing samples also decreased, the decrease of their availability is related to different immobilization mechanisms (and not by a dilution factor). In fact, the decrease of the available content of Co, Mg and Mn is related to the increase of CEC (r = ≈ –0.8), while in the case of Ni is related to the pH and organic C content (r = –0.83 and –0.86, respectively).

Table 3. Concentration of elements (mg/kg) in the available fraction of the collected materials (mean ± SD; n = 4).

Element	Tailing	Recovered tailing	Technosol
Al	138 ± 1.2*	523 ± 71.6*	62.1 ± 1.1
As	< 0.1	< 0.1	0.1 ± 0.02
Ca	582 ± 27.3*	2642 ± 489*	2449 ± 89.1
Cd	(17.3 ± 4.9) x10^{-2}	(15.3 ± 1.0) x10^{-2}	(0.6 ± 0.3) x10^{-2}
Co	5.3 ± 0.9*	1.2 ± 0.2*	(13.8 ± 0.5) x10^{-2}
Cr	(11.8 ± 1.0) x10^{-2*}	(15.5 ± 2.4) x10^{-2*}	(13.8 ± 0.5) x10^{-2}
Cu	0.4 ± 0.1*	2.1 ± 0.6*	0.6 ± 0.02
Fe	24.7 ± 1.1*	71.4 ± 1.9*	23.5 ± 0.9
K	18.0 ± 0.5*	209 ± 3.1*	352 ± 20.5
Mg	1215 ± 148*	578 ± 84.5*	514 ± 24.2
Mo	< 5.0 x10^{-2}	(4.3 ± 1.5) x10^{-2}	(28.3 ± 1.9) x10^{-2}
Mn	227 ± 63.1*	53.8 ± 8.2*	1.0 ± 0.04
Na	67.3 ± 8.5*	194 ± 20.0*	197 ± 20.9
Ni	10.7 ± 2.4*	5.1 ± 0.6*	< 5.0 x10^{-2}
Pb	< 5.0 x10^{-2}	< 5.0 x10^{-2}	< 5.0 x10^{-2}
Sb	< 1.0	< 1.0	< 1.0
Se	< 20.0 x10^{-2}	< 20.0 x10^{-2}	< 20.0 x10^{-}
Zn	5.1 ± 0.7*	11.1 ± 1.1*	0.1 ± 0.02

Values in each parameter followed by an asterisk indicate significant differences between Tailing and Recovered tailing (p < 0.05).

The concentrations of available Al and Fe were higher for Recovered tailing (Table 3), although the content of the exchangeable Al was similar for the Tailing and Recovered tailing (Table 1). This result reflects two main aspects: i) the leaching of Al and Fe forms from the Technosol to the recovered tailing, and ii) the significant effect of the plants exudates on the availability of these elements. The andic properties of the soils are mainly provided by the presence of Al and Fe oxyhydroxides (IUSS Working Group WRB, 2015). Generally, these nanosized oxyhydroxides present large specific surface area, variable surface charge, high affinity for metals and metalloids and, consequently, high adsorption capacity (Barrón and Torrent, 2013; Bolan et al., 2014). Thus, in a leaching environment, the superficial application of Technosol with andic properties allowed the migration of these nanosized particles to the tailing materials (under the Technosol), leading to the immobilization of PHEs in the treated tailing materials. The high concentrations of Al and Fe extracted by low-molecular weight organic acids, analogous to the root exudates in the rhizosphere, on Recovered tailing reflect not only the presence of these Fe and Al oxyhydroxides but also the effect that plant exudates may have on these nanosized particles. In fact, the dissolution of Fe and Al oxyhydroxides can be greatly increased with some organic acids (Jones et al., 1996; Wang et al., 2015). The concentrations of available Al and Fe in the treated tailings corresponded to 1 % of the pseudototal concentration, which does not constitute any environmental risk.

A significant enhancement of the availability of some macronutrients and micronutrients, such as Ca, Cu, Fe, K, Mo and Zn, occurred in the treated tailings due to the application of Technosol (Table 3). In the case of K and Mo, as well as extractable P (Table 1), the increase of the availability is associated to increase of the organic matter content ($0.86 < r < 0.99$). The increase of the bioavailable nutrients (Table 3), extractable P and organic matter content (Table 2), compared to non-treated tailing, is considered an advantage for the improvement of biological properties in the system and will facilitate the establishment and sustainable development of a plant cover.

3.2 Biological characteristics of the materials

The rehabilitation of the tailings was also evaluated by biological indicators, which reflect soil functional diversity, changes in microbial community composition and microbial status (Karlen et al., 1997; Kumar et al., 2013; Martinez-Salgado et al., 2010; Romero-Freire et al., 2016). The higher enzymatic activities and basal respiration found in the Technosol (Figs. 1 and 2A) indicated the good performance of the overall microbial communities involved in the organic matter degradation, mineralization process, and nutrient cycling. Moreover, the accumulation curve of the CO_2 released from the Technosol presents two well-defined stages of the growth of the active aerobic microorganisms (beginning at hour 32th and 150th). This high value of basal respiration (similarly to dehydrogenase activity) can be associated to the organic C concentration. A large content of organic matter can supply enough substrate and energy for microbial growth and enzyme production (Romero-Freire et al., 2016; Xu and Qi, 2001). Neutral pH values and high nutrient concentration in available forms can also promote the activity of the microbial communities in the Technosol and, consequently, a great CO_2 release (Oertel et al., 2016; Xu and Qi, 2001). Such conditions will limit the proliferation of the microbial CH_4 generators (Fig. 2B).

