UNIVERSIDADE FEDERAL DE LAVRAS

EVANISE SILVA PENIDO

CONVERSÃO PIROLÍTICA DE LODO DE ESGOTO A BIOCARVÃO E SEU USO NA REMEDIAÇÃO DE AMBIENTES CONTAMINADOS

LAVRAS - MG

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Dissertação apresentada à Universidade Federal de Lavras, como parte das exigências do Programa de Pós-Graduação Multicêntrico em Química de Minas Gerais, área de concentração em Química, para a obtenção do título de Mestre.

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Aos meus pais, Robson e Ana, ao meu irmão Alberson e ao meu companheiro, Alan Filipe,

DEDICO

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Agradeço a Deus por Sua proteção divina. Aos meus pais e toda minha família.

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RESUMO

O lodo de esgoto é um resíduo produzido em grandes quantidades pelas estações de tratamento de esgoto. Buscar soluções alternativas de reuso desse tipo de resíduo, além de agregar valor ao material, contribui para garantir o desenvolvimento sustentável e a proteção ambiental. Conduziu-se, este trabalho, com o objetivo de produzir biocarvão, a partir da conversão pirolítica do lodo de esgoto, o qual foi aplicado em processos considerando a remediação de ambientes contaminados com metais pesados. No primeiro estudo, biocarvões (ativo e não ativo) foram testados quanto a suas capacidades de remover Cr(VI) em solução. O processo de funcionalização com ácido fosfórico aumentou a capacidade de adsorção e acarretou na criação de grupos funcionais (P^+-O^- e P-O-P) na superfície do material. Os dados das isotermas de adsorção (a 25˚C) foram melhores ajustados pelo modelo SIPS, indicando uma superfície heterogênea. A remoção do Cr(VI) em meio aquoso aumenta em valores de pH mais baixos e é proporcional à elevação da temperatura. Os parâmetros termodinâmicos indicam que o processo de adsorção é espontâneo e de natureza física. Na segunda parte do trabalho, foi estudada a capacidade de remediação do biocarvão de lodo de esgoto quando aplicado em solos provenientes de uma área de mineração de Zn, a qual apresenta elevados teores de metais pesados (Cd, Pb e Zn). A aplicação de biocarvão de lodo de esgoto acarretou no aumento do pH e da condutividade elétrica dos solos e diminuiu os teores de Cd, Pb e Zn que são disponíveis para as plantas, ocasionando, assim, maiores crescimentos e desenvolvimentos quando comparados com solos que não receberam nenhum tratamento. Nesse contexto, conclui-se que a conversão pirolítica do lodo de esgoto para a formação de biocarvão é um processo promissor para gerenciar e agregar valor a esse resíduo, contribuindo para a preservação e remediação ambiental, principalmente em ambientes contaminados por metais pesados.

Palavras-chave: Lodo de esgoto. Resíduo. Biocarvão. Contaminação. Remediação ambiental.

ABSTRACT

Sewage sludge is a waste product produced in large quantities by sewage treatment plants. Alternative solutions for the reuse of this type of waste can add value to the material and contribute to sustainable development and the environment. The aim of this study was to produce biochar from the pyrolytic conversion of sewage sludge and use it for the remediation of environments contaminated with heavy metals. In the first study, biochars (active and non-active) were tested for their ability to remove Cr(VI) from solution. The treatment with phosphoric acid increased the adsorption capacity and resulted in the creation of functional groups (O^--P+ and P-O-P) on the surface of the material. The data of adsorption isotherms (at 25˚C) were better adjusted by the SIPS model. The temperature and pH are determining physical parameters for the removal of Cr(VI), which increases at lower pH and with increasing temperature. The thermodynamic parameters indicate that the adsorption process is spontaneous and physical. In the second part of the study, we assessed the ability of remediation of sewage sludge biochar when applied as an amendment in soils from a Zn mining area, which has high contents of heavy metals (Cd, Pb and Zn). The application of sewage sludge biochar resulted in the increase of pH and electrical conductivity of the soils and decreased the Cd, Pb and Zn that are available to plants, causing higher growth and plant development compared with soils that did not receive any treatment. In this context, we conclude that the pyrolytic conversion of sewage sludge to biochar is a promising process to manage and add value to this waste, contributing yet to the preservation and environmental remediation, especially in environments contaminated by heavy metals.

Keywords: sewage sludge, waste, biochar, contamination, environmental remediation

SUMÁRIO

PRIMEIRA PARTE

1 INTRODUÇÃO

As grandes produções de resíduos têm gerado a necessidade de buscar soluções alternativas de reuso e de descarte, para que não haja o comprometimento do meio ambiente e da saúde da população. O lodo de esgoto é um resíduo produzido em grandes quantidades pelas estações de tratamento de esgoto e sua destinação é um problema ambiental para as empresas de saneamento, públicas ou privadas. Recentemente, uma nova resolução da Organização das Nações Unidas (ONU), anunciada em Assembleia Geral no dia 17 de dezembro de 2015, reconheceu o saneamento básico (coleta de esgoto e tratamento) como Direito Humano (NAÇÕES UNIDAS NO BRASIL, 2016). Entretanto, quando todos os esgotos coletados forem devidamente tratados, a geração de resíduos aumentará substancialmente e buscar soluções para seu aproveitamento é de extrema importância. Uma alternativa sustentável para o reaproveitamento desse tipo de resíduo é a sua utilização como matéria-prima para a produção de biocarvão, que se trata de qualquer fonte de biomassa que passou por tratamento térmico na ausência de oxigênio (pirólise). Dependendo de suas características, que são decorrentes dos processos de produção, o biocarvão pode atuar como remediador de ambientes contaminados com metais pesados, tais como Cromo, Cádmio, Chumbo e Zinco, os quais possuem alta toxicidade, reatividade e bioacumulação, causando sérios riscos à saúde e ao meio ambiente (GUILHERME et al., 2005). Neste estudo, objetivou-se produzir, caracterizar e avaliar o potencial remediador de biocarvão produzido a partir da pirólise do lodo de esgoto, em ambientes contaminados por metais pesados.

Na primeira parte, descreve-se um estudo de adsorção de cromo hexavalente por biocarvões produzidos a partir de lodo de esgoto. O lodo de esgoto foi coletado na estação de tratamento de esgoto de Vazante, Minas Gerais. As amostras coletadas foram secas em estufa (60°C), peneiradas e armazenadas. Foram produzidos biocarvões (ativo e não ativo), por meio da conversão pirolítica do lodo de esgoto. Para a funcionalização química da superfície do material carbonáceo, foi utilizado ácido fosfórico (H_3PO_4). Os biocarvões foram caracterizados e testados quanto a sua capacidade de adsorver cromo do meio aquoso. Foram avaliados os seguintes parâmetros: massa de biocarvão, cinética de adsorção, efeito do pH e da temperatura. Verificou-se que o biocarvão funcionalizado possui maior capacidade de adsorção de Cr(VI) e as melhores condições de análise foram em pH 2 e dose 1 g L^{-1}. O aumento da temperatura eleva a capacidade de adsorção, evidenciando um processo endotérmico e de natureza espontânea.

Na segunda parte, foi estudada a capacidade de remediação do biocarvão de lodo de esgoto quando aplicado em solos provenientes de uma área de mineração de Zn, a qual apresenta elevados teores de metais pesados (Cd, Pb e Zn). Foi realizado experimento em casa de vegetação com solos coletados em uma área de mineração de Zn, localizada em Vazante, Minas Gerais. O biocarvão de lodo de esgoto foi aplicado ao solo em diferentes doses (30 e 60 g kg^{-1}). Biocarvões e lodo de esgoto *in natura* também foram utilizados no experimento. Os lixiviados foram coletados durante 4 semanas e analisados quanto ao pH, condutividade elétrica e teores totais de Cd e Pb. Após um mês, porções de solo foram coletadas para a análise dos teores fitodisponíveis de Cd, Pb e Zn, utilizando os métodos de extração Mehlich-1 e DTPA, e pH, sendo, posteriormente, realizada a semeadura de 15 sementes de uma gramínea (Mullato II), que se trata de um cruzamento entre *B. ruzi*ensis x *B. decumbens*, para a avaliação de: i) índice de velocidade de germinação; ii) porcentagem de germinação; iii) altura; vi) massa seca das plantas. Pelos resultados encontrados, verificou-se que os tratamentos, principalmente o biocarvão de esgoto, diminuíram os teores fitodisponíveis de Cd, Pb e Zn e melhoraram o desenvolvimento das plantas em relação ao controle (solo sem tratamento).

2 REFERENCIAL TEÓRICO

Esta seção tem o objetivo de apresentar uma revisão da literatura acerca do problema pesquisado.

2.1 Lodo de esgoto

O lodo de esgoto é um resíduo semissólido, pastoso e de natureza predominantemente orgânica, oriundo das estações de tratamento de esgoto (ETE), gerado em grandes quantidades, principalmente nos grandes centros urbanos (PEDROZA et al., 2010). Seu acúmulo em pátios de secagem pode representar um grande problema ambiental.

No Brasil, apenas 39% dos esgotos são tratados (TRATA BRASIL, 2015). Na região Norte, apenas 14,7% do esgoto são tratados, sendo a pior situação entre todas as regiões. No Nordeste apenas 28,8% do esgoto é tratado, Sudeste 43,9%, Sul 43,9% e Centro-Oeste 45,9%, sendo a região com melhor desempenho; porém a média de esgoto tratado não atinge nem a metade da população (TRATA BRASIL, 2015). Considerando que a produção de lodo no Brasil está entre 150 a 220 mil toneladas de matéria seca por ano, uma vez que todos os esgotos sejam coletados e tratados no Brasil, estima-se que a sua geração supere 400 mil toneladas de lodo por ano (PEDROZA et al., 2010; VIEIRA et al., 2011).

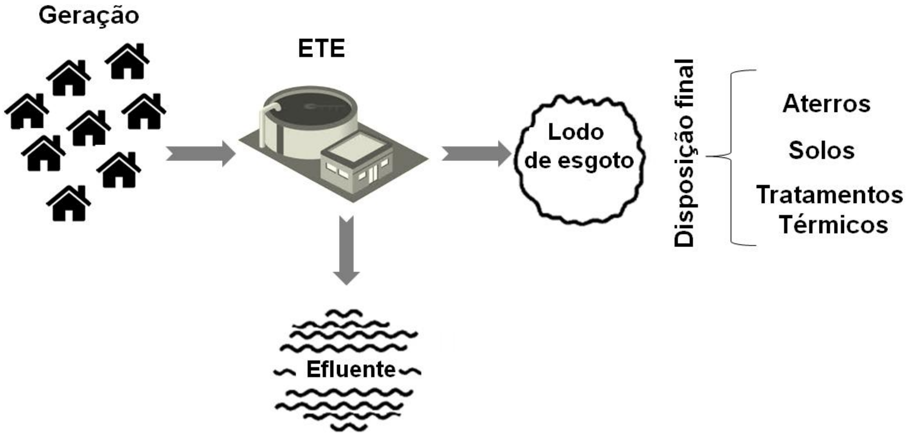
As características do lodo de esgoto dependem da qualidade do esgoto e do tipo de tratamento. Em razão das suas diferentes fontes, lodos de esgotos variam em conteúdo e composição de água, materiais orgânicos e inorgânicos (GONG et al., 2014). Em geral, o lodo de esgoto é rico em matéria orgânica e nutrientes, tais como N, P, S, Ca, Mg, K, Mn, Cu, Zn e Mo (GRAY, 2010) além de organismos patogênicos e contaminantes orgânicos e inorgânicos (MAZZEO et al., 2015). A sanidade do lodo de esgoto está relacionada com o perfil da população que gerou o esgoto, com o tipo de tratamento e com as condições ambientais às quais é submetido. Os agentes bacterianos mais frequentes são: *Salmonella spp*., *Vibrio cholarae*, *Leptosira sp*., *Shigella sp*., *Escherichia coli*. Quanto aos protozoários, são encontrados: *Cryptosporidium, Entamoebahistlytica, Giárdia lambia, Balantidium coli e Toxoplasma gondii*. Os helmintos mais frequentes são: *Ascaris lumbricoides, Ascaris sum, Toxocara sp., Trichuristrichiura, Taeniasolium, Taeniasaginata, Necator americanus e Hymenolepis nanam, Hymenolepis diminuta*. Dentre os agentes virais podem ser citados: vírus da hepatite A, rotavírus, enterovírus e reovírus (UNITED STATES OF AMERICA, 2003).

Com o aumento populacional e leis de saneamento básico mais rígidas, a disposição final dos resíduos do sistema de tratamento de esgoto tem se tornado um problema de ampla escala, considerando o descarte desses materiais ou utilização como matéria-prima, além de custos elevados. Sua gestão normalmente representa até 60% dos custos operacionais de uma ETE (KANDASAMY; ISKENDER, 2015).

A Lei 12.305, de 02 de agosto de 2010, instituiu a Política Nacional de Resíduos Sólidos e dispõe de diretrizes relacionadas à gestão e gerenciamento desses resíduos, identificando, ainda, as responsabilidades dos geradores e do setor público (BRASIL, 2010).

Dentre os objetivos da lei, destacam-se: Incentivo à indústria da reciclagem, tendo em vista fomentar o uso de matérias-primas e insumos derivados de materiais recicláveis e reciclados; proteção da saúde pública e da qualidade ambiental e, ainda, incentivo ao desenvolvimento de sistemas de gestão ambiental e empresarial voltados para a melhoria dos processos produtivos e ao reaproveitamento dos resíduos sólidos, incluídos a recuperação e o aproveitamento energético (BRASIL, 2010). Assim, com o o maior rigor nas exigências das legislações brasileiras, as estações devem destinar, de forma adequada, esses resíduos, sendo que o tratamento e a disposição do lodo devem ser geridos de forma a minimizar problemas ambientais como o odor e o lançamento de contaminantes e patógenos no ambiente. Na Figura 1, ilustra-se a geração, tratamento pelas ETEs e prováveis usos do lodo de esgoto.

Figura 1 - Geração, tratamento e disposição final do lodo de esgoto.



A forma mais comum de destinação do lodo de esgoto é em aterros sanitários ou em aterros exclusivos próximos as ETEs (DIAMANTIS et al., 2013; VIEIRA et al., 2011). Porém, esse tipo de destinação possui desvantagens, como: a exalação de forte odor, patógenos, contaminação das águas subterrâneas e poluição visual (DIAMANTIS et al., 2013). Existe uma tendência no sentido de proibir a destinação do lodo em aterros sanitários, uma vez que estudos indicam a possibilidade de reuso e sua agregação de valor em outras atividades, como o desenvolvimento de adsorventes, por exemplo (AHMAD et al., 2014). Em decorrência da sua composição em termos de matéria orgânica e nutrientes para as plantas, o lodo de esgoto pode ser também aplicado na agricultura. Quando aplicado ao solo, o lodo de esgoto pode aumentar a matéria orgânica, aumentar a fertilidade e melhorar características físicas, tais como taxa de infiltração, capacidade de retenção de água, respiração e agregação (ANGIN, 2013).

A resolução número 375 do CONAMA, de 29 de agosto de 2006, define critérios e procedimentos para o uso agrícola de lodos de esgoto gerados em estações de tratamento de esgoto sanitário e seus produtos derivados. Os valores máximos dos teores de vários elementos-traço estipulados são, em (mg kg^{-1}): As (41), Ba (1300), Cd (39), Pb (300), Cu (1.500), Cr (1.000), Hg (17), Mo (50), Ni (420), Se (100) e Zn (2.800) (BRASIL, 2006).

Outra destinação para o lodo de esgoto é a utilização de tratamento térmico em altas temperaturas, transformando-o em biocarvões. Métodos termoquímicos são alternativas promissoras para a reutilização do lodo de esgoto, quando comparado com as rotas tradicionais, em razão da sua inerente melhoria na redução do volume de resíduos e produção de energia (JAYARAMAN; GOKALP, 2015).

Alguns estudos evidenciam o uso de lodo de esgoto como matéria-prima alternativa para a produção de materiais adsorventes, gerando, assim, produtos de baixos custos e com valor agregado (HU et al., 2009; WAQAS et al., 2014; YUAN et al., 2015; ZHANG; WANG, 2016; ZIELINSKA et al., 2015). Assim, a conversão pirolítica de lodo de esgoto para biocarvão trata-se de um método promissor para gerenciar esse resíduo.

2.2 Pirólise

A pirólise é a conversão termoquímica de biomassa em ambiente sem oxigênio a temperaturas acima de 300°C (KYLECROMBI; MASEK, 2015). Sob essas condições, materiais orgânicos se decompõem em gases não condensáveis, líquidos orgânicos e um sólido carbonáceo. Como todos esses coprodutos apresentam valor agregado, a pirólise é um processo altamente eficiente para a conversão de biomassa (KYLECROMBI; MASEK, 2015). Tais coprodutos são obtidos em diferentes proporções dependendo dos parâmetros a serem levados em consideração durante a pirólise, que são a taxa de aquecimento, temperatura final, tempo de residência, a atmosfera da pirólise e o tipo de reator/forno (VAN HECKE et al., 2013)

A pirólise é basicamente constituída por duas etapas: primária e secundária. Na pirólise primária, a biomassa sofre clivagem, formando seus principais constituintes, pelo efeito do calor. Diferentes grupos carboxílicos, carbonilas e hidroxilas também são formados na primeira fase da pirólise. O processo envolve a desidratação, descarboxilação e desidrogenação da biomassa. Após a conclusão da pirólise primária, o processo de pirólise secundária é iniciado, quando ocorre o craqueamento de compostos pesados, convertendo a biomassa em carvão e gases como CH_4 e CO_2. Algumas biomoléculas volatilizadas se recondensam numa fase aquosa denominada bio-óleo (TRIPATHI; SAHU; GANESAN, 2016).

Dependendo das suas condições, a pirólise de biomassa pode ser representada pela seguinte reação:

$$(C_6H_6O_6)n \rightarrow (H_2+CO+CH_4+\cdots+C_5H_{12})_{(g)}+(H_2O+CH_3OH+CH_3COOH+\cdot\cdot)_{(l)}+C$$

Sendo que a primeira parte no lado do produto representa diferentes gases produzidos durante o processo. A segunda parte do lado do produto mostra a mistura de vários tipos de produtos líquidos e o último termo representa o rendimento sólido, ou seja, o biocarvão (PUSHKARAJ et al., 2011).