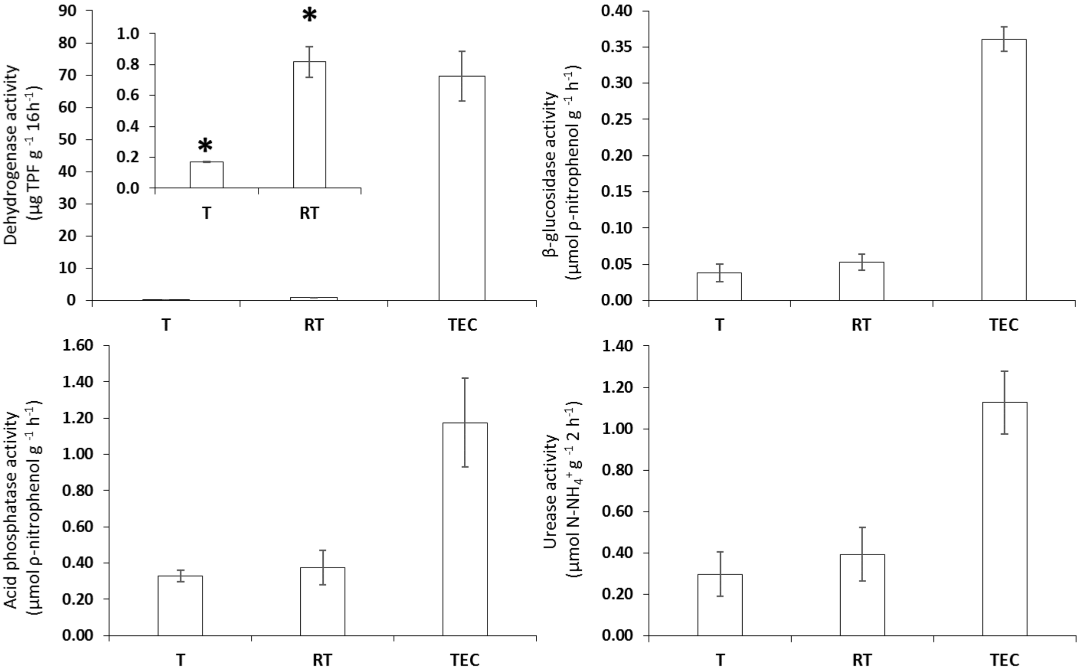

Figure 1. Enzymatic activities (dehydrogenase, β-glucosidase, acid phosphatase and urease) in the materials from the Tailing (T), Recovered tailing (RT) and Technosol (TEC) (Mean ± SD; n = 3). Values followed by an asterisk indicate significant differences between the Tailing and Recovered tailing ($p < 0.05$).

The dehydrogenase activity and basal respiration in Recovered tailing were higher than in Tailing (Figs.1 and 2A), indicating the stimulation of the overall active microbial community. However, no significant differences between Recovered tailing and Tailing were found for the enzymatic β-glucosidase, acid phosphatase and urease activities. Similar results were obtained by Asensio et al. (2013) for urease and acid phosphatase activities. According to these authors, the activity of the enzymes involved in N and P cycling increase significantly only during the first stage of the ecological rehabilitation process, when the substrate presents great availability. These enzymes have great sensitivity to changes in the physic-chemical characteristic materials (Karlen et al., 1997; Kumar et al., 2013; Santos et al., 2014b, 2016), although the microorganism activities tend to balance if conditions in the materials are maintained.

The PCA analysis was conducted in order to evaluate the relationship between chemical characteristics and enzymatic activities of the microbial communities. The first component, PC1, explained 73.94 % of the data variation (Figure S1). This component showed that dehydrogenase activity is closely related to the pH, organic C content and some macronutrients and micronutrients in available fraction (e.g. Ca, Cu, Fe, Na and Zn), while it is negatively influenced by the concentrations of Co, Mg, Mn and Ni in available fraction. However, the activities of the other enzymes were not justified by any studied chemical characteristics of the materials. It is also possible to observe a clear separation among materials, being especially important here the difference observed between the treated and non-treated tailings.

It is possible to assess the functionality of the different microbial communities and to establish the gaseous equilibria by analysing the amounts of CO_2 and CH_4 released by the tailing materials (Fig. 2). In Tailing, the absence of organic matter as C source (Table 1) may lead to a minimum presence of CO_2 producers. This sample seems to have CH_4 producers (methanogenic community), which are able to use rapidly the initial CO_2 existent in box to produce CH_4. The increase of this compound stimulates the methanotrophic community (CH_4 users), establishing the equilibrium between both microbial communities. The activity of the methanogenic community requires acidic and anaerobic conditions. The weak structure and moisture of the tailing materials favours the later conditions (Smith et al., 2003). However, these anaerobic conditions were temporary, since methanotrophic community is a CH_4 sink under aerobic conditions (Fiedler et al., 2005).

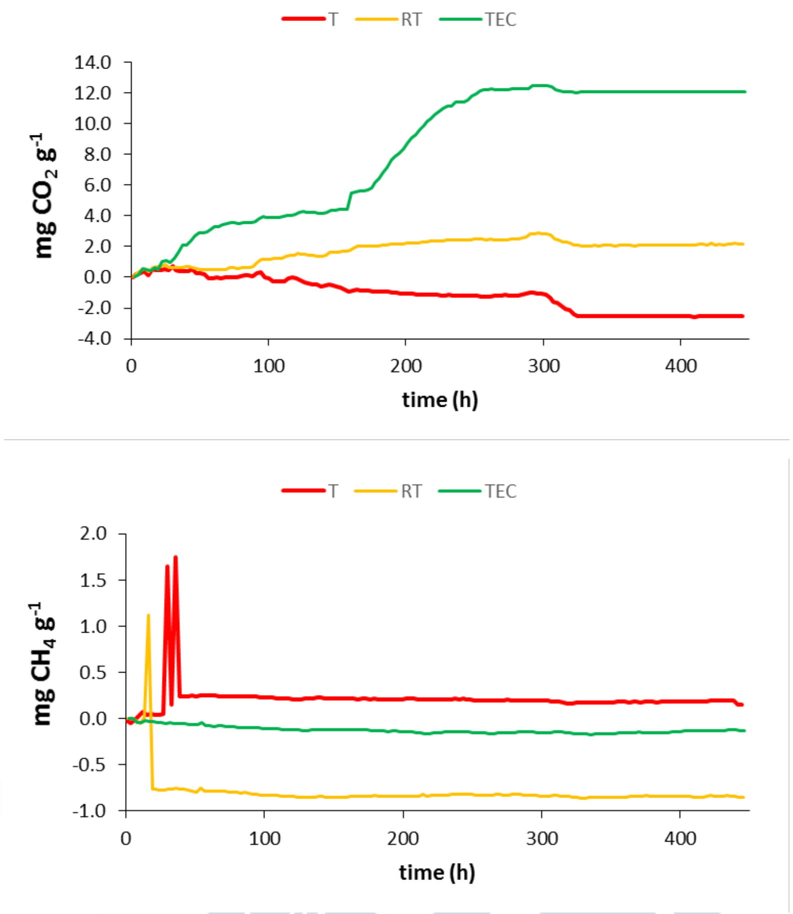

Figure 2. Concentrations of a) CO_2 (basal respiration) and b) CH_4 released from the Tailing (T), Recovered tailing (RT) and Technosols (TEC), as a consequence of microbial activity (Mean ± SD; n = 3).