2.3 Biocarvão

Biocarvão ou biochar (do grego bios = vida e do inglês char = carvão), como é conhecido internacionalmente, é qualquer fonte de biomassa que passou por tratamento térmico na ausência de oxigênio (LEHMANN et al., 2012).

Ameaças globais tais como as alterações climáticas, a degradação do solo, contaminação ambiental e escassez de água podem levar a danos econômicos, sociais e ambientais. Por isso, o biocarvão está recebendo a atenção da comunidade política e científica, em razão de seu potencial para melhorar a produtividade do solo (LYCHUK et al., 2014), remediar ambientes contaminados (INYANG; DICKENSON, 2015) e mitigar as mudanças climáticas (WOOLF et al., 2010). Tais benefícios, acompanhados com o fato de que o biocarvão pode ser produzido por várias fontes de biomassa de baixo custo, estimulam pesquisas sobre biocarvão (JEFFERY et al., 2015).

Srinivasan et al. (2015) investigaram a conversão de vários tipos de biomassa (serragem de pinho, grama, cama de frango, lodo de esgoto) para a produção de biocarvão e encontraram que tal conversão constitui uma solução de gestão de resíduos eficaz, viável e ecologicamente correta, uma vez que é possível reutilizar resíduos e proteger o ambiente de contaminantes.

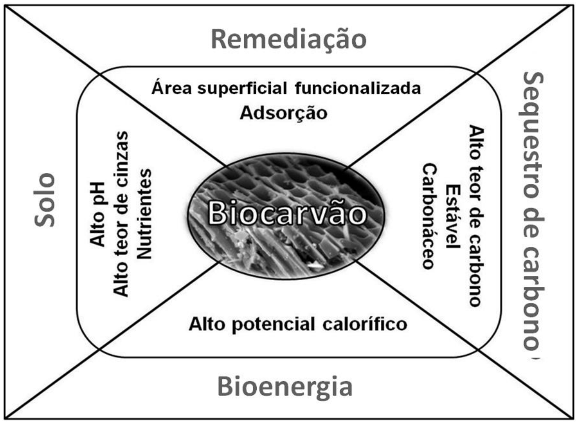
2.3.1 Biocarvão de lodo de esgoto

Um dos estudos pioneiros no emprego de lodo de esgoto pirolisado para fins de redução de poluentes foi realizado por Beeckmans e Ng em 1971. Os autores mostraram a capacidade de adsorção do biocarvão de lodo de esgoto na remoção do corante orgânico violeta de cristal, considerando a aplicação potencial desse material no tratamento das águas residuais (BEECKMANS; NG, 1971).

Atualmente, muitos estudos vêm sendo realizados com biocarvão de lodo de esgoto com ampla variedade de aplicações ambientais, por exemplo, adsorção de HPAs (KHAN et al., 2015), aplicação no solo (YUAN et al., 2016), captura de amônia (ZHANG; WANG, 2016), catalisadores (YUAN et al., 2013), adsorção de metais pesados (ROZADA et al., 2008). Caracterizações e compreensão das propriedades (AGRAFIOTI et al., 2013; GAO et al., 2014) são necessárias. Em uma situação de crescente interesse no uso do lodo de esgoto para a produção de biocarvão, é importante analisar como as propriedades iniciais do lodo determinam as propriedades dos biocarvões produzidos. Zielinska et al. (2015) encontraram que não só as propriedades do lodo, mas também a temperatura de pirólise apresentam papel importante no controle das propriedades do material carbonáceo final.

A escolha do biocarvão para diferentes aplicações depende da função de destino. Na Figura 2, exemplificam-se as várias aplicações para biocarvões com base em suas propriedades específicas, como obtido pelo trabalho de Srinivasan et al. (2015).

Figura 2 - Diferentes aplicações de biocarvões e a relação com suas propriedades.



Fonte: Adaptado de Srinivasan et al. (2015)

2.4 Materiais carbonáceos com área superficial funcionalizada: aplicação na remediação ambiental

A utilização de biocarvões funcionalizados como adsorventes tem aumentado, em razão da sua estrutura porosa e a natureza química da superfície. Assim, um número crescente de pesquisas tem sido direcionado tanto para o desenvolvimento de métodos de modificações das propriedades químicas da superfície quanto para a porosidade dos materiais compostos por carbono (ARAÚJO et al., 2016).

Muito embora possam, eventualmente, ocorrer em etapas separadas, em que a ativação ocorre em processo separado da funcionalização, novos estudos apontam para métodos de funcionalização/ativação que sejam concomitantes. Nesse contexto, esses processos podem ser divididos em químicos e físicos com base nas interações entre as moléculas ativas e os átomos de carbono da matriz orgânica. Dentre eles, a funcionalização química baseia-se na ligação covalente entre as entidades funcionais e o carvão final (MA et al., 2010).

2.4.1 Processos de funcionalização/ativação da superfície

Carvões ativados são considerados excelentes adsorventes para uma ampla variedade de contaminantes, em razão de suas estruturas e funcionalidades (BANDOSZ, 2006). A estrutura porosa dos carvões ativados pode ser manipulada, por meio da alteração dos parâmetros de ativação, tais como o tipo de ativação (física e/ou química), agente de ativação (proporção de impregnação) e pirólise (temperatura, tempo etc) (MARSH, 2006).

Ros et al. (2006) realizaram tanto ativações físicas quanto químicas no lodo de esgoto e concluíram que a ativação física é ineficaz para a preparação de adsorventes adequados, enquanto que ativações químicas aumentam a área de superfície específica, que é comparável com os carvões ativados comerciais utilizados para o adsorção de poluentes. Vários agentes oxidantes, tais como o $ZnCl_2$, H_2SO_4, H_3PO_4, KOH e NaOH têm sido utilizados para a modificação química de lodos (HUNSOM; AUTTHANIT, 2013; NUNTHAPRECHACHAN; PENGPANICH; HUNSOM, 2013).

Chen, Jeyaseelan e Graham (2002) constataram que o carvão ativado proveniente de lodo de esgoto é um adsorvente promissor com propriedades distintas e acredita-se ser seguro na maioria das aplicações de tratamento de efluentes industriais. Fan e Zhang (2008) encontraram que carvão ativado a partir de lodo de esgoto exibiu maior capacidade de adsorção do corante orgânico *alkaline black* quando comparado com carvão ativado comercial, mesmo sendo o carvão ativado comercial mais microporoso.

A funcionalização da superfície de biocarvões pode melhorar suas capacidades de adsorção de íons metálicos. Um aspecto importante é o controle da sua química de superfície (GODINO-SALINO et al., 2009).

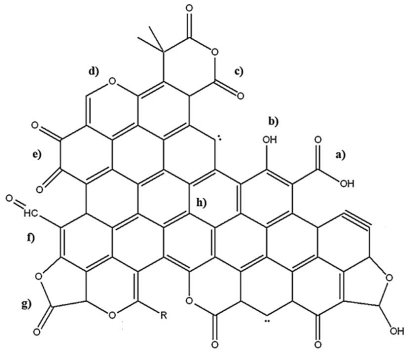
Decorrente de uma química de coordenação flexível, existem infinitas possibilidades de estruturas, possuindo boa habilidade de reagir com outros heteroátomos, tais como fósforo. Tais heteroátomos podem exercer grande influência nas propriedades físico-químicas dos carvões, principalmente considerando as especificidades de cada aplicação (BANDOSZ, 2006).

2.4.2 Desenvolvimento de poros e funcionalização da superfície mediado pelo H_3PO_4

Os biocarvões preparados por ativação química utilizando ácido fosfórico contêm quantidades elevadas de complexos de fósforo estáveis, que apresentam algumas propriedades interessantes, tais como resistência à oxidação e acidez superficial elevada (ROSAS et al., 2012).

A química de superfície de materiais de carbono é governada por átomos de carbono basais ou de bordas, bem como pela presença de defeitos. Essas imperfeições e defeitos, ao longo das bordas das camadas de grafeno, são os sítios mais ativos, em razão da elevada densidade de elétrons desemparelhados. A estrutura física dos carvões possuem anéis aromáticos, ou seja, carbonos de hibridização sp^2, unidos por interações de Van der Waals (BANDOSZ, 2006). Em relação às funcionalidades, grupos oxigenados, tais como ácidos carboxílicos, lactonas e fenóis, são os mais comuns e proporcionam caráter ácido ao carvão. Na Figura 4, são ilustradas as espécies oxigenadas presentes na superfície de carbono.

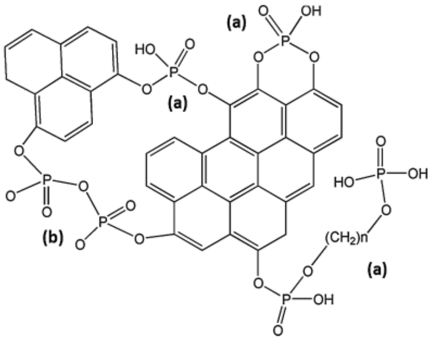
Figura 3 - Espécies oxigenadas presentes na superfície de carbono: (a) ácido carboxílico, (b) fenol, (c) anidrido carboxílico, (d) éter, (e) quinona, (f) aldeído, (g) lactona e (h) a densidade de elétrons π sobre o plano basal.



Fonte: Adaptado de Bandosz (2006).

O fósforo é utilizado como agente ativante, pois atua na clivagem das ligações, formando pontes de fosfato e polifosfatos que se distribuem ao longo da matriz, levando a uma estrutura porosa (BANDOSZ, 2006). Na Figura 5, ilustram-se as espécies de fósforos presentes na superfície de carvões funcionalizados.

Figura 4 - Estrutura de compostos de fósforo-carbono como descritos na literatura: (a) ésteres fosforocarbonáceos, e (b) espécies de pirofosfato.



Fonte: Adaptado de BANDOSZ (2006).

Materiais de carbono contendo fósforo mostram um número de características específicas, tais como (i) grupos superficiais ácidos, (ii) propriedades de adsorção iônica e (iii) aumento da estabilidade (AXET et al., 2016).

2.4.3 Biocarvão aplicado em processos de adsorção de cromo hexavalente em meio aquoso

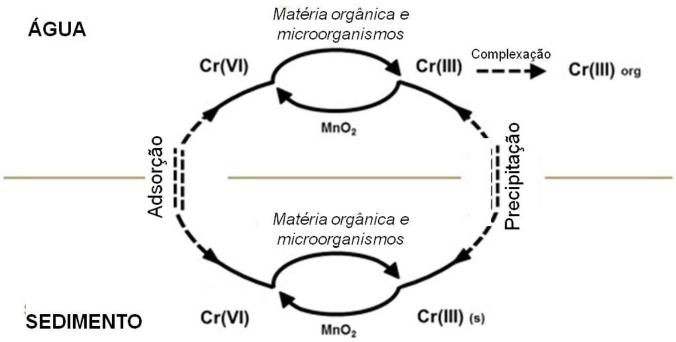
Cromo (Cr) e seus compostos são liberados em ambientes aquáticos, tanto através de fontes antropogênicas quanto por processos naturais. Em combinação com outros elementos, o Cr ocorre, naturalmente, no meio ambiente. As fontes naturais que contribuem para um aumento de sua concentração em sistemas aquáticos são: desagregação das rochas, precipitação úmida e atmosférica (por exemplo, poeira vulcânica e incêndios florestais). As atividades industriais também contribuem para a contaminação ambiental com Cr. Aplicações incluem curtimento de couro, inibição de corrosão metálica, lama de perfuração, corantes têxteis, catalisadores, madeira e tratamento da água (DHAL et al., 2013).

Grandes quantidades de compostos de cromo são liberadas para o meio ambiente, o que acarreta em efeitos adversos sobre o ecossistema. A toxicidade, biodisponibilidade e propriedades de transporte dependem da forma específica na qual o cromo esteja presente no ambiente. Diferentes espécies de Cr possuem formas antagônicas de comportamento. Os dois estados de oxidação mais comuns de cromo são Cr(III) e Cr(VI).

Em geral, compostos de Cr(III) são relativamente imóveis e pouco solúveis em comparação com a elevada mobilidade e solubilidade do Cr(VI), sendo, consequentemente, os compostos mais biodisponíveis de Cr. Essas diferenças estendem-se também quanto à reatividade química e bioquímica de ambas as espécies. Cromo (III) é um nutriente essencial para o corpo humano. Em contraste, o Cr(VI) é tóxico, em razão de seu elevado potencial de oxidação e a capacidade de penetrar nas membranas biológicas (DHAL et al., 2013).

Ao examinar a distribuição das espécies de cromo em ambientes aquáticos, percebe-se a sua solubilidade e capacidade de ser absorvido por materiais do solo ou aquíferos. Esses fatores são regidos pela química desse tipo de água e pelas propriedades do ambiente. As transformações e movimento das espécies de cromo no ambiente são ilustrados na Figura 6.

Figura 5 - Ciclo do Cr no sistema água-sedimento.



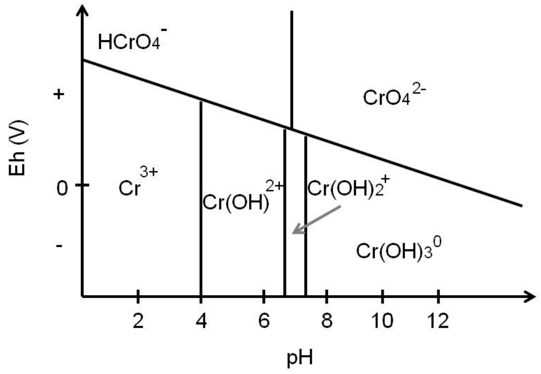
Fonte: Adaptado de Markiewicz et al. (2015)

Em geral, o Cr(III) é imóvel na maioria das águas subterrâneas em virtude da formação de compostos fracamente solúveis. Cromo hexavalente, por sua vez, tende a ser a forma mais móvel do Cr em ambientes aquáticos. A oxidação de Cr(III) a Cr(VI) é limitada pela concentração de cromo solúvel, o pH, a área de superfície disponível e a força iônica (MARKIEWICZ et al., 2015).

O equilíbrio químico entre as espécies de Cr depende fortemente do valor de pH. Em soluções mais ácidas (pH~4), Cr(III) é a espécie predominante e sua hidrólise gera $Cr(OH)^{2+}$ e $Cr(OH)_2^{+}$. Dentro de um intervalo de pH de neutro até alcalino, o Cr(III) tende a se precipitar como $Cr(OH)_3$. Como consequência, em um intervalo de pH típico para águas naturais (variando de pH 4 a 9), $Cr(OH)_2^{+}$ e $Cr(OH)_3$ são as formas predominantes. No caso de Cr(VI), H_2CrO_4 é observado apenas abaixo de pH 2. Como um resultado da sua dissociação, os seguintes produtos são formados: $HCrO_4^{-}$ a um pH variando de 1 a 6, enquanto CrO_4^{2-} é encontrado em valores de pH superiores a 6,5.

O potencial redox (Eh) e o pH desempenham um papel crucial na interconversão dos dois estados estáveis de cromo. Na Figura 7, mostra-se o diagrama com o comportamento de Cr(III) e Cr(VI) para as espécies de cromo em ambientes aquáticos. Sob condições acídicas, o Cr(VI) exibe um elevado valor positivo de Eh, o que significa que é um agente oxidante forte e é facilmente reduzido por doadores de elétrons, tais como matérias orgânicas ou inorgânicas. Em pH neutro, a proporção Cr(III)-Cr(VI) está relacionada com a oxigenação da solução. Já, em alcalinos, o carácter oxidante do cromo hexavalente é muito menos eficaz e, portanto, tem uma tendência a permanecer nesse estado, em vez de ser reduzido (MARKIEWICZ et al., 2015).

Figura 6 - Espécies trivalentes e hexavalentes de cromo em ambientes aquáticos em função do Eh vs pH, assumindo a presença de a penas H_2O, OH^- e concentração de Cr total = 10^{-6} mol L^{-1}.



Fonte: Markiewicz et al., 2015

Estudos epidemiológicos mostraram que a exposição a Cr (VI) pode induzir uma variedade de problemas clínicos como, por exemplo algumas doenças dérmicas (MARJIEWICZ et al., 2015).

De acordo com os padrões de água potável estabelecidos pela Agência de Proteção Ambiental dos Estados Unidos, o nível admissível de cromo é de 0,10 mg L^{-1} (UNITED STATES OF AMERICA, 2004). Já, nos efluentes, o limite de Cr(VI) em águas é regulado abaixo de 0,05 mg L^{-1} pela USEPA e a União Europeia, enquanto Cr total, incluindo Cr(III), Cr(VI) e suas outras formas, é regulada inferior a 2,0 mg L^{-1} (BARAL; ENGELKEN, 2002). No Brasil, a resolução 397 do CONAMA estabelece limites máximos de lançamento de Cr(VI) e Cr(III) em efluentes de 0,1 mg L^{-1} e 1,0 mg L^{-1}, respectivamente (BRASIL, 2008).

Como medida de remediação de ambientes contaminados com cromo, estudos mostram que biocarvão é uma alternativa viável para a utilização em processos de adsorção de Cr em solução (CHEN et al., 2015; LIOU, 2010).

2.5 Materiais carbonáceos com elevado teor de cinzas: aplicação no solo

A aplicação de biocarvão ao solo é amplamente defendida por uma variedade de razões relacionadas com a sustentabilidade. Os benefícios incluem: 1) sequestro de carbono, 2) melhoria da fertilidade do solo, em razão dos nutrientes encontrados no material, 3) imobilização de poluentes e 4) gestão de resíduos (JEFFERY et al., 2015).

Nesse contexto, são duas as principais vantagens do biocarvão de lodo de esgoto: ser livre de patógenos e melhorar a estrutura, auxiliando ainda nas propriedades biológicas e na qualidade do solo (ROGOVSKA et al., 2014). Paz-Ferreiro et al. (2012) mostraram que a aplicação de biocarvão de lodo de esgoto tem maior efeito sobre a qualidade do solo do que a aplicação de lodo de esgoto *in natura*.

2.5.1 Metais pesados em solos

Os poluentes podem exercer efeito tóxico ao ecossistema, principalmente, considerando a lixiviação, por meio do perfil solo para as águas subterrâneas, bem como a transferência para as culturas/biota. Metais pesados poluentes, tais como Cd, Pb e Zn causam impactos negativos aos ecossistemas. Tais elementos podem ser encontrados tanto naturalmente nos solos, por exemplo, quando provenientes de processos naturais tais como intemperismo de rochas e lixiviação no perfil do solo quanto por razões antrópicas, como, por exemplo, atividades de mineração (GUILHERME et al., 2005; KABATA-PENDIAS; PENDIAS, 2000).

A legislação brasileira estabelece três valores orientadores considerando os teores de metais pesados no solo: Valores Orientadores de Referência de Qualidade (VRQs), de Prevenção (VP) e de Investigação (VI) (BRASIL, 2009). Valores orientadores são concentrações de substâncias químicas que fornecem orientação sobre a qualidade e as alterações do solo e da água subterrânea. O valor de Investigação (VI) representa o valor acima do qual haverá risco à saúde humana e ao desenvolvimento dos demais organismos vivos. O Valor de Prevenção representa um valor intermediário entre o VRQ e o valor de investigação (VI), sendo o valor limite de metal no solo, que não interfere em sua capacidade de comprometer suas funções (BRASIL, 2009).

Na Tabela 1, abaixo, indicam-se os valores orientadores estabelecidos pelo CONAMA para Cd, Pb e Zn em solos. Os valores de qualidade são determinados de acordo com o Estado (BRASIL, 2009).

Tabela 1 - Valores orientadores para solos (BRASIL, 2009).

	VP	VI[*]
	------------ mg kg^{-1}	------------
Cd	1,3	20
Pb	72	900
Zn	300	2.000

[*] Para áreas industriais

2.5.2 Atividades de mineração e a contaminação por metais pesados

As atividades de mineração exercem papel importante para a economia e trazem benefícios tanto para a sociedade quanto para o desenvolvimento do país. Entretanto, tanto atividades de extração quanto de beneficiamento de metais, promovem grande contaminação do ambiente por metais pesados, gerando áreas degradadas com grandes quantidades de rejeitos. Tais contaminações trazem prejuízo ao solo e ao ecossistema, uma vez que esses poluentes podem ser transferidos para a água, plantas e outros meios (GALL; BOYD; RAJAKARUNA, 2015)

A área de mineração de Zn de Vazante, localizada no Estado de Minas Gerais (MG), Brasil, é um dos maiores depósitos não- sulfídricos de zinco conhecidos do mundo (HITZMAN et al., 2013). Esse depósito é responsável por uma importante parcela da produção de Zn no Brasil (MONTEIRO et al., 2006).

Os metais pesados em solos podem estar associados a diversas formas químicas. Em solos não poluídos, esses metais estão contidos principalmente nos minerais primários ou ligados a óxidos, formando espécies com baixa mobilidade. Porém, solos que sofrem ações antrópicas, como as atividades de mineração, possuem a tendência de apresentar formas mais móveis de metais pesados, que podem representar frações disponíveis para plantas. Borges Júnior et al. (2008), ao avaliar a distribuição e as formas de ocorrência de Zn para identificar a origem de valores anômalos em solos adjacentes a áreas de mineração no município de Vazante-MG, encontraram teores altos de Zn. Além do Zn, os elementos-traço Pb e Cd podem também estar presentes em altas concentrações em áreas de beneficiamento de zinco. Lopes et al. (2015) investigaram extrações únicas e sequências de Zn, Pb e Cd em solos da área de beneficiamento de Zn, naquela mesma cidade e encontraram altos teores totais desses elementos nos solos e diferentes distribuições, considerando o fracionamento nas seguintes formas: a) fase trocável, b) ligados a carbonatos, c) ligados a óxidos facilmente redutíveis, d) ligados à matéria orgânica, e) ligados a óxidos redutíveis e f) fração residual. Métodos de extrações sequenciais são importantes, pois fornecem informações sobre a mobilidade e disponibilidade dos elementos.

Biocarvões possuem grande potencial para a remediação de solos contaminados por atividades de mineração, uma vez que podem reduzir a contaminação e minimizar danos causados ao meio ambiente. Zhu et al. (2014) descobriram que a adição de biocarvão no solo ácido, altamente intemperizado, influenciou na germinação das sementes, crescimento das plantas, cobertura vegetal, bem como na eficiência do uso de nitrogênio e potássio.

3 OBJETIVO

Conduziu-se, este estudo, com o objetivo de produzir, caracterizar e avaliar o potencial remediador de biocarvão produzido a partir da pirólise do lodo de esgoto, em ambientes contaminados por metais pesados. Foram produzidos dois artigos científicos, apresentados no capítulo a seguir.

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SEGUNDA PARTE – ARTIGOS

ARTIGO 1 - CHROMIUM ADSORPTION ONTO FUNCTIONALIZED SEWAGE SLUDGE BIOCHAR

(VERSÃO PRELIMINAR)

Artigo redigido conforme regras gerais da Elsevier

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Highlights

- Production of biochar is a way of recycling and adding value to sewage sludge;
- Treatment with H_3PO_4 increased adsorption capacity and functionalized the biochar surface;
- Temperature and pH are determinant factors for the removal of Cr(VI) from solution;

Abstract

Initially only used in agriculture, the range of uses for biochar now covers a wide range of different fields. Biochar has been prepared from sewage sludge of a municipal wastewater treatment plant. The aim of this work was to study the adsorption of chromium onto biochar and active biochar that has been treated with H_3PO_4 by investigating the effects of adsorbent dose, pH, contact time and temperature. An adsorption mechanism was proposed. The surface of the biochar was functionalized with phosphorus compounds, resulting in an active biochar with higher Cr(VI) removal capacity when compared to non-active biochar. Chromium (VI) removal increases under acidic conditions and equilibrium data (at 25°C) fitted well with SIPS isotherm. Temperature and pH are determinant factors for the removal of Cr(VI) from solution, which strongly increases at lower pH values and increases with the increase of temperature. Both Cr(III) and Cr(VI) was found on the biochars surface. The adsorption mechanism onto the biochar surface involves both complexation and electrostatic reactions.

Keywords: Hexavalent chromium, sewage sludge biochar, surface functionalization

Introduction

In recent years sewage sludge is being generated in large quantities due to population growth and higher effluent criteria implemented by the authorities. Sewage sludge is the solid or semi-solid that results from the treatment of domestic and/or industry wastewater in sewage treatment plants (Qian et al., 2016).

The characteristics of sewage sludge depend on the quality of sewage and type of treatment. In general, sewage sludge is a residue composed by organic matter, nitrogen, phosphorus, potassium, calcium, sulphur and magnesium (Gray et al., 2010). However, it can also contain pathogens, inorganic as well as organic contaminants (Mazzeo et al., 2015; Kulling et al., 2001). Therefore, appropriate final disposal of sewage sludge has been considered an environmental issue.

The most common form of disposal of sewage sludge is in landfills. However, this kind of allocation has disadvantages, as the exhalation of strong odor, pathogens, groundwater contamination and visual pollution (Diamantis et al., 2013). Due to its composition in terms of organic matter and plant nutrients, sewage sludge can also be applied to soils. The drawbacks regarding soil application are the pathogens and the availability of potential toxic metals, which often restricts its uses (Angin, 2013; Singh; Agrawal, 2008).

Because sewage sludge is carbonaceous in nature and rich in organic materials, its conversion into biochar can be a cost-effective potential method for its disposal and reuse. Biochar is a carbon rich solid by-product resulting from the pyrolysis of biomass under oxygen-free conditions (Lehmann, 2007; Tripathi et al., 2016).

Thermochemical methods, such as pyrolysis, are promising alternatives for sewage sludge reuse, due to its inherent improvement in the reduction of waste volume level and energy production Jayaraman; Gokalp, 2015).

Turning sewage sludge into biochar also eliminates pathogens and hazardous compounds present in the raw sewage sludge (Harder et al., 2016; Clarke; Smith, 2011). Earlier research shows that when converting sewage sludge into biochar, the bioavailability and mobility of heavy metals is reduced in biochars compared to raw sewage sludge (Hossain et al., 2010). The use of biochar as a cost effective sorbent for heavy metal adsorption from contaminated water and soils have been reported (Inyanga et al., 2015; Xie et al., 2015; Mohan et al., 2011; Ahmad et al., 2014). Surface functionalization of biochars can improve their adsorption capacities to metal ions. An important aspect in designing suitable active biochars for metal ion-capture is the control of their chemical surface (Godino-Salino et al., 2009).

Industrial effluents contain a variety of toxic heavy metals ions that cause contamination of water. Due to its accumulation in the environment and toxicity for plants and humans, heavy metals are of great concern among public and regulatory authorities. The presence of heavy metals, such as Cr, in the environment is a major concern due to their toxicity because, unlike organic pollutants that are mostly susceptible to biological degradation, metals do not degrade, remaining in the environment for years, posing long-term risks to life (Keng et al., 2014).

Chromium is introduced into the environment both naturally, by volcanic activity, mineral weathering and erosion and by industry, which includes mining, smelting, fossil fuels combustion, solid waste incineration and the manufacture (Krause-Nehring; Brey, 2012).

In aquatic environments chromium is present mainly as hexavalent and trivalent species. The toxicological properties of chromium depend strongly on its oxidation state (Markiewicz et al., 2015). Chromium (III) is considered an essential nutrient for many organisms (Pechova, 2007). Hexavalent chromium, however, can cause severe environmental and public health problems. Cr(VI) is highly soluble and mobile and is found in the form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions (Hu et al., 2009).

The Agency for Toxic Substances and Disease Registry (ATSDR) classifies Cr (VI) as top 17th hazardous substance. Because of Cr(VI) severe toxicity, the World Health Organization (WHO) and US Environmental Protection Agency (USEPA) set the maximum permissible limit of chromium in drinking water at 0.05 mg L^{-1}.

Many processes have been reported to eliminate Cr(VI) from aqueous solutions, for example, chemical electrochemical precipitation, ion exchange, membrane separation, reverse osmosis, nanofiltration and adsorption (Jain et al., 2015; Yoon et al., 2009; Al-Rashdi et al., 2013; Akbal et al., 2013). Among them, adsorption is the most effective and widely used technique for Cr(VI) removal due to its low operation cost, easy handling, short operation time and no formation of secondary toxic compounds (Xu et al., 2014; Di Natale et al., 2015).

Herein, a study on the adsorption of chromium on active and non-active biochar produced from sewage sludge, which is a low-cost locally available biomass, were conducted to determine the efficiency in removing chromium from aqueous solution. The effects of adsorbent dose, pH, contact time and temperature were investigated and an adsorption mechanism was proposed.

Experimental

1 Sewage Sludge

Sewage sludge was obtained from the municipal wastewater treatment plant, located in Vazante, Minas Gerais, Brazil (coordinates 17.98ºS e 46.9°W). Prior to analysis and pyrolysis, dewatered sludge was dried at room temperature, crushed and sieved (2 mm). The sample was then dried at 60˚C for 48 hours and stored in air tied plastic bags.

2 Sewage Sludge biochar preparation

The preparation of active biochar from sewage sludge can be divided into three stages, including base-leaching, activation, and acid-washing. Firstly, the sewage sludge was washed with 0.5 mol L^{-1} NaOH and heated in a round bottom flask at 100˚C for 1 h. The basic solution was filtered and the remaining solid was washed with distilled water for complete base removal, reaching pH 7. The material was dried at 105˚C for 24 h and concentrated H_3PO_4. The impregnation ratio was 1:2 (biochar weight: H_3PO_4) based on the results from Liou (2010). The material was oven dried for 24 h to remove residual water.

The impregnated material was then subjected to a heat treatment in a tubular furnace under inert atmosphere of N_2 at a flow rate of 100 mL min^{-1} and temperature ramp of 10˚C min^{-1} from room temperature to 500˚C and remained at this temperature for 2 hours. The char was then washed with distilled water until it reached neutrality. Lastly, the washed samples were dried at 105˚C and ground to form powder.

Only the pyrolysis step, under the same conditions mentioned above, was applied to the non-active sewage sludge char.

The yield of the process was calculated according to equation 1

$$\text{Yield (\%)} = \left(\frac{w_2}{w_1}\right) \times 100 \tag{1}$$

where w_1 corresponds to dry sewage sludge weight before pyrolysis and w_2 is the weight of the produced biochar.

Herein, sewage sludge is identified as SS, non-active sewage sludge biochar as SSB and active sewage sludge biochar as ASSB.

3 Biochar characterizations

Samples were mixed with distilled water in a ratio of 1:2.5 and agitated for 30 min and then conductivity and pH were measured. The pH drift method, developed for activated carbons, was used to determine the point of zero charge (pH_{PZC}). Biochars were washed with 0.1 mol L^{-1} HCl (26 $g_{biochar}$ L^{-1}), stirred during 1h, rinsed with distilled water and dried over night (60˚C). This step is important because it removes potential side effects on pH drift from salt dissolution processes. Thereafter, 5 mmol L^{-1} $CaCl_2$ solution was boiled to remove CO_2, cooled to room temperature (25˚C) and 20 mL was placed in contact 0.06 g of each biochar, with pH ranging from 2 to 10 (pH was adjusted using either 0.5 mol L-1 HCl or NaOH), agitated during 24 hours. The final pH was measured and plotted against initial pH. The pH_{PZC} of biochar was determined when $pH_{final} = pH_{initial}$ (Bayazit; Kerlez, 2014). The contents of C, H and N in biochar were determined by elementary analysis (EuroVector EURO EA 3000 Elemental Analyzer). Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX – model Zeiss LEO EVO 40 XVP) was used to characterize the chemical composition and structural morphologies of the materials. Biochar nitrogen adsorption analysis to calculate BET surface was carried out at 77 K (Quantachrome Instruments). Thermal stability was determined through thermogravimetric analysis (TGA) (Shimadzu DTG50). The analysis was carried out by rising temperature from room temperature to 800˚C, at a heating rate of 10°C min^{-1}, using either nitrogen or synthetic atmosphere. FTIR was used to identify the functional groups on the raw sludge and on biochars before and after Cr(VI) adsorption. The spectra were investigated in the 4000 - 400 cm^{-1} region under a 4 cm^{-1} resolution by using a Digilab Excalibur, FTS 3000. Biochar surface acid functional group distribution was determined using the Boehm titration method, as described by Goertzen et al. (2010). X-ray photoelectron spectroscopy (XPS) was performed to analyze the composition and chemical state of the surface elements of the materials using a UNI-SPECS UHV with k alpha Mg source, h_v 1253.6eV.

4 Bach adsorption experiments

Batch adsorption studies with active and non-active biochars were conducted to investigate the parametric effects of contact time, pH, mass of char and temperature. Chromium stock solution of 1000 mg L^{-1} of Cr(VI) was prepared by dissolving potassium dichromate ($K_2Cr_2O_7$, reagent grade) in distilled water and diluted to the required concentrations before use.

The effect of biochar dose was studied in the range of 0.5 - 8 g L^{-1} at 5 mg L^{-1} of Cr(VI) without pH adjustment. In order to investigate the pH influence on the adsorption process, the pH of the solution was adjusted to desired values, ranging from 2.0 to 8.0, with either 0.1 mol L^{-1} NaOH or 0.1 mol L^{-1} HCl and a dose of char of 1 g L^{-1} and 5 g L^{-1} Cr(VI) solution was used. To evaluate the effect of time on Cr adsorption, a kinetic experiment was carried out using a 5 mg L^{-1} Cr(VI) solution at constant pH of 2.0 and sorbent dose of 1 g L^{-1} at 25°C. The solutions were agitated and drawn from the mixture at pre-determined regular time intervals. For isotherm studies, a dose of adsorbent of 1.0 g L^{-1} was added to Cr(VI) solutions with initial concentration ranging from 5–50 mg L^{-1} at pH 2 and at a choice of temperature (15 – 40°C) in a water bath coupled with a magnetic shaker.

For all tests, after the asorption equilibrium was reached, the solution was separated from the char by membrane filtration (Millipore 0.45 μm pore size). Control tests were run in parallel, without addition of sorbent, for comparison. Each test was replicated three times and the average values of the measured variables were considered.

4.1 Isotherms and fitting

The amount of Cr(VI) adsorbed per unit mass of adsorbent was calculated from the following expression:

$$q_{eq} = \frac{(C_0 - C_{eq}) \times V}{m} \tag{2}$$

where q_e (mg g^{-1}) was the amount of Cr(VI) adsorbed; C_0 and C_{eq} (mg L^{-1}) were the initial and equilibrium Cr(VI) concentrations in the aqueous solution; V (L) was the volume of the solution and m (g) was the adsorbent dose.

Isotherm models are widely employed for fitting the data. The Langmuir (1916) and Freundlich (1906) equations are most widely used to examine the relationship between the amount sorbed (q_e) and the aqueous concentration C_e at equilibrium.

Langmuir equation may be written as:

$$q_e = \frac{Q^0 b C_e}{1 + b C_e} \tag{3}$$

where C_e is the equilibrium concentration (mg L^{-1}); q_e the amount of metal ion sorbed (mg g^{-1}); Q^0 the amount of metal ion adsorbed for a complete monolayer (mg g^{-1}); b is the sorption equilibrium constant.

The Freundlich equation may be written as:

$$q_e = K_F C_e^{1/n} \tag{4}$$

The constants K_F and 1/n of the Freundlich model are the constants indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}) and the constant indicative of the intensity of the adsorption, respectively.

By studying the distribution of adsorption energies of the sites of an adsorbent surface, Robert Sips (1948) proposed an empirical isotherm equation, expressed as

$$q_e = Q^0 \frac{kC_e^{ns}}{1+kC_e^{ns}} \tag{5}$$

which n_s is the Sips constant.

4.2 Thermodynamics

The enthalpy, ΔH° (kJ mol^{-1}), the free energy ΔG° (kJ mol^{-1}) and entropy ΔS° (kJ mol^{-1} K^{-1}) for the adsorption process can be calculated using the following equations.

$$\Delta G° = -RT\ln k_{ads} \tag{6}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{7}$$

where $\ln k_{ads}$ is the Langmuir constant b multiplied by the water density (10^6 mg L^{-1}), as described by Yu et al. (2015), R is the gas constant (8.31 J mol^{-1} K^{-1}) and T is the temperature.

The Van't Hoff equation can therefore be derived from both equations above

$$\ln k_{ads} = -\frac{\Delta H^\circ}{R}\left[\frac{1}{T}\right] + \frac{\Delta S^\circ}{R} \qquad (8)$$

From the Van't Hoff plot between ln k versus 1/T the values of ΔH° and ΔS° can be determined from the slope and intercept respectively.