In the rehabilitated tailing, the methanogenic and methanotrophic communities coexist until total consume of CH_4. The main microbial communities in this treated tailing were CO_2 producers, which are associated to organic matter decomposition and mineralisation processes.

3.3 Chemical characterization of the simulated leachates

In general, the concentrations of elements in the leachates were smaller than the corresponding concentrations of available fraction in the solid samples. Concentrations of As and Pb were always below the detection limit in all cases. Leachates from the Technosol had adequate pH values and nutrient concentrations, and also small PHEs concentrations. Leachates from the non-treated tailings presented moderately acid pH values, indicating a low sulfide reactivity of the mine wastes. Moreover, high concentrations of sulfates and several PHEs (e.g. Al, Cd, Co, Cr, Ni, Zn) were observed, which agrees well with the high EC observed (Table 4). The chemical composition of these leachates showed lower pH values and PHE concentrations (> 10-fold) than that of runoff waters for the tailings collected in the field (Arán et al., 2016). In fact, under field conditions, the elements leaching from wastes and soils can vary due to several factors (e.g. climatic conditions, heap design) (Chezom et al., 2013). Moreover, percolated leachates from mine wastes presented significantly higher concentrations than simulated leachates, even for microcosm assays under greenhouse-conditions (Santos et al., 2017b). The large concentrations of PHEs found here in the leachates indicate a potential spread of toxic elements from the tailings to the adjacent areas.

In general, the leachates from the treated tailing showed significant enhancement of the chemical quality compared with the non-treated tailing (Table 4), minimizing the potential spread of pollutants. No significant differences were observed between the leachates of the treated and non-treated tailings for the pH, Cu, Mo, PO_4, Sb and Se. However, the concentrations of Ca, Fe, K and NO_3 in Recovered tailing leachates increased between 2- and 41-fold depending on element (Table 4). The concentrations of F, Cl and Na were significantly higher in Recovered tailing leachates, compared with tailing leachates. However, these concentrations are still below the legislation limits established for several water uses (BOE, 2003, 2015). Concentrations of K and NO_3 in the leachates are correlated with the organic matter (r = 0.90 and 0.85), but for the other elements is difficult to establish correlation with the chemical characteristics of the materials.

The concentration of sulfate in Recovered tailing leachates showed a decreased of 24 %, while a larger decrease, between 38 % and 92 %, was found for several PHEs (Al, Cd, Co, Cr, Mn, Ni, and Zn). The pH of the system and the formation of organometallic complexes justify the decrease of Mg in the leachates ($r \approx -0.80$) (Adriano et al., 2004), whereas the increase of CEC found in the treated tailing led to the decrease of Cd, Co, Cr, Mg, Mn, Ni and Zn concentrations in the leachates ($-0.81 < r < -0.92$). The presence of Al and Fe oxyhydroxides in Recovered tailings also contributes to the immobilization of these PHEs. Moreover, the formation of sulphate solid phases explains the decrease of this anion. In Recovered tailing, the significant decrease of NH_4 in its leachates, along with the increase of NO_3, can be related to the promotion of the nitrifying microbial community in the materials. The increase on the activity for this microbial community results in higher rates of net nitrification over ammonification.

Table 4. Chemical characteristics of the simulated leachates from collected samples (mean ± SD; n = 4)

	Tailing	Recovered tailing	Technosol
pH	4.7 ± 0.4	5.0 ± 0.3	7.8 ± 0.3
EC (mS/cm)	1.5 ± 0.3	1.4 ± 0.2	1.0 ± 0.1
	Elements concentration (mg/kg)		
Al	4.8 ± 0.1*	0.8 ± 0.1*	1.5 ± 0.1
As	< 0.1	< 0.1	0.1 ± 0.03
Ca	695 ± 46.8*	2987 ± 89.0*	1021 ± 48.0
Cd	(12.7 ± 0.6) x 10^{-2}*	(4.0 ± 1.0) x 10^{-2}*	< 1.0 x 10^{-3}
Cl	49.4 ± 8.2*	106 ± 6.2*	104 ± 4.7
Co	3.9 ± 0.1*	0.3 ± 0.01*	0.02 ± 0.01
Cr	(4.3 ± 0.6) x 10^{-2}*	(2.7 ± 0.6) x 10^{-2}*	(2.0 ± 0.1) x 10^{-2}
Cu	(14.0 ± 4.6) x 10^{-2}	(14.3 ± 1.5) x 10^{-2}	(12.7 ± 1.2) x 10^{-2}
F	1.6 ± 0.5*	3.2 ± 0.4*	22.5 ± 4.1
Fe	< 1.0 x 10^{-2}*	(20.3 ± 16.2) x10^{-2}*	(4.0 ± 1.0) x10^{-2}
K	35.9 ± 15.6*	191 ± 8.6*	302 ± 0.6
Mg	1105 ± 24.1*	613 ± 11.6*	331 ± 2.2
Mo	< 5.0 x 10^{-2}	(3.7 ± 1.2) x 10^{-2}	(36.3 ± 1.2) x 10^{-2}
Mn	167 ± 5.2*	30.1 ± 0.7*	0.1 ± 0.01
Na	63.9 ± 0.6*	201 ± 4.5*	186 ± 2.4
Ni	7.3 ± 0.2*	1.8 ± 0.1*	< 0.05
NH_4	16.3 ± 1.4*	5.6 ± 3.1*	7.7 ± 2.4
NO_2	< 0.4	< 0.4	2.7 ± 0.1
NO_3	17.2 ± 6.1*	446 ± 36.6*	879 ± 22.1
Pb	< 0.1	< 0.1	< 0.1
PO_4	< 0.5	0.5 ± 0.4	1.9 ± 2.5
SO_4	(8.1 ± 0.7) x10^{3}*	(6.1 ± 0.3) x10^{3}*	(2.8 ± 0.2) x10^{3}
Sb	(8.7 ± 1.5) x 10^{-2}	(11.7 ± 1.5) x 10^{-2}	(16.7 ± 1.5) x 10^{-2}
Se	0.2 ± 0.1	0.3 ± 0.1	0.2 ± 0.02
Zn	4.0 ± 0.2*	0.8 ± 0.03*	0.1 ± 0.1

EC: Electrical conductivity. Values in each parameter followed by an asterisk indicate significant differences between Tailing and Recovered tailing ($p < 0.05$).