5. Chromium analysis

The concentrations of Cr(VI) were analyzed by measuring the absorbance of the purple complex of Cr(VI) with 1,5 diphenylcarbohydrazide at 540 nm using a UV spectrophotometer (Shimadzu Corporation, 1800).

To determine the total chromium, Cr (III) was converted to Cr(VI) at high temperature (120°C) by adding potassium permanganate (20 g L^{-1}). Sodium azide (2 g L^{-1}) was slowly added to remove the excess of potassium permanganate until the solution was yellowish or transparent (depending on the Cr(VI) concentration). Cr(III) was obtained by difference.

Results and discussion

The yield of biochar was determined as the ratio of the produced biochar weight to the dry weight of sewage sludge subjected to pyrolysis. For the active biochar (ASSB), the yield was calculated by subtracting the chemical reagent weight from the biochar mass that was produced. The yield of non-activated biochar (SSB) was 54% and 49% for active biochar (ASSB).

Zhang and Wang (2016) reported a yield of 32.2 (wt%) when converting sewage sludge into biochar through pyrolysis at 500˚C, nitrogen flow of 50 cm^3 min^{-1}, heating rate of 5˚C min^{-1}, carried out with ceramic cups in muffle furnace. By loading the sewage sludge sample in a horizontal quartz reactor placed in an electrical furnace at 500˚C, with 1000 mL min^{-1} flow rate of nitrogen, Yuan et al. (2015) obtained a yield of 69.5% for sewage sludge biochar production. Zielińska et al. (2015) subjected sewage sludge to the process of pyrolysis in a furnace of own construction, at 500˚C, heating rate of 25˚C min^{-1} with constant flow of nitrogen, for 5h (slow pyrolysis) and found yields ranging from 45.07 to 54.29%. Furthermore, the pyrolysis yields obtained in this work were distinctly higher than those found by (Lu et al., 2013; Grafioti et al., 2013; Gao et al., 2014), at the same temperature (500˚C) and nitrogen atmosphere.

Since pyrolysis transforms sewage sludge into three different components: water vapor, biogas and biochar in different proportions, biochar production depends on both the feedstock composition and the pyrolysis conditions. For example, Lu et al. (2013) observed that the sludge from a waste water treatment plant with pure domestic wastewater influent and less mixed industrial wastewater produced the highest biochar yield due to differences in chemical composition (ash content).

Biochars Characteristics

Table 1 shows the compositions and properties of sewage sludge (SS) and biochars before and after adsorption. The active biochar (ASSB) have less C, compared to sewage sludge and non-active biochar (SSB). Chromium adsorption did not change the contents of C, H and N.

Table 1. Composition and properties of sewage and biochars before and after adsorption

	pH	pH_{PZC}	BET	C	H	N
			m^2g^{-1}	----------	%	----------
SS	6.00	-	5.18	20.1	4.6	10.4
SSB	8.23	7.79	46.47	19.5	1.2	2.0
SSB_{Cr}	8.17	7.50	16.97	19.0	1.0	1.9
ASSB	7.89	7.50	42.69	11.7	0.8	0.6
$ASSB_{Cr}$	7.20	6.60	7.65	11.9	0.7	0.6

The point of zero charge (pH_{pzc}) is important when considering adsorption process and it describes the condition when the balance of electrical charge density on a surface is zero. The pH_{pzc} values of the biochars are show in Table 1. The surface of biochar is mainly positively charged when pH is below the pH_{pzc}. Thus, a significant electrostatic attraction existed between the positively charged surface and the Cr(VI) ions, which was in favor of the adsorption of chromium ions since Cr(VI) existed in different anionic forms in solution.

The surface characteristics of sewage sludge and biochars before reaction with Cr(VI) are shown in Fig. 1. The raw sewage sludge (SS) has an aspect of decomposed organic matter (Fig. 1a) and both biochars (active (ASSB) and non-active (SSB)) have a rough surface and a more porous structure compared to raw sewage sludge, which is due to the release of volatile matter out of the biomass. Furthermore, the chemical treatment process generated cavities of different sizes and with irregular shapes (Fig. 1c).

As shown in Table 2, SEM/EDX semi quantitative analysis shows that raw sewage sludge and biochars consist, primarily, of Si, Fe, Al, Ca, K and Mg, regarding inorganic contents. Chromium was detected for both active and non-active biochars after adsorption, with higher percentages of Cr for active biochar, due to higher adsorption capacity. Because of the H_3PO_4 treatment, phosphorus was detected in the active biochar.

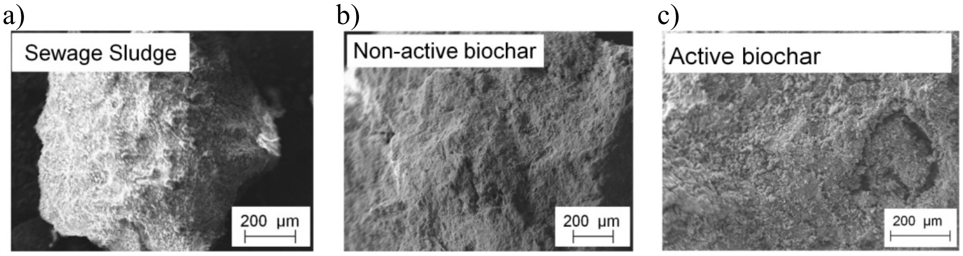


Fig. 1. Scanning Electron Microscope (SEM) image of the surface of a) sewage sludge, b) non-activated biochar and c) activated biochar.

Table 2. Element composition of the material determined by SEM/EDX

Material	Si	Fe	Al	Ca	K	Mg	P	Cr
	----------	----------	----------	%	----------	----------	----------	
SS	7.84	4.89	4.09	2.18	1.50	0.97	*ND	ND
SSB	8.20	7.62	5.62	3.73	1.54	0.98	ND	ND
SSB_{Cr}	9.40	6.69	6.02	2.99	0.99	0.88	ND	0.14
ASSB	10.62	2.93	1.92	0.69	ND	ND	7.03	ND
$ASSB_{Cr}$	11.72	2.23	2.03	0.63	ND	ND	7.05	0.57

*ND – not detected. (Limit detection = 0.1 %)

Figure 2 shows the EDX micrograph and spectra after chromium adsorption onto active biochar. The surface mapping showed that chromium was homogeneously distributed on the surface of biochar after adsorption (Fig. 2b).

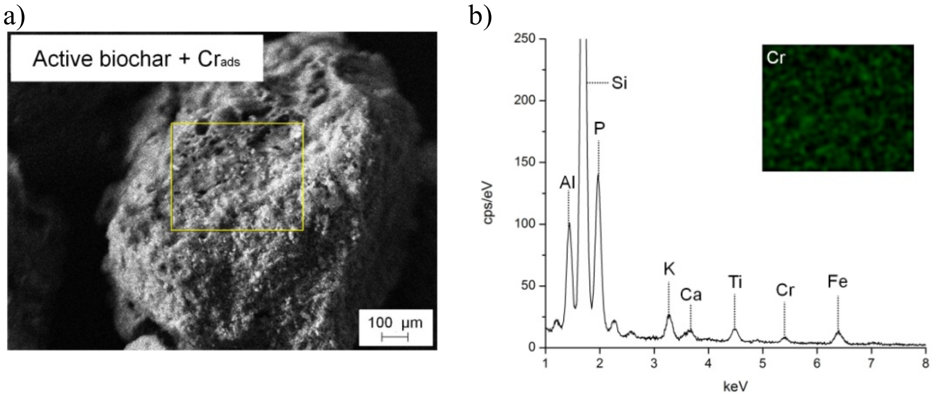


Fig. 2. SEM/EDX spectra after chromium adsorption onto active biochar: a) micrograph of active biochar loaded with Cr, b) EDX spectrum of the yellow square inside a, indicating the presence of P and Cr. The image inside b represents Cr distribution on the activated biochar

The BET-N_2 surface area of the raw sewage sludge increased when it was converted to biochar, from 5.18 m^2 g^{-1} for SS to 46.47 m^2 g^{-1} for SSB and 42.69 m^2 g^{-1} for ASSB (Table 1). The BET-N_2 surface area is higher for the non-active biochar than the active biochar. Willocq et al. (2008) state that the chemical modification of the carbonaceous surface is the most crucial factor responsible for the loss of surface area, probably because the accessibility of the micro- and mesopores is restricted. The authors also found that the chemical functionalization with phosphine groups is effective due to a very high density of functional groups on a carbonaceous surface even if its presents a low specific surface area.

The BET-N_2 surface area of biochars is still relatively low, although some porosity development is observed after the thermal treatment (Fig. 3). However, the increase in the BET specific surface area shown for ASSB compared to the raw material (sewage sludge) is noteworthy due to the simplicity of the preparation method, which uses an inexpensive and effective acid.

Ros et al. (2006), also using sewage sludge as biomass, found no porosity development after chemical activation with H_3PO_4 implying that it is not a suitable method for the preparation of adsorbents. However, the main objective of this work was to functionalize the surface in order to increase active sites for Cr adsorption, using a cost-effect method to improve the biochar surface. Furthermore, specific surface areas of approximately 300 m^2 g^{-1} have been reported for the activation of organic sewage sludge with phosphoric acid (Zhang et al., 2005). In addition to the different chemical composition of the organic sewage sludge used, the reason for such differences compared to our work, could be the higher pyrolysis temperature (650˚C) employed by the authors and the use of NaOH for washing the samples, which increases the cost of the process.

The materials combine microporosity and mesoporosity, as indicated by the N_2 adsorption at low relative pressure and the isotherm slope, respectively.

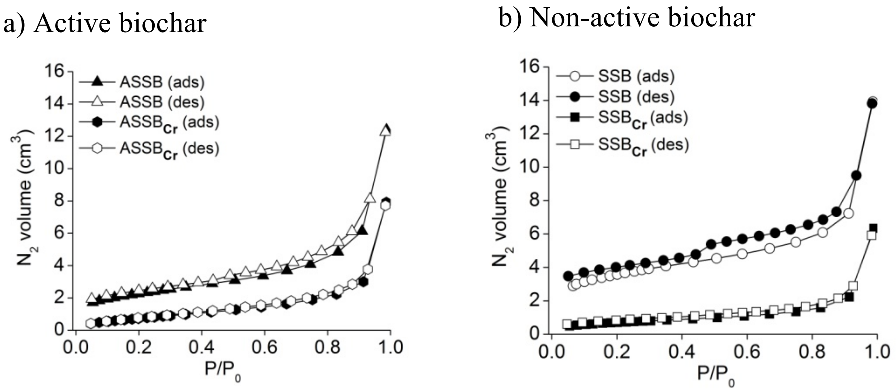


Fig. 3. N_2 adsorption isotherms at 77 K of adsorbents before and after Cr adsorption, a) active biochar and b) non-active biochar.

Fig. 4 shows the TG and DTG results. In the TG–DTG curves for sewage sludge (SS), three distinct regions are identified and can be defined as the beginning of the decomposition, main decomposition and final. The first stage corresponds to the dehydration and drying process, which takes place up to 140˚C. In pyrolysis, the second stage finishes at ~480˚C, with a mass loss of 55 %.

The final decomposition is of inorganic matter, resulting in fixed carbon and ash content. Therefore, the pyrolysis of sewage sludge starts above 200˚C and finishes around 500˚C. Similar results were found by Magdziarz and Werle (2014).

The plot of mass loss of the ASSB (Fig. 4a) is shifted to higher temperatures, up to 480˚C. Mass loss may be assigned to the ultimate oxidation of the carbon material after reaction with H_3PO_4, due to the decomposition of the phosphate bridges (accompanied by a contraction of the material and a decrease of the microporous volume) (Xu et al., 2014). Higher temperatures could cause loss of phosphorus functional groups, which could improve the biochar area. However, active sites would be lost.

Pyrolysis temperature for the production of active sewage sludge biochar was then chosen considering the characteristics above cited. Cheng et al. (2014) reported that a more highly cross-linked structure is developed after acid treatment, which is less prone to volatile loss.

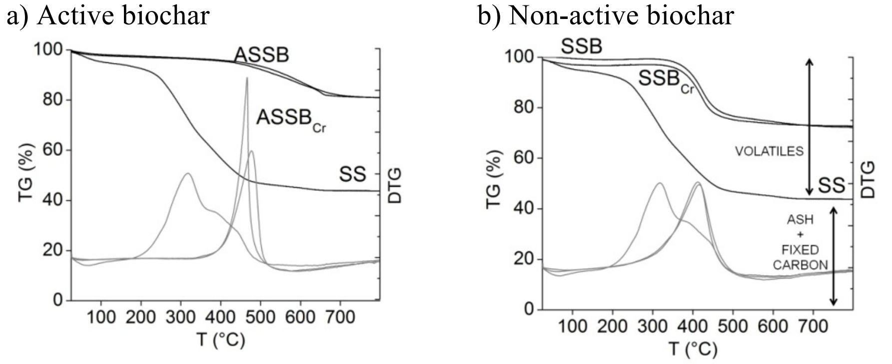

a) Active biochar
b) Non-active biochar

Fig 4. TG and DTA analysis curves of sewage sludge (SS) and biochars in nitrogen atmosphere. a) Active biochar and b) Non-active biochar

Fig. 5 shows the FTIR spectra of the sewage sludge and sewage sludge biochars before and after Cr adsorption. The spectra contain similar features, with different intensities and shifts. According to the spectra, carboxyl and hydroxyl groups were present in abundance. The peak at 3417 cm^{-1} is more intense for the biochars compared to raw sewage sludge because of the increase of oxygen-containing functional groups. The intensity is even higher for active biochar (ASSB). At ∼1600 cm^{-1} is the combination of C=C stretching vibration of the aromatic ring structures and conjugated systems such as diketone, ketoester, quinone (1550–1680 cm^{-1}). Bands at ∼1050 cm^{-1} can be assigned to C-O-C lactone structures, stretching C-O vibrations of phenol structures and ethers and bending O-H of phenol structures. Those peaks are more intense for ASSB. Regarding the raw sewage sludge sample, Shi et al. (2014) assigns wide band at 3232 cm^{-1} for hydroxyl groups of adsorbed water on the surface. The peaks appearing at the wavenumbers of ∼3420 cm^{-1} and ∼1040 cm^{-1} are attributed to OH stretching vibration and C-O stretching vibration (Chen et al., 2015). The peaks at ∼1040 cm^{-1} slightly shifted to the higher wavenumbers after functionalization. Bands at 2954 cm^{-1} and 2847 cm^{-1} are assigned to symmetric and asymmetric vibrational stretching -CH3 aliphatic -CH3. The bands are absent for biochars, since methyl groups are weak functional groups that break down with pyrolysis temperature. The broad band near at 1083 cm^{-1} may be attributed to the P–O bond of phosphate in biochar, which was consistent with the P contents of active biochar indicated by the EDX results as well as the activation agent (Ding et al., 2016).

Bands below 600 cm^{-1} can be attributed to stretching of metals bonding with halogens (Hossain, 2011). The peaks are more intense for active biochar loaded with Cr ($ASSB_{Cr}$) and non-active biochar loaded with Cr (SSB_{Cr}).

Leng et al. (2015) assigned the peaks at 1655 and 1540 cm^{-1} to be protein origin (amide I and amide II correspondingly). Changes in intensity and shifts after adsorption indicate that adsorption mechanisms might be related to the functional groups of biochar.

FTIR spectra of active biochar present additional absorption bands at 1150 and 990 cm^{-1} (as arrows indicate in Fig. 5), which have been reported as being characteristic of phosphorus and phosphor-carbonaceous compounds on the surface of carbons. The peak at 1150 cm^{-1} can be attributed to the ionized linkage P^{+}-O^{-} or P-O-C, indicating the existence of electrostatic interaction between the positively group on activated biochar surface and the negatively charged Cr(VI). Kyzas et al. (2016) discuss that the peak at 1060 cm^{-1} could be due to a combination of the P^{+}-O^{-} bond in acid phosphates esters and the symmetrical vibration of the polyphosphate chain P-O-P.

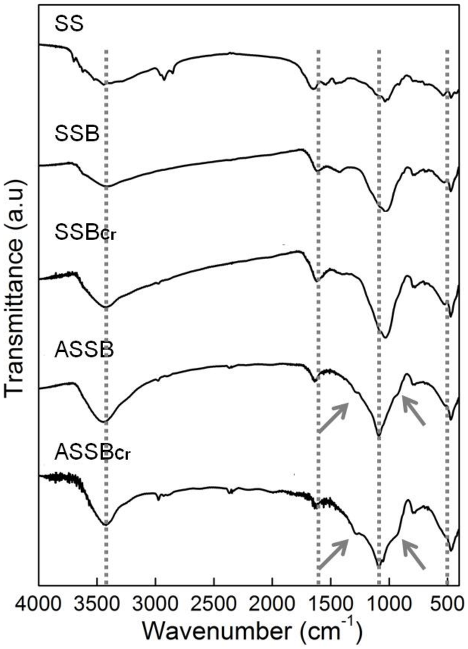
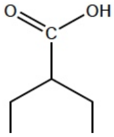
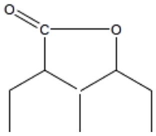
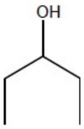


Fig. 5. FTIR spectra of sewage sludge and biochars

Table 3 shows Boehm titration results for biochars. As it can be seen, the content of total oxygen-containing groups is higher for the active biochar. There are more carboxylic groups compared to lactone and phenol, being lactone the lowest.

Machida et al. (2006) showed that the presence of mineral impurities (e.g. ash and metal oxides), acidic oxygen groups (e.g. carboxylic and lactonic groups) and basic nitrogen groups can enhance the adsorption capacity of carbonaceous materials.

Table 3: Contents of oxygen-containing functional groups of the biochars derived from sewage sludge

Biochar	 **Carboxylic Acid**	 **Lactone**	 **Phenol**
	------------------------ mmol$_{\text{H}}^{+}$ g^{-1} ------------------------		
SSB	1.21 ± 0.09	0.06 ± 0.01	0.20 ± 0.08
ASSB	1.69 ± 0.12	0.09 ± 0.01	0.65 ± 0.11

The XPS analysis results are found in Fig. 6, 7, 8 and 9. Results indicate that the biochars from sewage sludge are rich in surface functional groups, which was also supported by FTIR and Boehm's method.

XPS spectra of C1s excitation (Fig. 6) showed complicated envelope that indicated several carbon species on the materials surface. The characteristic signals found for carbon for the biochars are: graphite (284.6 eV, relative area = 63), carbon species in alcohol, phenols, ether groups, and/or C-O-P linkage (286.3 eV, relative area = 28), carboxylic groups or esters (288.6 eV, relative area = 9). After Cr adsorption, a new signal appears at 289.6 eV and can be assigned to COO groups (Jianzhong Xu et al., 2014).

The O1s spectra (Fig. 7) of active biochar presented 3 signals that include oxygen in carbonylic groups (C=O) and non-bridging oxygen in the phosphate group (P=O) (531.3eV, relative area = 44), oxygen in phenolic, lactonein and C-O-P groups (532.8 eV, relative area = 41) and noncarbonyl oxygen in carboxylic groups (534.5 eV, relative area = 15).

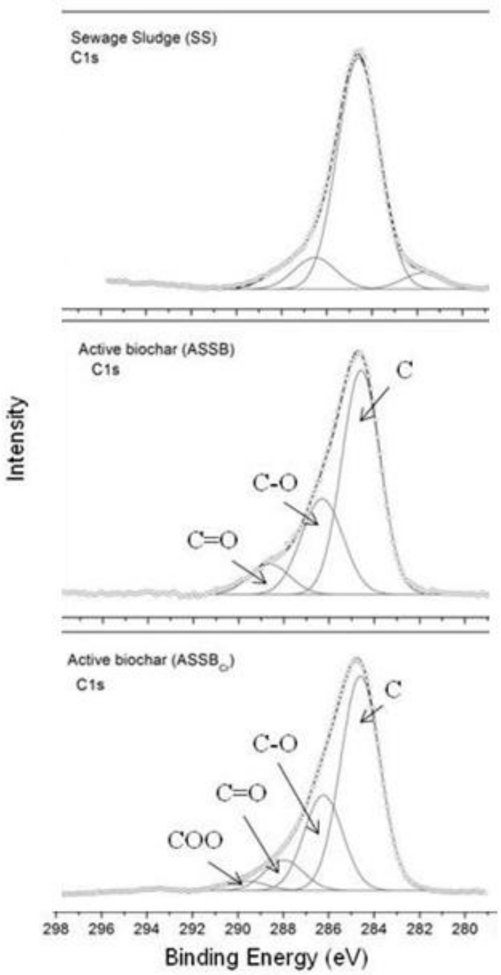


Fig. 6. Deconvolution of XPS C1s for Sewage Sludge and Active biochar (before and after adsorption)

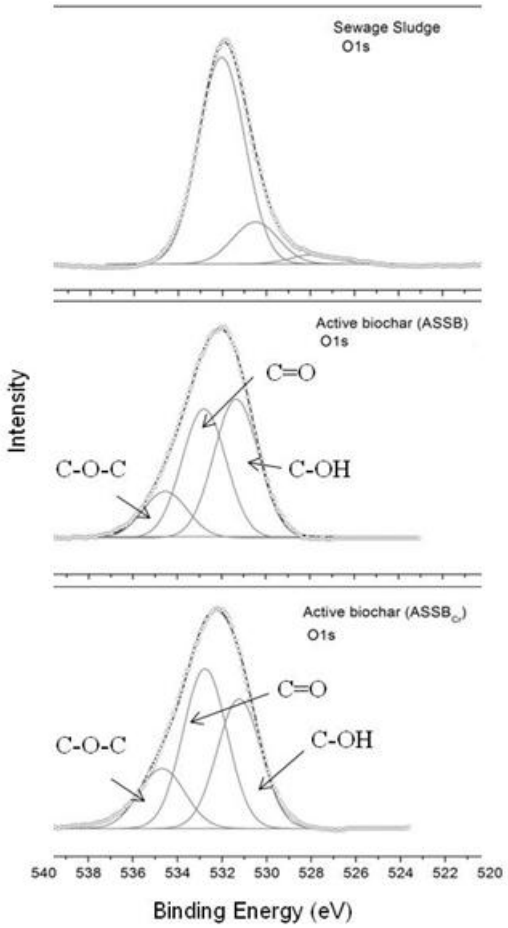


Fig. 7. Deconvolution of XPS O1s for sewage sludge and Active biochar (before and after adsorption)

The spectra for P2p (Fig. 8) shows only one signal at 133.6 eV and according to Castro-Muñiz et al. (2011) comes from metaphosphates. The signal is shifted to lower binding energy after Cr adsorption, indicating that phosphorus functional groups are involved in the adsorption process, proving that the active sites enhanced the Cr adsorption capacity of the sewage sludge biochar.

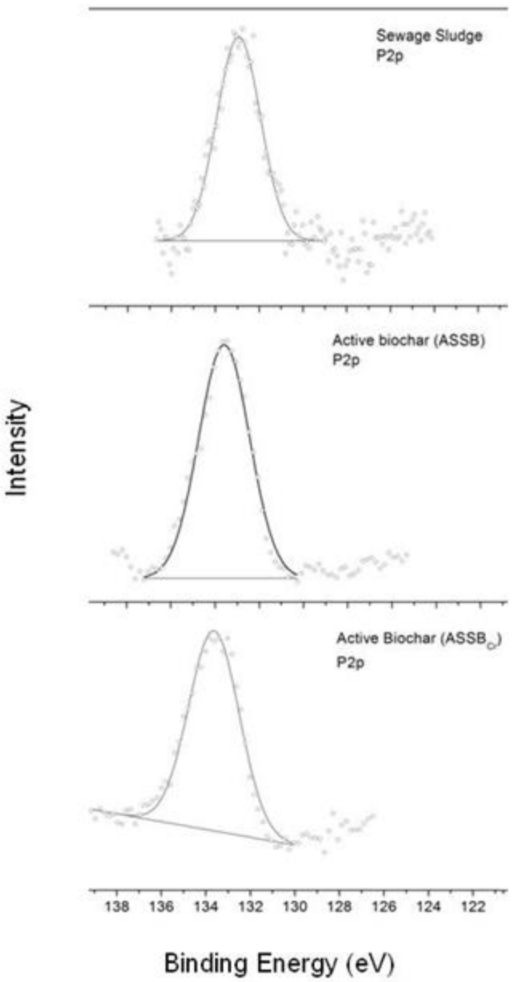


Fig. 8. Deconvolution of XPS P2p for sewage sludge and Active biochar (before and after adsorption)

Two Cr signals can be seen in XPS spectrum (Fig. 9) of active biochar loaded with chromium (ASSBCr). Cr(III) was found at 576.9 eV (relative area = 72) and Cr(VI) at 579.7 eV (relative area = 28), since Cr_2O_3 was characterized by higher binding energies than the hexavalent form (Park et al., 2008).

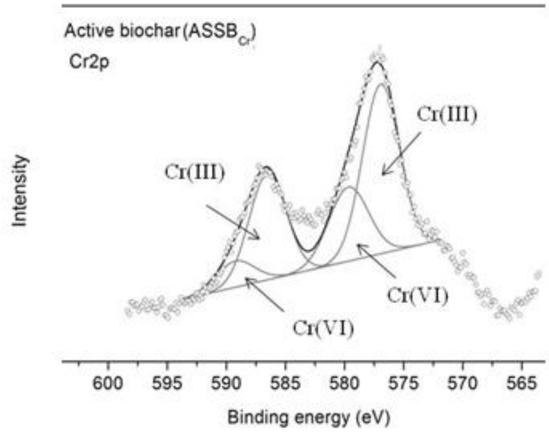


Fig. 9. Deconvolution of XPS Cr2p for sewage sludge and Active biochar (after adsorption)

Batch studies

Control tests confirmed that the initial chromium concentration, the Cr(VI)/Cr(III) ratio and pH did not change when there was no biochar in the solution. Therefore, the pH variation, the decrease of chromium concentration and the occurrence of redox reactions during adsorption are exclusively due to biochar presence.

Changes in Cr concentrations over time are shown in Fig. 10. According to our results, the removal of Cr(VI) by the biochars increased with time and then decreases slowly until saturation levels were completely reached at the equilibration point, which was 3 hours for the active biochar (Cr(VI) removal up to 83.4 %) and 2 hours for non-active biochar (Cr(VI) removal up to 67.0 %), remaining thereafter almost constant. The removal was rapid in early stages and was almost constant for longer contact time. Based on this study, 5 h was used in all following experiments to ensure that equilibrium was reached.

a) Active biochar b) Non-active biochar

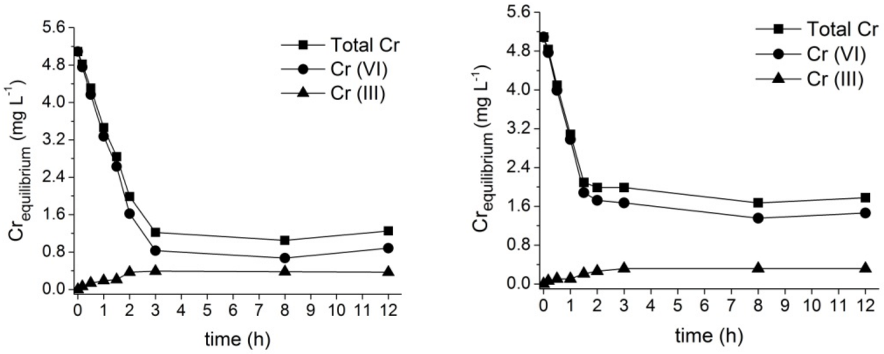


Fig. 10. Effect of reaction time on Cr removal by (a) active and (b) non-active biochars from sewage sludge. Adsorption tests were conducted in pH range 2, adsorbent dose (1 g L^{-1}), Cr(VI) initial concentration (5 mg L^{-1}), contact time (12 h) and temperature (25 ± 1˚C)

As the solution pH considerably affects chromium speciation the effect of pH on adsorption was carried out and Fig. 11 shows that maximum Cr(VI) removal by active biochar was 88.6 % and 71.0 % for non-active biochar, at pH 2.

As solution pH increased, removal of Cr(VI) decreased significantly. This finding has been reported by other investigators who have found that Cr(VI) adsorption by active carbon is enhanced in the acidic range of pH (Pang et al., 2015; Wu et al., 2016).

The pH dependence of chromium adsorption can be related to the type and ionic state of functional groups present on the adsorbents and chromium speciation in solution. The optimum solution pH for removal of Cr by both biochars was pH 2. At low pH values, Cr(VI) exists in the form of oxyanions such as $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-}. Under acidic conditions, Cr(VI) is reduced to Cr(III) in the presence of carbonaceous materials (Sharma et al., 2008)

The higher values of Cr (III) can be explained by the reduction of Cr (VI), according to following equation

$$\mathrm{Cr_2O_7^{2-} + 6e^- + 14H^+ \rightleftharpoons 2Cr^{3+} + 7H_2O} \qquad (\mathrm{E = 1.3\ V}) \qquad (9)$$

Also, at lower pH, the negatively charged carboxilate anions in the biochars structure are neutralized by H^+ ions, decreasing the repulsion between $Cr_2O_7^{2-}$ and surface active sites. On the other hand, at high pH there is abundance of negatively charged hydroxyl ions in the solution, which causes hindrance between negatively charged ions and negatively charged adsorbent, resulting in a decrease of adsorption.

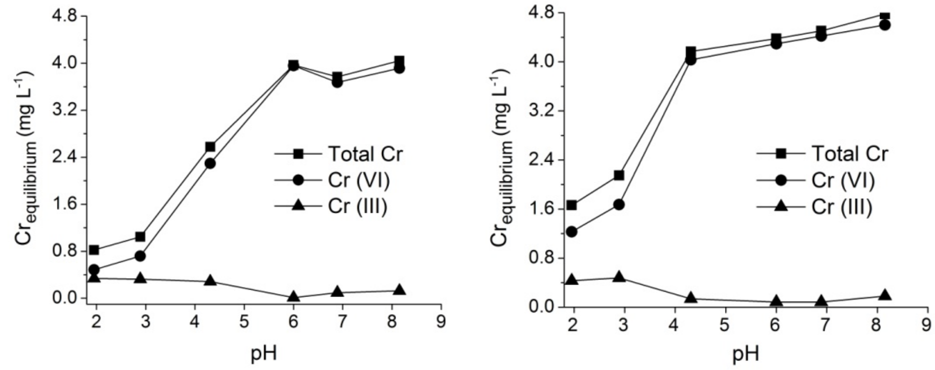
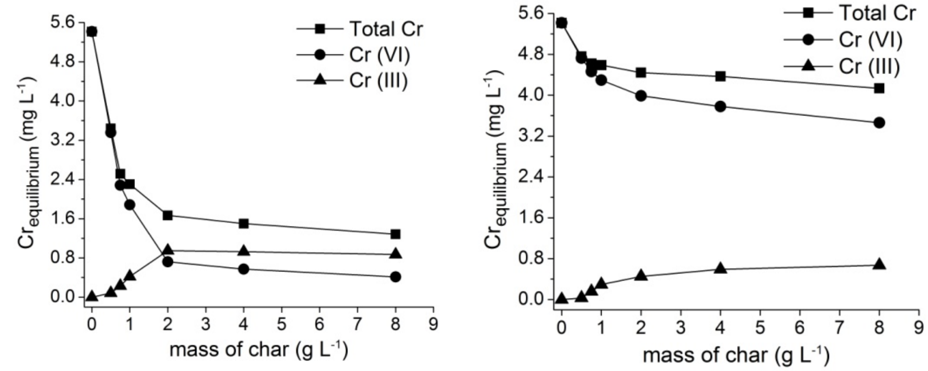

a) Active biochar
b) Non-active biochar

Fig. 11. Effect of pH on Cr removal by (a) active and (b) non-active biochars from sewage sludge. Adsorption tests were conducted in the pH range of 2 – 8 while keeping adsorbent dose (1 g L^{-1}), Cr(VI) initial concentration (5 mg L^{-1}), contact time (5 h) and temperature (25 ± 1˚C) constant

Regarding adsorbent dose, the results, presented in Fig. 12, showed that Cr(VI) removal increased with the increase of adsorbent dose, while Cr(III) decreased. At higher adsorbent dose, more exchangeable sites are available for adsorption. At high adsorbent dose Cr removal was higher for active biochar than for non-active. We observed that for the non-active biochar, the higher the adsorbent dose the higher was the solution pH after adsorption, which could explain the low removal percentage with the increase of adsorbent dose

Adsorption capacity, obtained from isotherms, decreased with increase in adsorbent dosage (data not shown) and might be related to the over-crowding of adsorbent particles, reaching their overlapping (Namasivayam et al., 1998). Gupta et al. (2010) explain that at low doses, all types of sites are entirely exposed and the adsorption on the surface is saturated faster, showing a higher q_e value. However, at a higher adsorbent dose, the availability of higher energy sites decreases and there are more fractions of lower energy sites occupied, resulting in a lower q_e value.



a) Active biochar

b) Non-active biochar

Fig. 12. Effect of biochar dose on Cr removal by (a) active and (b) non-active biochars from sewage sludge. Adsorption studies were carried out at an initial Cr(VI) concentration of 5 mg L^{-1} with adsorbent doses ranging from 0.5 to 8 g L^{-1}

Effect of temperature and thermodynamic studies

Changes of the temperature modified the equilibrium capacity of the adsorbent. Chromium adsorption onto both biochars increased with increasing temperature (Fig. 13) and can be referred as endothermic (ΔH>0). Maximum adsorption was found at 40˚C.

The values of the thermodynamic parameters are recorded in Table 4. The negative values of ΔG˚ indicate the spontaneous nature of the process. As the change in free energy for physical adsorption is usually between -40 and 0 kJ mol^{-1}, and between -80 to -400 kJ mol^{-1} for chemisorptions, we concluded that Cr adsorption onto biochar might be physical in nature (Kara et al., 2015). More negative values are found as solution temperature increases, showing that an increase in temperature favors the adsorption process.

The positive values of ΔS˚ represent an increase in the degree of freedom of the adsorbed species and increasing randomness at the solution/solid interface during the adsorption. Since the biochars are rich in inorganic elements and heterogeneous in nature, we hypothesized that Cr ions might replace some other molecules/ions previously adsorbed on the surface of the biochars.

Table 4: The thermodynamic values of the adsorption for the different solution temperatures used for Cr(VI) removal with the biochars

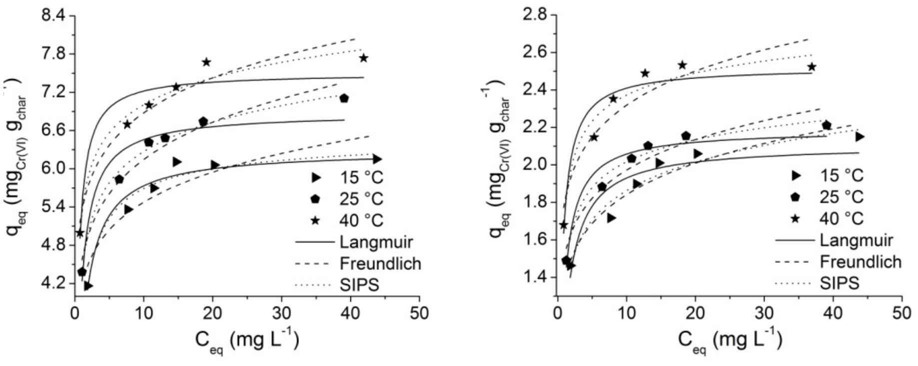
Biochar	**Solution temperature** (K)	**ΔG˚** (kJ mol^{-1})	**ΔH˚** (kJ mol^{-1})	**ΔS˚** (J mol^{-1} K^{-1})
SSB	288.15	-33.28	20.71	210
	298.15	-35.16		
	313.15	-38.98		
ASSB	288.15	-33.16	27.38	187
	298.15	-35.26		
	313.15	-37.41		

Isotherms

Active biochar had a larger adsorption capacity than non-active biochar, with the highest Q^0 and k values regardless of temperature (Fig. 13).

The near unity regression coefficient values (R^2) related to the SIPS model indicate its general better fitting to Cr(VI) adsorption onto biochars at 25˚C (Table 5). The SIPS and Langmuir parameter Q^0 and the Freundlich k parameter are higher for active biochar than for non-active biochar, confirming that the functionalization process resulted in a larger Cr(VI) capacity adsorption.