3.4 Ecotoxicological characterization

The assessment of the ecotoxicological risk of Recovered tailing and Tailing combined several endpoints of two plant species used in different bioassays (OECD bioassays) and a microcosm assay (pot experiment) under greenhouse conditions. Through bioassays using leachates (filter and hydroponic bioassays) the ecotoxicological risk of the materials to adjacent areas can be evaluated by acting as a source of contamination (van Gestel et al., 2001). Nonetheless, the organisms can be affected not only by the presence of PHEs in soluble forms but also by those elements associated to exchangeable complex of inorganic and organic colloids (available fraction). Consequently, the assays using the solid matrix are essential. Soil test was conducted during a short period of time under growth chamber conditions. The ecotoxicological effects of the materials on the same plant species were also evaluated through a microcosm assay (pot experiment) for a slight longer period and under greenhouse conditions, which can simulate more real conditions (e.g. light intensity, relative air humidity and temperature). Including different matrix, assay conditions, plant species and plant endpoints, it was intended to make a more rigorous assessment of the system and the rehabilitation process.

The different sensitiveness depended on the assay (between type, matrix, time period and growth conditions) and/or plant species (*L. perenne* and *T. pratense*). Similar results were reported in bioassays conducted with other plant species (*Lactuca sativa* L., *Avena sativa* L. and *Zea mays* L.) to assess the ecotoxicological effect of recovered materials (*gossan* mine wastes and contaminated soils) by Technosols and amendments (Abreu et al., 2014; Santos et al., 2013). According to the same authors, the plant response to elements depends on biological tolerance of the plant group (dicot *Vs* monocot) and species.

No visual signs of nutritional deficiency and phytotoxicity were observed in both species from the three bioassays. In general, Technosol did not show any ecotoxicological risk since several endpoints of both species in the three bioassays were similar compared to negative control. Even the plants growing in its leachates and microcosm assay reached the greatest survival and development (Figs. 3-4 and Table 5). The only exception was observed for the *T. pratense* in the soil bioassay where the germination in Technosol was slightly lower than those in the negative control (Sand: 92 ± 13 %). The slight reduction of the *T.*

pratense germination can be related to its sensitivity to the higher EC in the Technosol, as a result of high nutrient concentration (Tables 2 and 3). In fact, *T. pratense* presented the highest sensitivity, compared to other *Leguminosae* species, in its germination by the increase of the application rate of municipal waste compost (Marchiol et al., 1999), which always increases the elements content and EC in soil solution (Peverly et al., 1994).

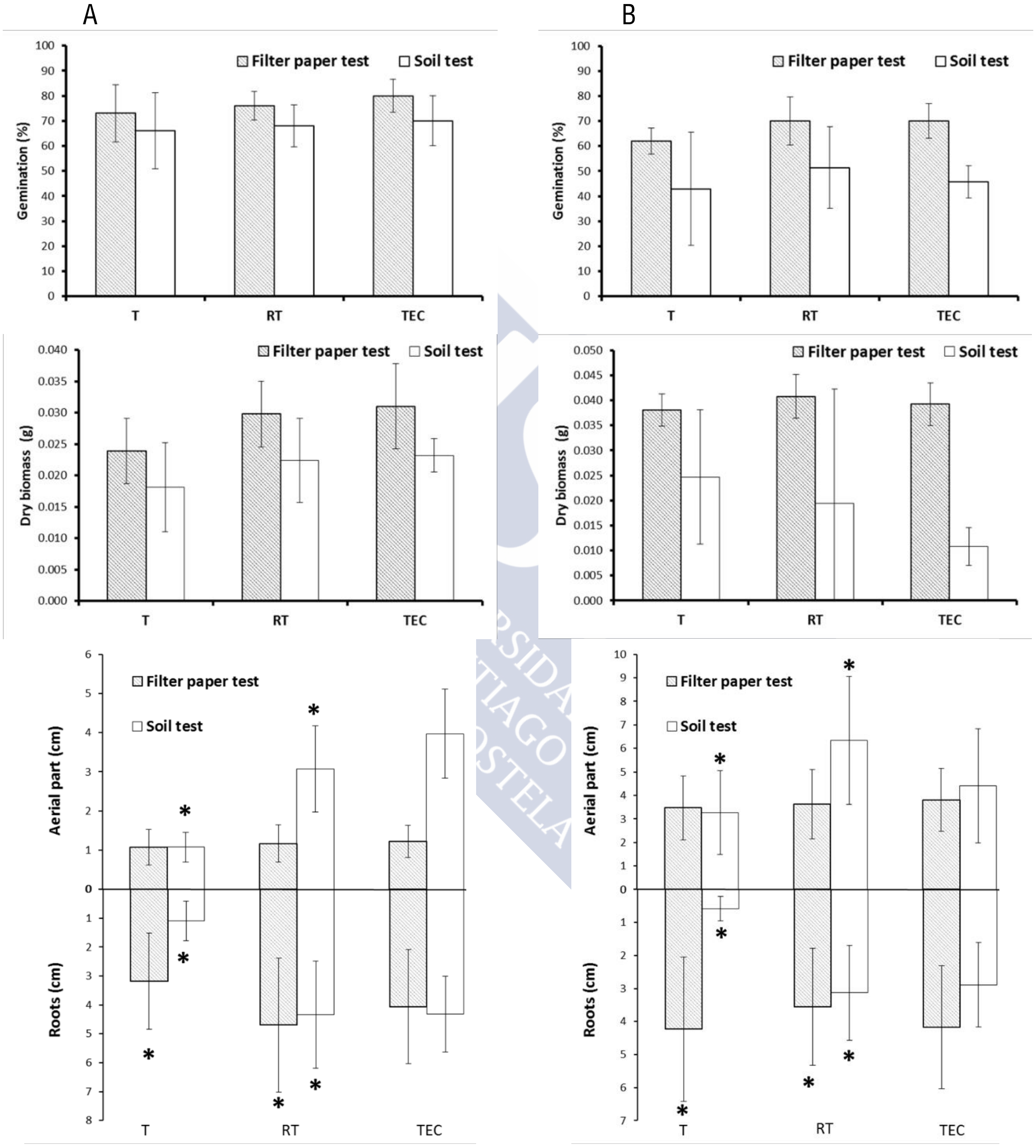

Figure 3. Plant endpoints obtained in the filter paper and soil bioassays with Trifolium pratense (A) and Lollium perenne (B)in Tailing (T), Recovered tailing (RT) and Technosol (TEC), (Mean ± SD; n = 4 and 5 for each bioassay respectively). Values followed by an asterisk indicate significant differences between Tailing and Recovered tailing ($p < 0.05$).