SIPS isotherm is a combination of the Langmuir and Freundlich isotherm type models, which describes heterogeneous surfaces much better. At low sorbate concentrations it reduces to a Freundlich isotherm, while at high sorbate concentrations it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm (Perez-Marin et al., 2007).



a) Active biochar

b) Non-active biochar

Fig. 13. Isotherms for the a) active biochar and b) non-active biochar at different temperatures (15, 25 and 40˚C). Straight lines represent the Langmuir fitting and dash lines represent the Freundlich fitting. Adsorption experiments were run at 15, 25, 40˚C, with an initial Cr(VI) concentration of 5 mg L^{-1}, adsorbent dose of 1 g L^{-1} and pH 2 for both adsorbents.

Table 5. Adsorption isotherms parameters

Biochar	Langmuir			Freundlich			SIPS		
	Q^0	b	R^2	K_F	1/n	R^2	Q^0	n_s	R^2
				15 °C					
SSB	2.10	1.08	0.830	1.38	0.13	0.930	1.28	0.90	0.923
ASSB	6.29	1.02	0.953	4.16	0.11	0.823	5.84	0.98	0.944
				25 °C					
SSB	2.19	1.60	0.930	1.51	0.12	0.925	1.69	0.94	0.973
ASSB	6.88	1.54	0.913	4.54	0.13	0.958	4.68	0.92	0.988
				40 °C					
SSB	2.52	2.16	0.904	1.80	0.11	0.876	2.01	0.94	0.930
ASSB	7.50	2.55	0.889	5.32	0.11	0.945	5.14	0.93	0.962

Proposed mechanism

A possible adsorption mechanism can be suggested based on biochar characterizations. Chromium (VI) from the initial solution can be physically adsorbed by electrostatic interaction onto the positively charged groups of the biochar since the initial pH solution is lower than pH_{PZC} of the active biochar. The surface of the biochar presents electron donors groups, as found by Boehm's titration for instance, that have the potential to reduce Cr(VI) to Cr(III). Furthermore, the low pH associated with the carbonaceous surface can also cause reduction conditions (Equation 10).

$$HCrO_4^- + 3/2C + H^+ \rightarrow Cr^{3+} + H_2O + 3/2CO_2 \tag{10}$$

Since the surface are mostly positively charged, electrostatic repulsions might occur between Cr(III) ions and the surface groups and Cr(III) is then released to the solution, as detected in the equilibrium solution after adsorption. Therefore, Cr(III) ions can be involved in complexation reactions with carbon surface groups (acid basic reactions). Similar mechanism was found by Duranoglu et al., 2012.

Comparative studies

Chromium (VI) adsorption capacities of activated carbons from various sources are showed in Table 6. It can be observed that a pH of 2.0 was found to be an optimum in nearly all cases. There is a large spread in Q^0 values, but the biochars of this study compare well with the active carbons from most of the raw materials listed in Table 6. Hence, sewage sludge biochars can be considered to be viable adsorbents for the removal of Cr(VI) from aqueous medium.

Table 6. Comparison of adsorption capacities of Cr(VI) with other adsorbents

Adsorbents	**Adsorption capacity (mg g^{-1})**	**pH**	**Reference**
Coconut shell carbon	4.72	4.0	(Babel et al., 2004)
Activated carbon fabrics (ACFs)	5.59	1.0	(Xu et al., 2014)
AG-5 activated carbon	1.00	1.9	(Zinicovscaia et al., 2014)
Walnut shell ctivated carbon	3.28	2.0	(Nethaji; Sivasamy, 2014)
Olive oil factory wastes	12.15	2.0	(Malkoc et al., 2006)
Distillery sludge	5.70	3.0	(Selvaraj et al., 2003)
Coconut tree sawdust activated carbon	3.46	3.0	(Selvi et al., 2001)
Activated clay	2.17	3-9	(Zhao et al., 2015)
Sewage sludge biochar	2.19	2.0	Present study
Active sewage sludge biochar	6.88	2.0	Present study

Conclusions

Sewage sludge biochars hold promising adsorption characteristics for chromium and can be used as a suitable adsorbent for the treatment of aqueous medium. The functionalization increased the adsorption capacity and added phosphorus functional groups to the surface as found by XPS, EDX and FTIR analysis. Chromium (VI) removal increases under acidic conditions and equilibrium data (at 25˚C) fitted well with SIPS isotherm, indicating a heterogeneous surface. Temperature and pH are determinant physical parameters for the removal of Cr(VI) from solution, which strongly increases at lower pH values and increases with the increase of temperature. The adsorption mechanism onto the biochar surface involves both complexation and electrostatic reactions and both Cr(VI) and Cr(III) are found at the surface of active biochar.

Using sewage sludge as a precursor for the preparation of biochars offers a cost-effective and environmental friendly way of recycling sewage sludge and reduces the environmental problems related to its disposal. Furthermore, the sewage sludge used in this work is locally available and the chemicals used for functionalization is not expensive.

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ARTIGO 2 - BIOCHAR AND SEWAGE SLUDGE AS AMENDMENTS FOR REMEDIATION OF CONTAMINATED SOILS FROM A ZN MINING AREA

(VERSÃO PRELIMINAR)

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Highlights

- The pyrolytic conversion of sewage sludge into biochar is a potential alternative to reuse and aggregate value to the residue ;
- Application of sewage sludge biochar decreased bioavailable levels of Cd, Pb and Zn;
- Sewage sludge biochar could be efficient for remediation of contaminated areas

Abstract

Establishing a vegetative cover directly over contaminated soils by applying amendments is a cost-effect remediation technique. In this work we aimed at studying the ability of biochars (from sewage sludge and wood chips), raw sewage sludge and their blending to improve soil function and revegetation processes after addition to heavy metals contaminated soils from a Zn mining area. A greenhouse experiment was set in order to analyze the leachates by measuring the pH, the electrical conductivity and total levels of Cd and Pb. After the incubation period, soils (Soil A and Soil B) were analyzed for pH, Mehlich-1 and DTPA extractable Cd, Pb and Zn. Plant development was evaluate by measuring: germination rate, germination (%), height (cm) and dry weight (mg). Biochar forms (mainly the sewage sludge biochar) were responsible for the greatest reduction of Cd, Pb and Zn bioavailability. The pyrolytic conversion of sewage sludge into biochar is a potential alternative to reuse and aggreagate value to the residue

Keywords: heavy metals, sewage sludge biochar, degraded areas

Introduction

Mining is an important economic activity in many developed and developing countries. However, mineral exploration cause soils to become highly degraded at both physical and chemical levels. Contamination with heavy metals, such as Cd, Pb and Zn, are of great concern because of their toxicity and persistence in the environment (Ettler, 2016; Kabatta-Pendias, 2011; Lago-Vila et al., 2016). As a result, it is important to focus on the development of soil remediation techniques, because conservation and reclamation efforts can ensure continued beneficial use of land. Furthermore, restoration of vegetation cover on contaminated land can fulfill the objectives of stabilization, pollution control, visual improvement and removal of threats to life (Mahar et al., 2016; Sheoran et al., 2010; Wong, 2003).

A cost-effective technology to recover contaminated soils involves the use of amendments from different types of waste material (Forján et al., 2016; Mahar et al., 2015). Applying organic materials to contaminated soil is considered to be an environmentally friendly technique. Nawab et al. (2016) found that organic amendments (activated carbons and farmyard manures) significantly reduced the availability of heavy metal(-loid) concentrations in soil and their bioaccumulation in plants.

Sewage sludge (SS), also known as biosolid, is a solid organic waste produced by wastewater treatment plants worldwide and its application on soil is a common practice, due to benefits for soil quality (Peña et al., 2015; Sampaio et al., 2016). However, there are drawbacks considering the application of sewage sludge, such as pathogens and organic and inorganic pollutants (Rastetter et al., 2015). Furthermore, SS tends to increase soil acidity, which could lead to greater solubility of metals and increase their availability to plants, particularly in soils with poor buffering capacity (Antoniadis et al., 2008).

Biochar is charcoal material produced by pyrolysis of biomass (Lehmann, 2007). Nowadays, the incorporation of biochar into soils and mine wastes has attracted interest because of its capacity to adsorb metals in contaminated soil, acting as a green environmental sorbent (Melo et al., 2016; Zornoza et al., 2016). Different studies (Beesley et al., 2010; Beesley et al., 2011; Park et al., 2011; Shen et al., 2016) have shown that biochar can reduce available contents of metals such as Cd, Pb and Zn, and increase the soil pH.

Because sewage sludge is carbonaceous in nature and rich in organic and inorganic materials, its conversion into biochar can be a cost-effective potential method for its disposal and reuse (Yuan et al. 2015).

Blending sewage sludge with biochar could also increase the success of revegetation efforts (Belyaeva; Haynes, 2012). Because of the contrasting chemical properties and nutrient contents in SS and biochar, land application of their blending could be a beneficial means of their disposal, once the mixture could improve soil quality (Sajwan et al., 2003).

Miller-Robbie et al. (2015) recently investigated the co-production and co-application to land of biochar and biosolids and found that biochar provides many benefits to biosolids management in terms of energy integration and reduction of greenhouse gas emissions. Their study contributes to a first analysis in evaluating the co-production of biochar and biosolids for potential environmental, economic, and health benefits.

Therefore, the main objective of this work is to study the ability of biochars (from sewage sludge and wood chips), raw sewage sludge and their blending to improve soil function and revegetation processes after addition to heavy metals contaminated soils from a Zn mining area.

Experimental

Study area and soil sampling

Soil samples were taken from a Zn mining area with approximately 18 ha located in Vazante, Minas Gerais state, Brazil (geographic coordinates 17° 59′ 11″ S, 46° 54′ 27″ W).

Soil samples were collected at 0-20 cm depth from two different locations inside the area (named CAVA 3) (Fig. 1), which was divided due to their differences in properties, such as total concentration of heavy metals and pH. Table 1 shows the physical and chemical attributes of the soils (Soil A and Soil B) used in this study.

Table 1. Physical and chemical attributes of the soils used in this study

Attributes	**Soil A**	**Soil B**
Organic matter (g kg^{-1})	10	1.4
pH	7.4	5.8
Clay (g kg^{-1})	145	560
Silt (g kg^{-1})	430	295
Sand (g kg^{-1})	425	145
Available P (mg dm^{-3})	44.1	3.5
Available K (mg dm^{-3})	28.1	14.8
Exchangeable Ca ($cmol_c$ dm^{-3})	2.6	0.9
Exchangeable Mg ($cmol_c$ dm^{-3})	1.7	0.7
Total Zn (mg kg^{-1})	26,145	530
Total Cd (mg kg^{-1})	102	1.6
Total Pb (mg kg^{-1})	5,887	1,253

Upon collection soil samples were dried in the shade and passed through 2 mm sieve prior to use and further analysis.

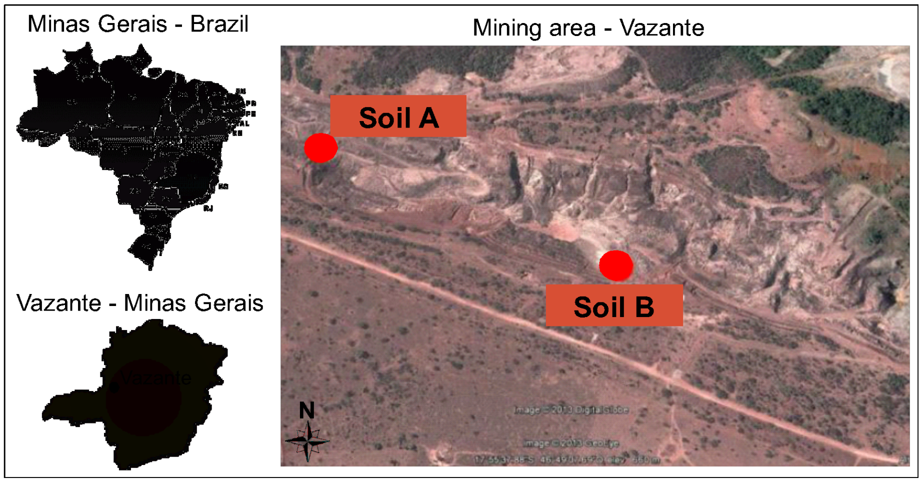


Fig. 1. Location of the soil samples collected from the mine area of Vazante, Minas Gerais state, Brazil

Amendments

Sewage sludge (SS) was obtained from the municipal wastewater treatment plant, located in Vazante, Minas Gerais State, Brazil.

Prior to analysis and pyrolysis, dewatered sludge was dried at room temperature, crushed and sieved (2 mm). The sample was then dried at 60˚C for 48 hours and stored in air tied plastic bags. The dried sewage sludge was subjected to a heat treatment (pyrolysis) in a tubular furnace under inert atmosphere of N_2 at a flow rate of 100 mL min^{-1} and temperature ramp of 10˚C min^{-1} from room temperature to 500˚C and remained at this temperature for 2 hours, producing sewage sludge biochar (SSB).

The wood biochar was collected at a coal production facility, also located in Vazante city. At the end of the coal production process, the furnaces are cleaned, generating, then, a residue. The residue was used in this work and was labeled wood biochar (WB).

Greenhouse experiment

This experiment was conducted with both Soil A and B. Each amendment was applied at two doses and wood biochar and sewage sludge was blended at different ratios. Table 2 shows the amendments and their dose for each treatment.

Table 2. Identification and doses of the amendments used in this study

Amendment	**Dose**	**ID**
Wood biochar	30 g kg^{-1} 60 g kg^{-1}	WB 30 WB 60
Sewage sludge	10 g kg^{-1} 20 g kg^{-1}	SS 10 SS 20
Sewage sludge biochar	30 g kg^{-1} 60 g kg^{-1}	SSB 30 SSB 60
Blending of wood biochar and sewage sludge	WB 30 g kg^{-1} + SS 10 g kg^{-1} WB 30 g kg^{-1} + SS 20 g kg^{-1} WB 60 g kg^{-1} + SS 10 g kg^{-1} WB 60 g kg^{-1} + SS 20 g kg^{-1}	WB 30 SS 10 WB 30 SS 20 WB 60 SS 10 WB 60 SS 20

Amendments were thoroughly mixed with 250 cm^3 of each soil, placed in 500 mL containers that were connected to bottles to collect the leachate. Glass wool and paper filter was placed at the bottom of each container. The pots were wrapped with aluminum foil, arranged in a completely randomized design and incubated at room temperature (25–30°C) for 4 weeks, at the greenhouse. Three replicate were used for each treatment and there were six replicates of nontreated control for each soil. Pots were constantly rewetted to keep 70% of water-holding capacity. During the incubation period, leachate was weekly collected in pore volume (150 mL) fractions for a total of 4 collections (week 1, week 2, week 3 and week 4) and analyzed for pH, electrical conductivity and total levels of Cd and Pb. At the end of the incubation period of 4 weeks, 10 dm^3 of soil were collected from each pot and analyzed for pH, Mehlich-1 and DTPA extractable Cd, Pb and Zn. Mehlich-1 is a extractant consisting of 0.05M HCI in 0.0125M H_2SO_4. The soil:extractant ratio was 1:5 and shaking time was 15 min. The DTPA (diethylenetriaminepentaacetic acid) is a solution containing 0.05M DTPA, 0.1 M TEA (Triethanolamine), and 0.01M $CaCI_2$ at pH 7.3. The soil: extractant ratio was 1:2 and shaking time was 2 hours.

Seed germination

After the incubation period of four weeks, pots were seeded with 15 Mullato II seeds, which is a *B. ruzizi*ensis x *B. decumbens* cross. Pots were constantly rewetted to keep 70% of water-holding capacity during the evaluation of germination and growth of plants. Germination rate (speed of germination) was obtained by dividing the number of germinated seedlings of each count by the number of days seeds have been sown. The values obtained at each count were then summed at the end of the germination test:

$$G_R = \left(\frac{\text{number of seedlings}}{\text{days to first count}} + \ldots + \frac{\text{number of seedlings}}{\text{days to final count}}\right) \qquad (1)$$

The germination percentage G(%) was determined for each pot according to the following equation:

$$G(\%) = \left(\frac{\text{number of seedlings}}{\text{total number of seeds}}\right) \times 100 \qquad (2)$$

For these evaluations, germination is interpreted as the appearance of a green shoot/leaf above the soil. The number of germinating seeds was weekly monitored during one month. After that period, plants heights (cm) were also measured. After 45 days weeks, the plant biomass was separated from the soil by hand, washed carefully, dried at 70˚C for 72 h, and weighed for dry biomass determination.

Analysis and characterization

Electrical conductivity and pH were measured. Levels of Cd, Pb and Zn were determined by either graphite furnace or flame ionization atomic absorption spectroscopy (Perkim Elmer). Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX – Zeiss LEO EVO 40 XVP) was used to characterize the chemical composition and structural morphologies of the materials. Thermal stability of sewage sludge was determined through thermogravimetric analysis (TGA) (Shimadzu DTG50). The analysis was carried out by rising temperature from room temperature to 900˚C, at a heating rate of 10°C min^{-1}, using nitrogen atmosphere.

Results and discussion

Soils and amendment characterization

The soils used in this study have different attributes such as contrasting pH and organic matter contents (Table 1). Furthermore, according to the Brazilian Environmental Agency (CONAMA, 2009), the total levels of Cd, Pb and Zn exceeds by far the quality reference values for unpolluted soils, mainly for Soil A, which indicates that there are potential risks, direct or indirect, to human health considering a standardized exposure scenario and soils may not be able to sustain its main functions (CONAMA, 2009).

Fig. 2 shows the morphological aspects, based on images obtained by SEM, which indicate that the wood biochar (WB) is predominantly composed of elongated fragments that can be structural remnants of the wood fibers (Fig. 2a). The sewage sludge biochar (SSB) presents a rough surface and a more porous structure compared to raw sludge, which showed a wrinkled surface due to the release of volatile matter out of the biomass (Zornoza et al., 2016).

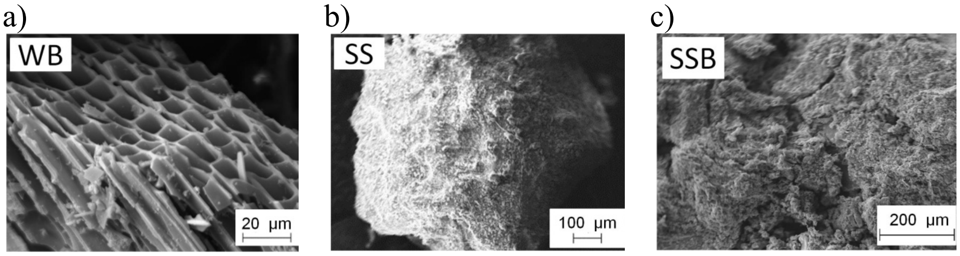


Fig. 2. Scanning Electron Microscopy (SEM) image of the surface of a) Wood Biochar (WB), b) Sewage Sludge (SS) and c) Sewage Sludge Biochar (SSB)

The chemical composition of the amendments is shown in Table 3. Wood biochar (WB) has the highest percentage of carbon (68.02 %) but lower values of the other elements compared to sewage sludge (SS) and sewage sludge biochar (SSB). With the exception of C and N, sewage sludge biochar presents higher percentages of the elements listed, due to the fact that the pyrolysis process concentrates the less volatile elements. Furthermore, the elements found in the amendments are mostly macro and micronutrients and reflect their directly reuse as a soil fertilizer.

Table 4 shows the total heavy metal contents in the amendments and the limits established by legislation. The application of sewage sludge to agricultural land is strictly governed by legislations, because of the potential for health hazards associated with its use. Herein, we compared the heavy metals contents in the sewage sludge with the European (EEC, 1986), American (US EPA, 1993) and the Brazilian legislation (CONAMA, 2006). Contents of Cu, Cd, Pb and Cr in the sewage sludge and sewage sludge biochar are within the levels set by all three regulations, which enable their use as soil amendments.

Table 3. Element composition of the amendments determined by SEM/EDX

Element	**WB**	**SS**	**SSB**
	----------------------------------	%	----------------------------------
C	68.02	40.87	29.04
N	<DL*	5.16	<DL
Ca	1.64	2.12	6.00
Mg	0.24	0.71	1.54
K	0.53	0.71	1.20
P	<DL	0.58	1.32
S	<DL	0.94	0.89
Fe	0.75	3.44	8.52
Mn	<DL	<DL	<DL
Zn	<DL	0.27	3.39
Cl	<DL	<DL	1.39
Si	2.18	4.20	8.36
Na	<DL	0.27	0.55
Al	0.76	4.06	6.77

WB – wood biochar, **SS** – sewage sludge and **SSB** sewage sludge biochar. *DL = detection limit (DL = 0.1 %)

Table 4. Total heavy metals contents of the amendments and according to legislations

Element	**Amendment**			**Legislation**		
	WB	SS	SSB	CONAMA (Brazil)	EEC (Europe)	US EPA (USA)
	---------------------------- mg kg^{-1} --------------------------------					
Cu	2.34	128	210	1,500	1,000	1,500
Cd	0.06	10.90	11.21	39	20 - 40	39
Pb	1.55	182	267	300	750	300
Cr	248	112	179	1,000	-	-

WB - wood biochar, **SS -** sewage sludge and **SSB -** sewage sludge biochar.

Thermogravimetric analysis provides a prior knowledge of initial and final temperatures for thermal degradation of sewage sludge. The results of TGA/DTA are shown in Fig. 3. The pyrolysis temperature (500˚C) to convert sludge into biochar has been estimated based on the results obtained by TGA. At the temperature of 500˚C the mass loss is almost constant, indicating no further mass loss. Heating the biomass at a temperature above the biochar limit of thermal stability results in the formation of more stable products and solid residue (Tripathi et al. 2016).

The TG curve of sewage sludge pyrolysis presents continuous mass loss. The TGA and DTA curves showed that sewage sludge shows three distinct zones of reaction that are the released moisture content and dehydration, volatile matter and fixed carbon decomposition, respectively. Similar results were found by Abbas (2014), Othman et al (2010), Silva et al (2012) and Magdziarz and Werle (2014).

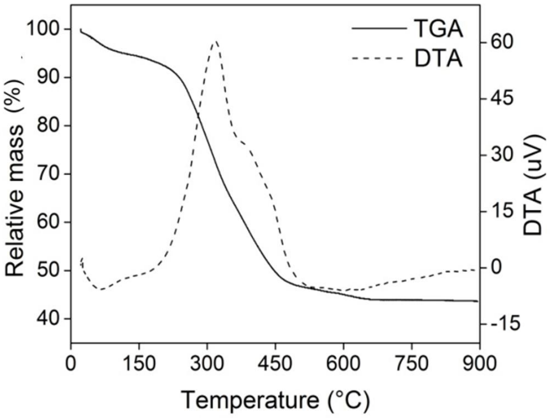


Fig. 3. TG and DTA curves corresponding to pyrolysis of sewage sludge

Greenhouse experiment: leachate analysis

Due to the high toxicity of the by-products and wastes generated by mineral processing operations (such as heavy metals), it is important to comprehend the various characteristics of the leachate, once it could be a source of groundwater contamination (Sethurajan et al., 2016).

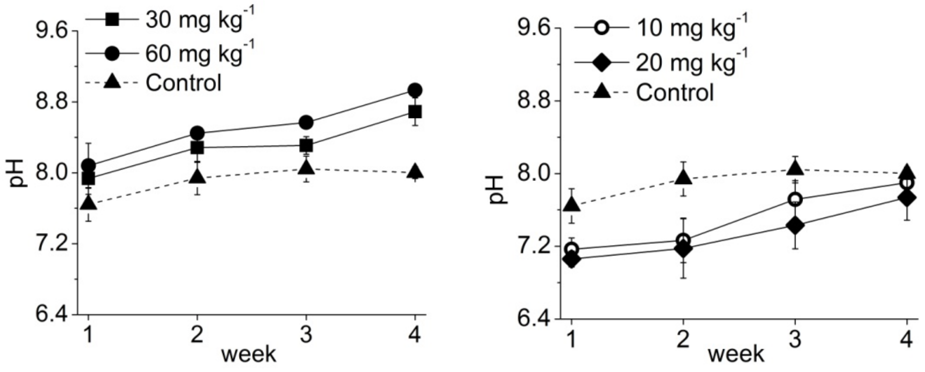
Since the release of heavy metals is greatly influenced by pH, it is necessary to consider the effect of pH to understand the leachability of metals. The pH of the leachate for each treatment and control during the incubation period of 4 weeks are shown in Fig. 4 for soil A and Fig. 5 for soil B. Results show that addition of wood biochar and sewage sludge biochar to both soils led to increased pH in the leachate compared to control. The higher the dose the higher the pH (Fig. 4a and c) and (Fig. 5a and c). The increased pH due to biochars addition to soil is related to the alkaline nature of these materials. During pyrolysis, some compounds containing Ca, Mg, K and Na are converted to hydroxides, oxides or carbonates and incorporated into the char (Houben; Evrard; Sonnet, 2013) and upon contact with water, have the ability to raise the pH. Hydroxides effect on the pH is because of the dissociation and release of hydroxyl and oxides react spontaneously with water to produce hydroxides. Therefore, both processes have the ability to increase pH.

Leachate pH decreased with the application of sewage sludge for both soils (Fig. 4a and 4c) and (Fig. 5a and 5c). At the dose of 20 mg kg^{-1} of sewage sludge the leachate pH of soil B decreased significantly after week two, reaching an average value of 5.6, which is considered acidic conditions (Fig. 5b).

The decrease in pH with increased application of sewage sludge may be related to the formation of organic acids during the mineralization of sludge, either due to the volatilization of ammonia or to increases in nitrification during incubation (Asik et al., 2015).

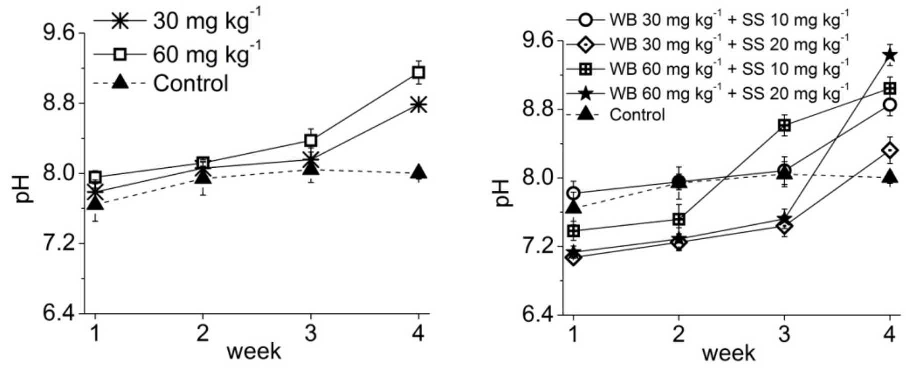
The pH curves for all treatments, except sewage sludge 20 mg kg^{-1} for Soil B (Fig. 5b), increased over time. Leachate pH from the blending WB 60 mg kg^{-1} + SS 20 mg kg^{-1} was the highest among all treatments applied to Soil A in week 4 (Fig. d).

Soil A



a) Wood biochar

b) Sewage sludge

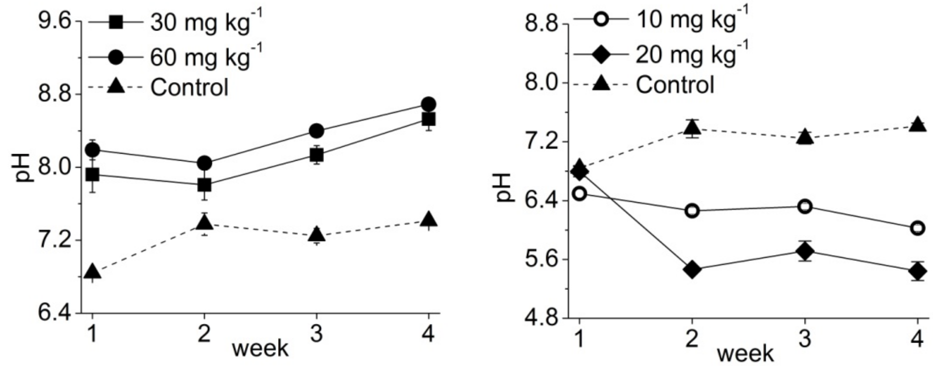


c) Sewage sludge biochar

d) Wood biochar + Sewage sludge

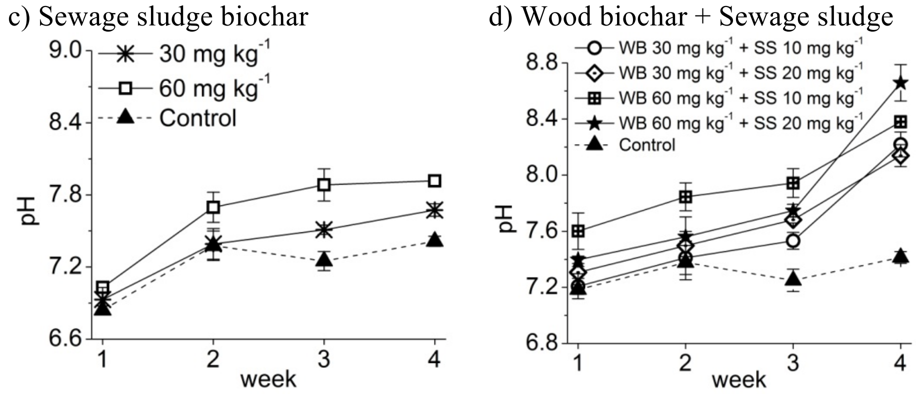
Fig. 4. Leachate pH during the incubation period of 4 weeks for soil A: a) Wood biochar, b) Sewage sludge, c) Sewage sludge biochar and d) Blending of wood biochar and sewage sludge

Soil B



a) Wood biochar

b) Sewage sludge



c) Sewage sludge biochar

d) Wood biochar + Sewage sludge

Fig. 5. Leachate pH during the incubation period of 4 weeks for soil A: a) Wood biochar, b) Sewage sludge, c) Sewage sludge biochar and d) Blending of wood biochar and sewage sludge. Note: Scales on Y-axis are different

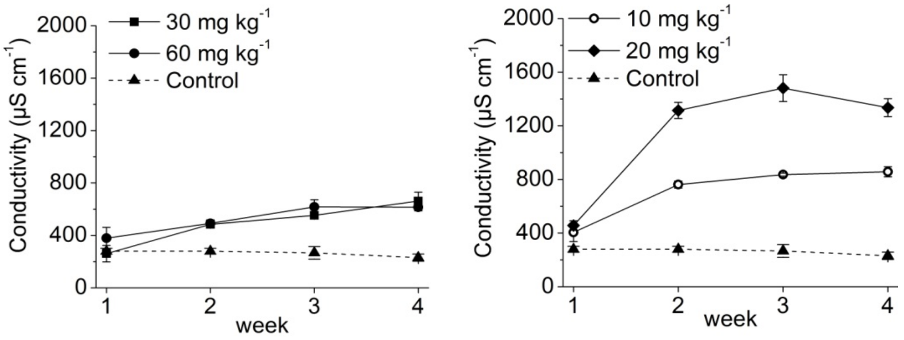
Herein, levels of salinity are expressed as electrical conductivity (EC). The electrical conductivity of the leachate over the period of four weeks of incubation, for Soil A and Soil B are shown in Fig. 6 and Fig. 7, respectively. The term salinity refers to the presence of the major dissolved inorganic solutes, such as Na^+, Mg^{2+}, Ca^{2+}, K^+, Cl^-, in aqueous extract of soil samples (leachate) (Rhoades, 1996).

The EC values increased significantly with application of all amendments. The highest EC values were observed after three weeks of incubation with the application of 20 mg kg^{-1} of sewage sludge, with values reaching up to 1,580 µS cm^{-1} for Soil A and up to 1,000 µS cm^{-1} for Soil B, (Fig. 6b) and (Fig. 7b), respectively. Sewage sludge biochar also presented high EC values (Fig. 6c) and (Fig. 7c). According to EDX analysis, SS and SSB are amendments with higher levels of elements than wood biochar, which could explain the low EC values (up to 600 µS cm^{-1} for Soil A (Fig. 6) and up to 400 µS cm^{-1} for Soil B (Fig. 7) when only wood biochar is used as amendment.

Soil A

a) Wood biochar

b) Sewage sludge



c) Sewage sludge biochar

d) Wood biochar + Sewage sludge

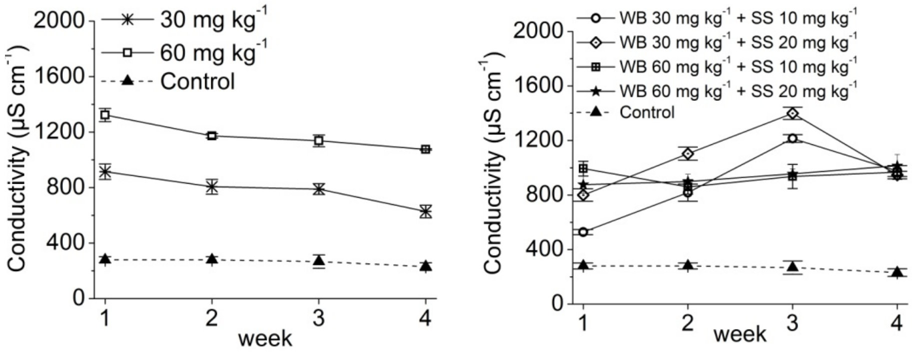
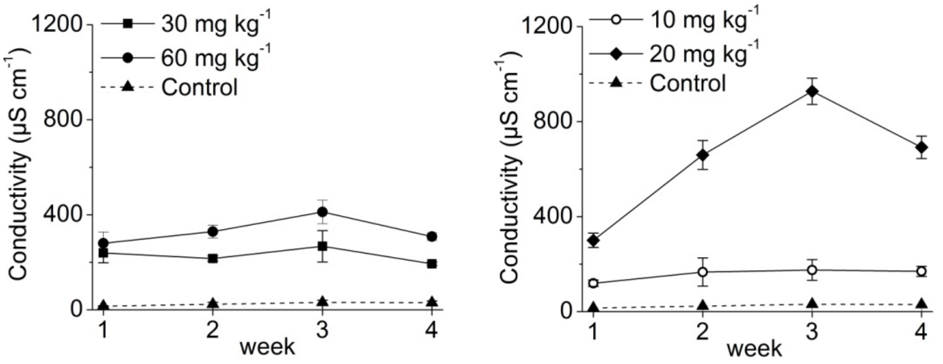
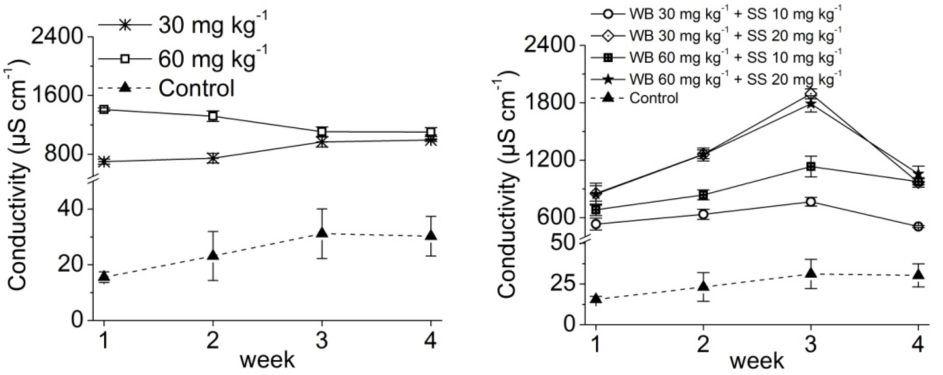


Fig. 6. Conductivity of the leachate during the incubation period of 4 weeks for soil A: a) Wood biochar, b) Sewage sludge, c) Sewage sludge biochar and d) Blending of wood biochar and sewage sludge

Soil B



a) Wood biochar b) Sewage sludge



c) Sewage sludge biochar d) Wood biochar + Sewage sludge

Fig. 7. Conductivity of the leachate during the incubation period of 4 weeks for soil B: a) Wood biochar, b) Sewage sludge, c) Sewage sludge biochar and d) Blending of wood biochar and sewage sludge. Note: Scales on Y-axis are different

Contents of Cd and Pb measured weekly in the leachates are given in Table 5. The levels of Cd and Pb in leachates are higher for Soil A compared to Soil B, because of the higher total contents of these elements (Table 1). Regardless the amendment applied levels of Cd and Pb decreased with time, which is comparable to natural environment where fresh leachant will continuously wash away the leachate, decreasing heavy metals concentration.