Similar results were obtained using the toxicity indexes RE and SG (Bagur-González et al., 2011) for both plant species growing in the Technosol leachates (filter bioassay) and materials (soil bioassay). Thus, the indexes calculated for the Technosol shows low ecotoxicity, between -0.14 and -0.24, depending on index and species) while its leachates did not represent any ecoxicological effect since the germination and roots elongation were stimulated (indexes > 0).

For both species, the germination percentage, aerial part elongation and dry biomass weight in filter paper and soil bioassays did not show significant differences between Tailing and Recovered tailing, and even with Technosol (Fig. 3). However, root elongation showed more sensitivity to the potential toxic effect of the materials and its leachates. Thus, the elongation of the roots in the Recovered tailing materials and their leachates (except for *L. perenne* in filter paper) presented significantly higher values than in the tailing without rehabilitation (Fig. 3). Moreover, the root elongation was similar between Recovered tailing and the Technosol.

The toxic effect, of the Tailing and Recovered tailing materials and their leachates, evaluated by toxicity indexes, depended on plant species, plant endpoint (germination and root elongation) and bioassay (filter paper and soil). Leachates from the Tailing and Recovered Tailing indicated low or no toxicity (0 < index values < 0.42, depending on species and endpoint). However, evaluating the solid materials, the Tailing present moderate (SG ≈ -0.3 for both species) and very high toxicity (RE ≈ -0.8) while the Recovered tailing had low or no toxicity (-0.25 < index values < 0.16 depending on species and endpoint).

In the hydroponic bioassay, the plant survival percentage of the plant survival in the Tailing and Recovered tailing leachates depended on plant species. Plant survival for *T. pratense* reached 85 % in both leachates, whereas the survival rate for *L. perenne* in the Recovered tailing was higher (100 %; similar to Technosol) than in Tailing leachates (90 %).

Ecotoxicological effect of the Tailing leachates was observed in the aerial part and dry biomass of *T. pratense* but not in the root elongation (Fig. 3). The Tailing leachates significantly inhibited the aerial part elongation and consequently the dry biomass. The reduction of the root–aerial part ratio (root elongation/shoot elongation) from 1.7 in the

Tailing to 1.2 in the Recovered tailing suggests a positive response of *T. pratense* and more favourable growing conditions. Nevertheless, ecotoxicological effect of the Recovered tailing leachates on same species, compared to the Tailing leachates, was not clear. The aerial part and root elongations were smaller compared to those found with Tailing leachates, but no significant differences were obtained for dry biomass. The lower plant survival of *L. perenne* in the Tailing leachates can explains its higher development (biomass and aerial part and roots elongations) due to small competition among individuals. For the same reason the root–shoot ratios (≈1.4) were similar between both treated and non-treated tailings.

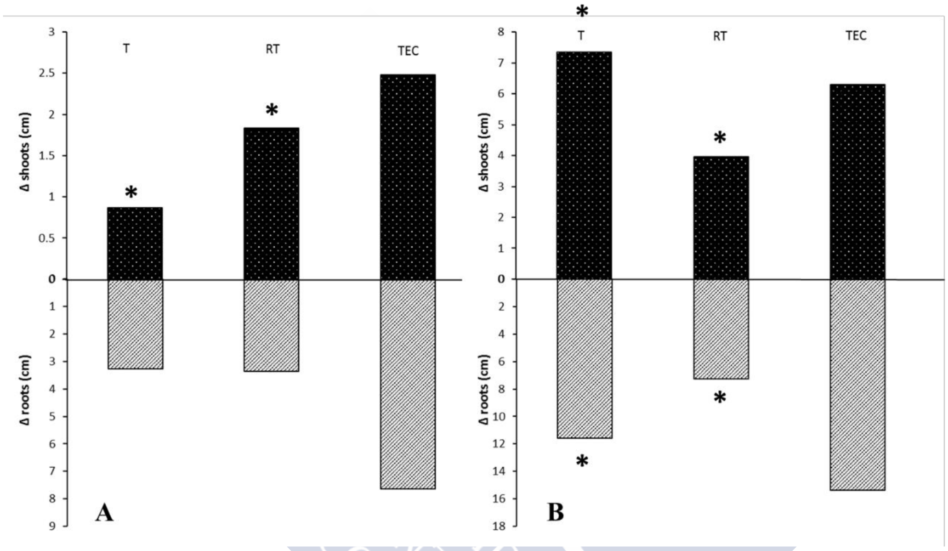

Figure 4. Plant endpoints obtained in the hydroponic bioassay with Trifolium pratense and Lollium perenne in Tailing (T), Recovered tailing (RT) and Technosol (TEC),(Mean ± SD; n = 5). Values followed by an asterisk indicate significant differences between Tailing and Recovered tailing (p < 0.05).

In the microcosm assay (pot experiment), the results were different to those compared to the soil bioassay and varied with plant species. In this assay, *T. pratense* showed strong sensitivity (at level of germination and dry biomass weight) to the Tailings conditions compared to *L. perenne*. As mentioned above, this was not clear in the soil bioassay. Plant cover and dry biomass of both species depends on the material, reaching the highest values in the Technosol. Even after 20 months of application, the Technosol still showed adequate physical and chemical characteristics, ensuring a significant germination, plant cover and biomass production. Therefore, this may lead in the future to the establishment of a pasture in the mining site (and surroundings) providing a suitable habitat and economic land use.

In non-treated tailing, a total inhibition of *T. pratense* germination and significant decrease of *L. perenne* germination was found. This inevitably affects the plant cover, with significant erosion risk and spreading of contaminated particulate material in the non-treated tailing (Table 5). Moreover, the few plants growing in this system showed visible symptoms of nutritional deficiency or phytotoxicity in the aerial part (e.g. chlorosis and narrow leaves; Kabata-Pendias, 2011). The combined effect of the poor structure, extreme chemical characteristics (e.g. high total and available concentrations of PHEs and low fertility; Tables 1 and 2) and emergence of significant amounts of salt efflorescence explains the total inhibition of seeds germination of *T. pratense* and low plant development of *L. perenne* (evaluated by dry biomass weight) in the Tailing materials. The germination and seedlings growth of both species was stimulated in the Recovered tailing (Table 5). The improvement of the structure and water holding capacity can explain the higher germination of both species in this sample. According to several authors, these characteristics are key factors for the stimulation of the germination and guarantees the seedlings growth during the first stage of the rehabilitation process (Santos et al. 2014b, 2016; Wang et al., 2008). The Recovered tailing allowed a quick plant cover. In fact, after 30 days of the sowing, no significant differences were obtained for the plant cover between the Recovered tailing and the Technosol (Table 5). Nonetheless, the plant biomass produced by both species at the end of the experiment was smaller in the treated tailing (Table 5). In the beginning of the plant growth no visual signs of nutritional deficiency or phytotoxicity were observed (as for bioassays) but at the end of the experiment the leaves of both species showed a light green colour (possibly due to N deficiency).

In order to determine the ecotoxicological influence of the chemical characteristics of the materials and their leachates a PCA analysis was conducted. For all ecotoxicological assays (bioassays and microcosm assay), PC1 explained more than 66.47 % of data variance and the separation of the materials was clearly observed (Figures S2-S4). For both species, the germinations from filter paper and soil bioassays, as well as dry biomasses from the three bioassays, were not affected by the studied characteristics of the materials, indicating the low ecotoxicological sensitivity of these plant endpoints. However, in microcosm assay the plant endpoints showed a clear ecotoxicological response related to the concentrations of available Co, Mg, Mn and Ni. The same result was obtained in the aerial part and roots elongations from soil bioassay.

Table 5. Plant cover and dry biomass of Lollium perenne and Trifolium pratense growing in study samples, after one month from sowing (mean ± SD; n = 4)

Plant parameters	Tailing	Recovered tailing	Technosol
		Lollium perenne	
Plant cover (%)	<1	65 ± 4.08	92 ± 4.01
Dry biomass (g/pot)	0.020 ± 0.008*	0.852 ± 0.084*	1.687 ± 0.091
		Trifolium pratense	
Plant cover (%)	—	90 ± 9.01	100 ± 0.00
Dry biomass (g/pot)	—	1.014 ± 0.542*	2.533 ± 0.754

Values in each parameter followed by an asterisk indicate significant differences between Tailing and Recovered tailing ($p < 0.05$).

In leachates, the sensitiveness to PHEs depended on plant species. According to PCA analysis, the ecotoxicological effects of the leachates (filter and hydroponic bioassays) on aerial part and roots elongations of the *T. pratense* were associated to the concentrations of Co, Mg, Mn and Ni (as observed for soil bioassay and microcosm assay) as well as the concentration Al, Cd, SO_4, NH_4 and Zn. However, these PHEs did not lead to ecotoxicological effects on *L. perenne*. Here, only the concentrations of some nutrients, such as Ca, NO_3, K and Na, can limit the elongations.

In general, the ecotoxicological effect evaluated by plant bioassays was not clear. However, the evaluation using pot experiments under greenhouse conditions showed an evident and strong ecotoxicological effect in the Tailings materials and a significant reduction of this effect in the Recovered tailing. Differences between OECD bioassays and pot experiments are related to time of contact and assay conditions.

4. CONCLUSIONS

The mine tailings present in the Fé mining area (Saelices el Chico, Spain) can lead to significant environmental risk to adjacent areas, due to concentrations of PHE’s (especially by the high concentrations of Co, Mg, Mn and Ni) in the leachates and the available fraction, and the total mass of the mine wastes. Therefore, it is essential the rehabilitation of the tailings to minimize the pollution effects.

The application of a Technosol with andic and eutrophic properties significantly improved the physico-chemical and biological characteristics of the tailing materials and their leachates. Also, the use of this material decreased the ecotoxicological impact of the mine tailings. Additional advantages in the rehabilitation process were the increase of organic matter content, increase of the concentration of nutrients in available forms and in the leachates, and the stimulation of the microbial activity (evaluated by dehydrogenase activity and basal respiration). After 20 months of application over the tailing, the Technosol still presents efficient characteristics to continue the tailing rehabilitation process as well as to. This will ensure the ecological functions and a stable vegetation cover. Moreover, no ecotoxicological effects were observed. Microcosm assays results evidenced the efficiency of the Technosol and its potential for pasture revegetation. Thus, it is essential to assess the PHEs concentration in these plants in order to evaluate the potential risk to domestic animals.

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Supplementary materials

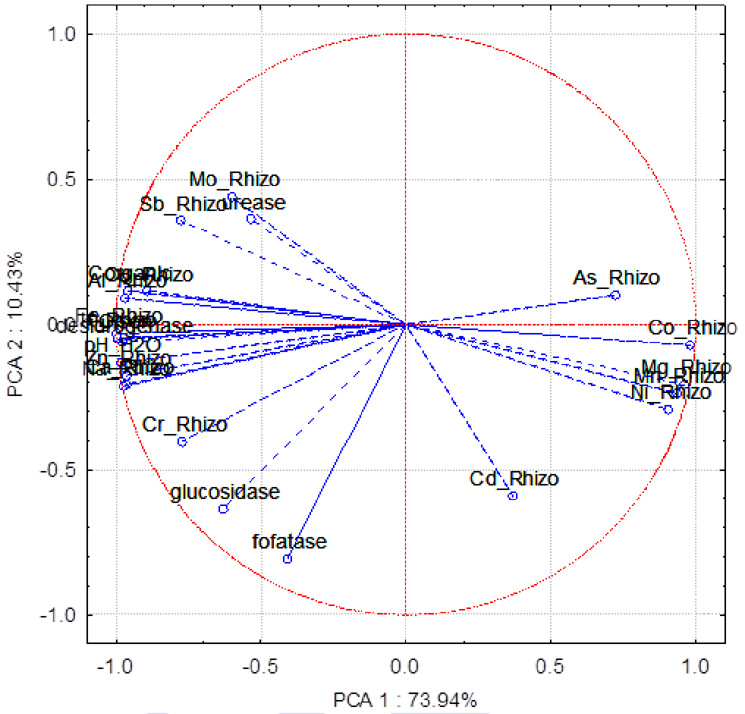

Figure S1. The PCA analysis between the chemical characteristics of the materials (Tailing and Recovered Tailing) and enzymatic activities of the microbial communities.

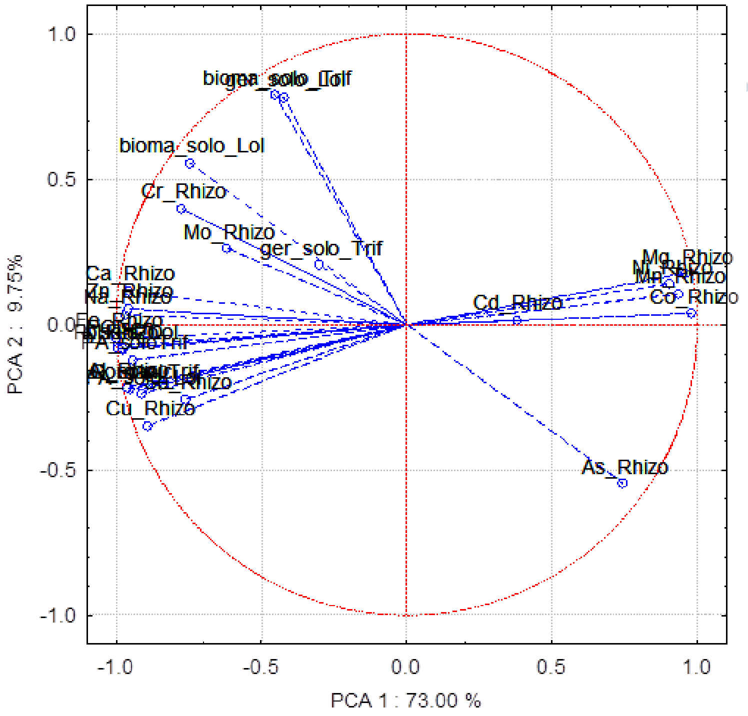

Figure S2. The PCA analysis between the chemical characteristics of the materials (Tailing and Recovered Tailing) and parameters from soil test assay.

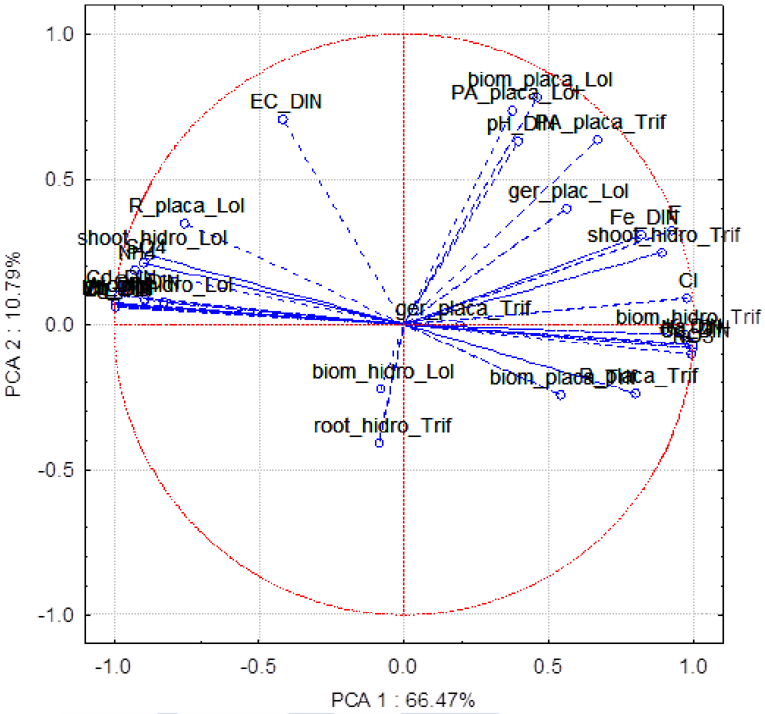

Figure S3. The PCA analysis between the chemical characteristics of the materials (Tailing and Recovered Tailing) and their leachates with parameters of the two bioassays (Hydroponic and filter paper).

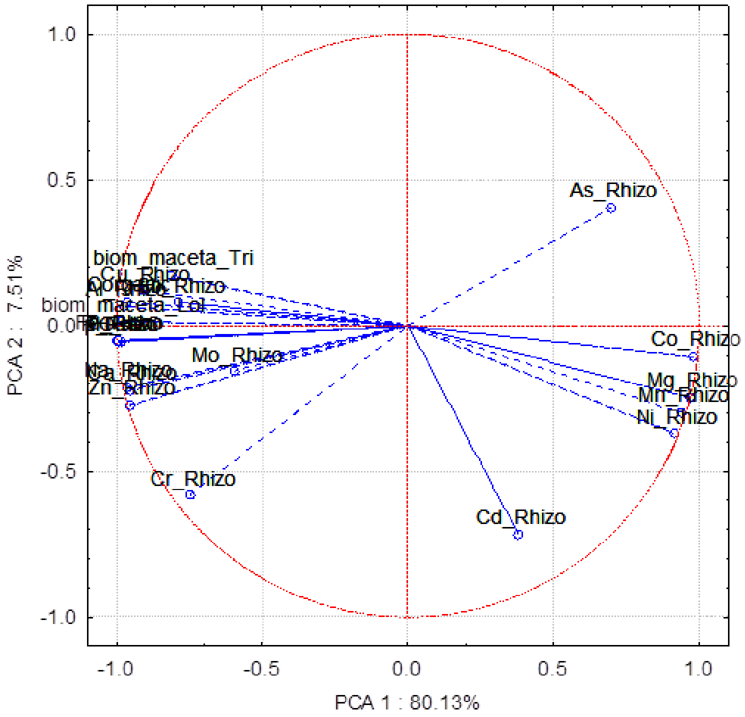

Figure S4. The PCA analysis between the chemical characteristics of the materials (Tailing and Recovered Tailing) with parameters of the microcosms assay.

GENERAL CONCLUSIONS

This Doctoral Thesis studies the effectiveness of the use of Technosols and biochar in the environmental recovery of soils and waters in contaminated areas. The following conclusions summarize the main results obtained:

i. The mine soils from Fé mining area are developed on different mixtures of host-rock and sulfide-rich waste materials. These soils present a high environmental risk since they generate acid mine drainage waters, rich in potentially toxic elements and sulfates. The mine soils were classified as different Spolic Technosols, depending on the additional properties or characteristics (Sulfidic, Salic) and Ekranic or Urbic Technosols. Precipitation of evaporate salts, mainly *epsomite* ($MgSO_4 \cdot 7H_2O$), are favoured in the warmer seasons. On the other hand, the natural soils adjacent (Lithic or Haplic Leptosols and Leptic or haplic Cambisols) to the Fé mine are poor in nutrients and organic matter content, which, together with the climatic conditions of the area, leads to scarce vegetative growth. These soils have a strong erosive tendency, with predominance of the processes of rexistasia over those of biostasia. These are only maintained very incipiently in the areas that preserve a permanent vegetal cover. Taking into account the limiting conditions of the soils, it is essential to act on these soils in order to minimize the oxidation of the sulfide-rich materials and to improve the soil fertility. The main actuation is to establish a stable and sustainable vegetation cover and to stimulate pedogenesis and biogeochemical processes, such as the nutrient cycle.

ii. The biochars showed a significant capacity to immobilize copper. This process is mainly controlled by adsorption and precipitation or co-precipitation mechanisms, which are influenced by the physicochemical properties of the biochar. The most important of these properties in relation to the high sorption capacity were the O/C ratio, the P content and the ash content. The sequence of sorption for the different biochars was the following: Rice Biochar > Chicken manure Biochar > Olive mill waste Biochar > Acacia Biochar > Eucalyptus Biochar > Corn cob Biochar. The controlling sorption mechanism in the biochars with the highest inorganic content was the precipitation or co-precipitation, as phosphates and carbonates. In the biochars with lower content in this fraction, the main mechanism was the adsorption. The effect of pH on the sorption capacity was independent of the nature of the feedstock material, and the copper retention of all types of biochar increased with pH. The distribution of copper between the different phases ($Cu_{Biochar}$, Cu_{DOM}, free Cu^{2+}) depended on the nature of the biochar, and prior evaluation of the material is necessary to guarantee efficient retention and immobilization. The physico-chemical and operation conditions of system (pH, flow rate…) affect the water treatment in continuous flow-systems. The flow rate of the system strongly influenced the amount of copper retained. An increase of 2.03 mg Cu g^{-1} was produced by the corncob biochar as the flux increased from 2.5 to 13 mL min^{-1}. Copper retention capacities found for the biochars studied ranged from 1.28 mg g^{-1} to 26.63 mg g^{-1}. A good correlation was found between the sorption parameters obtained in batch and column experiments. Biochars may therefore be an effective and economic alternative to common sorbent materials for use in water treatment systems to remove copper or other heavy metals. The results obtained with these biochars, in both static and dynamic systems, make them suitable materials to be used as constituents of Technosols and in soil remediation processes.

iii. Technosols with andic properties are considered an efficient adsorbent able to mitigate the effects of anion contamination, such as phosphate. This material effectively retained phosphate in both static and dynamic system, displaying higher (or comparable) retention capacities than other materials commonly used to remove phosphate from natural systems. The sorption capacity of the Technosol ranges from 7.18 and 18.51 mg PO_4 g^{-1} for static systems and from 2.04 to 6.21 mg PO_4 g^{-1} for dynamic systems. The main immobilization mechanisms controlling the immobilization of the phosphate ions in the Technosol are surface adsorption and precipitation (as Ca-P minerals). Phosphate sorption is dependent of the pH of the system and is also affected by the presence of different anions (carbonate, sulfate, chloride, chromate and molybdate). The flow rate and the thickness of the reactive layer in fixed-bed column systems were two important parameters that determined the capacity of retention of phosphate. An increment in the retention capacity, from 2.37 ± 0.06 to 6.19 ± 0.06 mg g^{-1}, as the flow rate decreased from 5.0 to 1.5 mL min^{-1}, as effect longer contact time. The effect of the thickness of the reactive layer on retention capacity was decreasing of a 14% when was halved this layer. Finally, the phosphate retention was higher in the samples in which the influent solution was acidic, and the retention capacity of the spolic silandic Technosol recovered well after several sorption-desorption cycles. This is positive aspect, since the Technosol can be then easily re-used in water treatment systems after washing. The use of this Technosol material represents an inexpensive method to resolve two important problems: eutrophication of aquatic systems and the scarcity of natural resources of phosphate for agricultural use.

iv. The application, under field conditions, of a Technosol with andic and eutrophic properties significantly improves the physico-chemical characteristics and the activity of microbial communities of the tailing materials from Fé mine (Salamanca, Spain). The concentration of potentially toxic elements in tailing leachates also decreases, minimizing pollution spreading and ecotoxicological impact. Additional advantages in the rehabilitation process were the increase of organic matter content, increase of the concentration of nutrients in available forms and in the leachates, and the stimulation of the microbial activity (evaluated by dehydrogenase activity and basal respiration). These improvements in the recovered tailings ensure the ecological function and a stable vegetation cover of the pastures. Finally, the Technosol presents an adequate long-term efficiency and shows good potential to continue the rehabilitation process of the mine tailing through the years. These results highlight the sustainability of this remediation technology for the rehabilitation of sulfide-rich tailings and adjacent soils affected by these tailings.

v. The evaluation of effective and sustainable remediation alternatives must be carried out from an integral and multidisciplinary perspective. The initial step of the rehabilitation methodology should be based on the characterization of the materials (soils, sediments, mine wastes, water...), and on the assessment of the nature and mobility of the contaminants present. Moreover, it is essential to evaluate other conditions of the studied area (climatic, geological, morphological, ecological, extension, influence area...). This integral evaluation allows proposing the use of independent or combined, of technologies (amendments, phytotechnologies, biochars, Technosols, reactive wetlands...). The monitoring of the rehabilitation process at medium- to long-time ranges, especially when reactive materials as sulfides are present in the system, is a key point to evaluate the real sustainability of the process. The goal of any recovery process should include the management and re-utilization of waste materials (including their mineral compounds, organic matter content and nutrients) and reconversion from degraded areas to productive areas with economic benefits.


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