Considering the toxicity of Cd and Pb, the maximum permissible level in drinking water has been established for several National and International health organizations. The limit for Cd concentration in drinking water, established by EPA, is 5 µg L^{-1} and for Pb is 10 µg L^{-1}. (USEPA, 2006).

In Brazil, the standard levels of Cd and Pb in river waters are 0,001 mg L^{-1} and 0,01 mg L^{-1}, respectively (CONAMA, 2005). The limits for groundwater considering human use are 5 µg L^{-1} for Cd and 10 µg L^{-1} for Pb (CONAMA, 2008).

Cadmium and Pb were found at concentrations below the probable no-effect levels and therefore should pose little impact to the aquatic environment when undergoing leaching. Levels higher than the limits established by the legislations for drinking water were found only when sewage sludge was applied. Same behavior has been found by other authors. For example, Schwab et al. (2007) found that organic amendments affected Cd and Pb leaching from mine tailings. Aged cattle manure and composted cattle manure significantly increased Cd concentration in the leachate compared to the control.

Table 5. Levels of Cd and Pb of the leachate of Soil A collected during the incubation time of four weeks

Amendment	**Soil A**			
	Week			
	1	**2**	**3**	**4**
	Cd			
	------------------------ µg L^{-1} ------------------------			
Control	2.05±0.13	2.29±0.15	2.06±0.10	2.60±0.11
WB 30	2.30±0.11	1.88±0.09	1.27±0.13	1.05±0.19
WB 60	1.62±0.23	1.52±0.22	1.45±0.22	1.22±0.16
SS 10	5.81±0.54	6.02±0.15	6.54±0.54	4.98±0.87
SS 20	14.07±0.67	12.44±0.54	12.06±0.27	9.86±0.99
SSB 30	4.51±0.23	3.82±0.56	2.90±0.59	1.82±0.32
SSB 60	4.07±0.44	2.59±0.33	2.03±0.27	1.23±0.14
WB 30 SS 10	3.21±0.41	5.14±0.27	4.08±0.11	4.21±0.56
WB 30 SS 20	5.57±0.19	6.42±0.18	6.32±0.56	4.86±0.37
WB 60 SS 10	4.15±0.58	2.80±0.67	2.14±0.39	1.80±0.53
WB 60 SS 20	2.82±0.99	4.10±0.22	2.40±0.69	2.10±0.23
	Pb			
	------------------------ µg L^{-1} ------------------------			
Control	31.07±0.43	12.67±0.66	<DL	<DL
WB 30	6.01±0.16	5.99±0.35	<DL	<DL
WB 60	5.53±0.23	5.01±0.17	<DL	<DL
SS 10	9.87±0.21	15.52±0.19	8.91±0.33	6.88±0.21
SS 20	11.98±0.20	16.42±0.61	13.42±0.44	9.86±0.19
SSB 30	7.32±0.11	6.67±0.10	<DL 0	<DL
SSB 60	6.92±0.51	5.71±0.67	<DL	<DL
WB 30 SS 10	7.65±0.45	6.23±0.42	5.98±0.18	<DL
WB 30 SS 20	9.22±0.29	6.52±0.27	6.55±0.49	<DL
WB 60 SS 10	5.67±0.37	5.02±0.64	5.00±0.62	<DL
WB 60 SS 20	7.98±0.54	5.32±0.66	5.12±0.47	<DL

DL: Cd = 0.56 µg L^{-1} and Pb = 4.90 µg L^{-1}

Values represent the average ± the standard deviation ($\overline{X} \pm SD$)

Table 6. Levels of Cd and Pb of the leached of soil B collected during the incubation time of four weeks

Amendment	Soil B			
	Week			
	1	2	3	4
	Cd ------------------------ µg L^{-1} ------------------------			
Control	<DL	<DL	<DL	<DL
WB 30	<DL	<DL	<DL	<DL
WB 60	<DL	<DL	<DL	<DL
SS 10	6.19±0.21	6.89±0.12	7.12±0.12	5.53±0.17
SS 20	7.20±0.16	7.98±0.29	8.06±0.09	6.99±0.31
SSB 30	5.17±0.11	4.84±0.07	3.76±0.12	1.34±0.16
SSB 60	3.56±0.15	2.82±0.21	2.29±0.11	1.28±1.09
WB 30 SS 10	<DL	<DL	<DL	<DL
WB 30 SS 20	0.67±0.11	1.42±0.12	1.19±0.16	1.17±0.14
WB 60 SS 10	<DL	<DL	<DL	<DL
WB 60 SS 20	1.84±0.17	0.75±0.26	0.75±0.12	0.81±0.13
	Pb ------------------------ µg L^{-1} ------------------------			
Control	<DL	<DL	<DL	<DL
WB 30	<DL	<DL	<DL	<DL
WB 60	<DL	<DL	<DL	<DL
SS 10	<DL	5.91±0.23	4.66±0.14	4.12±0.09
SS 20	<DL	7.60±0.32	6.92±0.22	6.01±0.19
SSB 30	<DL	<DL	<DL	<DL
SSB 60	<DL	<DL	<DL	<DL
WB 30 SS 10	<DL	<DL	<DL	<DL
WB 30 SS 20	<DL	<DL	<DL	<DL
WB 60 SS 10	<DL	<DL	<DL	<DL
WB 60 SS 20	<DL	<DL	<DL	<DL

DL: Cd = 0.56 µg L^{-1} and Pb = 4.90 µg L^{-1}

Values represent the average ± the standard deviation ($\overline{X} \pm SD$)

Greenhouse experiment: soil analysis

Soil pH is the most important factor controlling metal availability, which decreases with increasing pH (Asik et al., 2015). Fig. 8 shows the soil pH after amendments application and incubation period of four weeks, for Soil A and B.

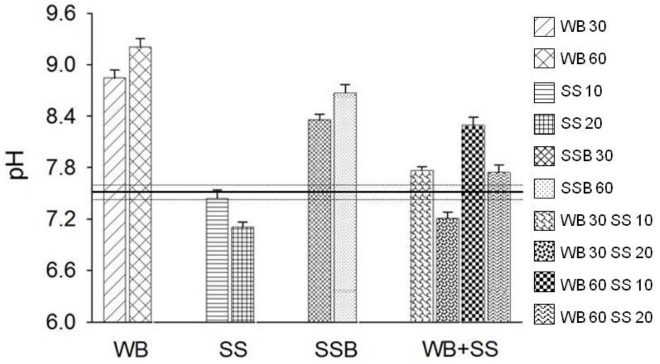
Application of the amendments was sufficient to change soils pH over the control. For Soil A, only sewage sludge (at both doses) and the blending of wood biochar and sewage at the dose of WB 30 g kg^{-1} + SS 20 g kg^{-1}, presented a pH lower than the control (without any amendment) (Fig. 8a).

The lowest pH values were observed on Soil B after application of sewage sludge at the dose of 20 g kg^{-1} (Fig. 8b). We hypothesize that over time, NH_4 could be oxidized to NO_3 and released H^+ ions.

For both soils, soil pH increased with increasing addition rate of wood biochar and sewage sludge biochar and decreased with higher rates of sewage sludge. Wood biochar at the dose 60 mg kg^{-1} was the most effective amendment for increasing soil pH. Yang et al. (2016) also found that there are higher increases in soil pH after application of fine rice straw biochar as addition rate increases.

Increased pH values could result in an increase in the number of negatively charged surface sites in the soil, increasing, therefore, the sorption capacity of the soil for cationic metals (Shen et al., 2016).

a) Soil A



b) Soil B

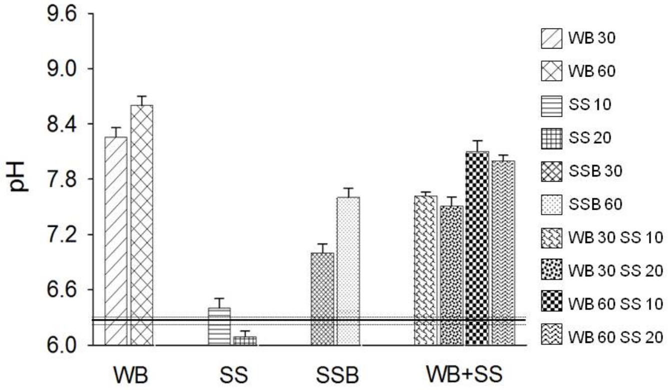


Fig. 8. Soil pH after the incubation period of four weeks: a) Soil A, b) Soil B. Straight lines represent the pH of the control and dash lines the standard deviation

Different studies (Beesley et al., 2010, Beesley; Marmiroli, 2011; Park et al., 2011) have shown that biochar can reduce available contents of Pb and Zn, and increase the soil pH.

The diethylene triamine pentaacetic acid (DTPA) and the Mehlich-1 bioavailability results are reported in Table 7 for Soil A and Table 8 for Soil B. Available Cd, Pb and Zn are higher for Soil A than for Soil B. With the exception of SS, the amendments tend to decrease available metals contents in the soils. DTPA is a chelating extractant while Mehlich-1 is an acid extractant and, in general, the latter has a higher extraction capacity than the former (Zhang et al., 2010). However, for Cd, in both soils DTPA had a higher extraction capacity (nearly an order of magnitude) than Mehlich-1. While, for Pb and Zn was the opposite. This is likely related to the forms and distribution among fractions these metals are present in the soils.

In soil A SSB 60 reduced the availability of the three metals the furthest. While for soil B such reduction was the highest with WB 60. In both cases biochar forms were responsible for the greatest reduction of metal availability. Puga et al. (2016) when working on soils from the same mining area of this study, also found that biochar from sugarcane straw reduces Cd, Pb and Zn concentrations in the leachate as well by DTPA extraction.

Soils with higher organic matter content have a higher capacity to retain metals (Park et al., 2011). Forján et al. (2016) showed that recovering mine tailing by applying organic amendment, consisting of a combination of a classic amendment using waste materials (solid urban waste, ashes from a paper factory, agri-food waste and sludges from a purification plant), together with biochar, increases the sorption capacity of Pb and Zn at 40% and 60%, respectively.

Surface application of amendments reduced the concentration of contaminants in the leachates. In the case of amendment incorporation, this may occur if the amendment provides binding sites for the contaminants or if the amendment alters the chemistry of the soil (Abbott et al., 2001). Reduced concentrations of available Cd, Pb and Zn in the soil indicate a reduction in phytotoxicity, improving the development of plants.

Table7. Extractable Cd, Pb and Zn of soil A for different treatments

Amendment	Soil A		
	MEHLICH-1		
	Cd	Pb	Zn
	mg dm^{-3}		
Control	7.13d	1,007d	6,337d
WB 30	5.63c	952c	5,625c
WB 60	3.83a	989d	4,433a
SS 10	5.73c	945c	6,453d
SS 20	5.80c	1,166f	5,835c
SSB 30	4.03a	894b	5,187b
SSB 60	3.93a	832a	4,157a
WB 30 SS 10	4.82b	958c	5,103b
WB 30 SS 20	4.13a	1,053e	5,913c
WB 60 SS 10	4.17a	949c	4,269a
WB 60 SS 20	4.73b	995d	5,085b
CV (%)	3.54	3.17	3.18
	DTPA		
	mg kg^{-1}		
Control	83.00f	588g	400e
WB 30	50.93d	516d	278c
WB 60	45.56c	450b	233b
SS 10	72.23e	559f	372d
SS 20	73.80e	585g	391e
SSB 30	48.43d	477c	237b
SSB 60	40.66b	406a	169a
WB 30 SS 10	42.40c	533e	282c
WB 30 SS 20	44.06c	503d	290c
WB 60 SS 10	33.57a	412a	232b
WB 60 SS 20	36.03a	481c	239b
CV(%)	5.23	2.38	4.26

Values represent the mean. Treatments with the same letter were not significantly different (Scott-Knott test, $p < 0.05$)

Table 8. Extractable Cd, Pb and Zn of soil B for different treatments

Amendment	**Soil B**		
	MEHLICH-1		
	Cd	**Pb**	**Zn**
	mg dm^{-3}		
Control	0.18	619g	85.26d
WB 30	<DL*	465c	43.17b
WB 60	<DL	294a	31.36a
SS 10	0.10	563f	98.39e
SS 20	0.12	580f	89.47d
SSB 30	<DL	401b	61.55c
SSB 60	<DL	388b	59.64c
WB 30 SS 10	0.09	503d	57.62c
WB 30 SS 20	0.10	574f	83.80d
WB 60 SS 10	<DL	539e	62.58c
WB 60 SS 20	<DL	514d	78.04d
CV(%)	-	2.43	5.47
	DTPA		
	mg kg^{-1}		
Control	0.66d	34.7d	18.5c
WB 30	0.40a	20.0a	12.0a
WB 60	0.36a	22.9b	10.4a
SS 10	0.50b	38.6d	19.6c
SS 20	0.57c	47.7f	27.3d
SSB 30	0.33a	20.0a	15.1b
SSB 60	0.40a	16.9a	18.2c
WB 30 SS 10	0.40a	31.2c	10.8a
WB 30 SS 20	0.40a	45.2f	18.5c
WB 60 SS 10	0.40a	35.7s	11.3a
WB 60 SS 20	0.40a	46.5f	18.1c
CV(%)	8.92	4.33	6.42

*DL for $Cd_{MEHLICH}$ = 0.01 mg dm^{-3}. Values represent the mean. Treatments with the same letter were not significantly different (Scott-Knott test, $p < 0.05$). No statistical test was applied for Cd extracted by Mehlich because of the low values

Plants development after amendments application

Establishing a vegetative cover directly over the soils will reduce the potential for erosion and contaminant transfer. In order to select the best amendment for plant growth and site remediation, we evaluated germination, germination percentage, height (cm) and plant dry mass, showed in Fig. 9.

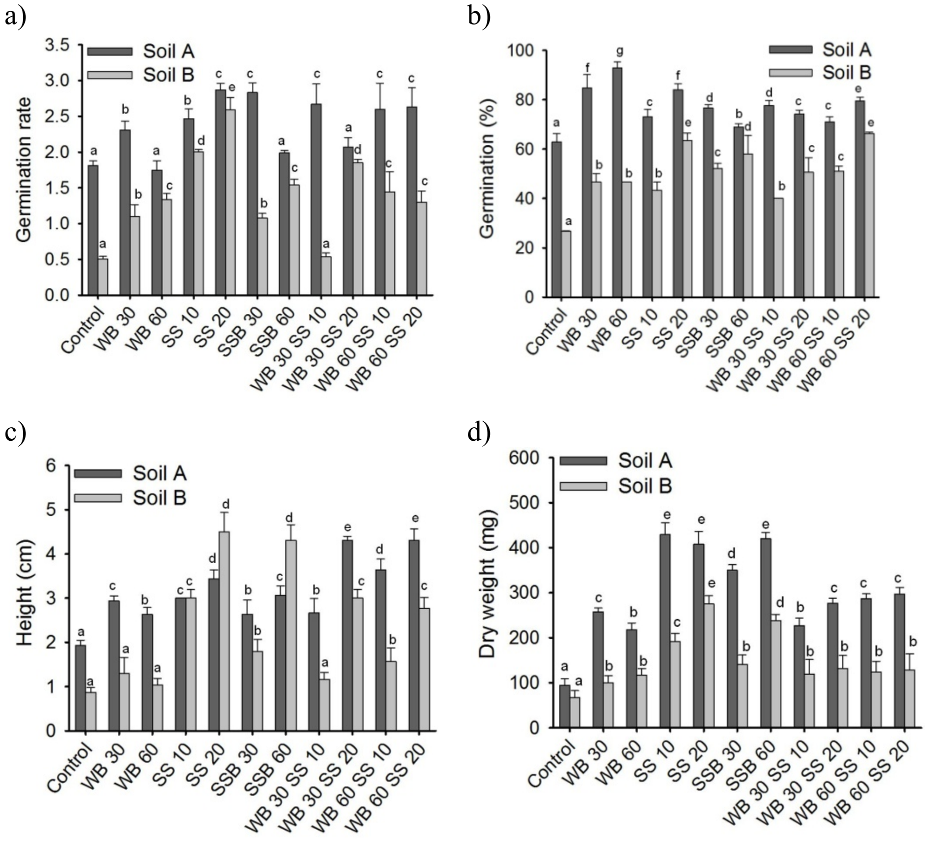


Fig. 9. Growth and development of Mullato II (*B. ruziziensis x B. decumbens* cross) for Soil A and Soil B. a) germination rate, b) germination (%), c) height (cm) and d) dry weight (mg). Treatments with the same letter were not significantly different (Scott-Knott test, $p < 0.05$) when comparing treatments of the same soil.

Germination rate and germination percentage were higher for Soil A than Soil B for all treatments, including the control. Furthermore, all amendments significantly differ from control, causing higher germination percentage. Wood biochar application caused the highest percentage of germination for Soil A, which was higher at the dose 60 g kg^{-1}. For Soil B. the highest percentage of germination were found when SS 20 and the blending WB 60 SS 20 were applied. This result is in agreement with the reduction of metal availability indicated by the extractants DTPA and Mehlich-1.

Sewage sludge biochar (SSB 60) also substantially increased germination for this soil (Fig. 9b). In general, plants heights are higher for Soil A than Soil B, with the exception of SS 20 an SSB 60, which presented the highest height (up to 4 cm) for Soil B. For Soil A, application of WB 30 SS 20 and WB 60 SS 20 caused plants to grow higher compared to other treatments and control (Fig. 9c). Soil A produced more plant biomass than Soil B when weighting the dry mass of plants (Fig. 9d). Sewage sludge (SS) and sewage sludge biochar (SSB) produced more biomass weight (up to 450 mg) for Soil A and Soil B (up to 300 mg).

Fig. 10 shows photographs of plants after 45 days since seeds were sowed, for Soil A and Soil B. The proliferation of plants in the plots and different heights, by a visual observation (Fig. 10), may be the result of the amendment's ability to reduce bioavailable metal concentrations in the soils. During the short-term experiment (60 days), all plants survived but leafs started yellowing, which might be related to nutrient deficiencies (eg. nitrogen). Brown et al. (2003) found that surface application of high N biosolids mixed with wood ash is effective in establishing a vigorous plant cover directly on metal mine tailings for at least two growing seasons after amendment application. Basta et al. (2015) found that soil amendments improved soil quality and nutrient pools, established a dense and high-quality vegetative cover, and improved earthworm reproductive measures. Amendments also increased soil enzymatic activities that support soil function.

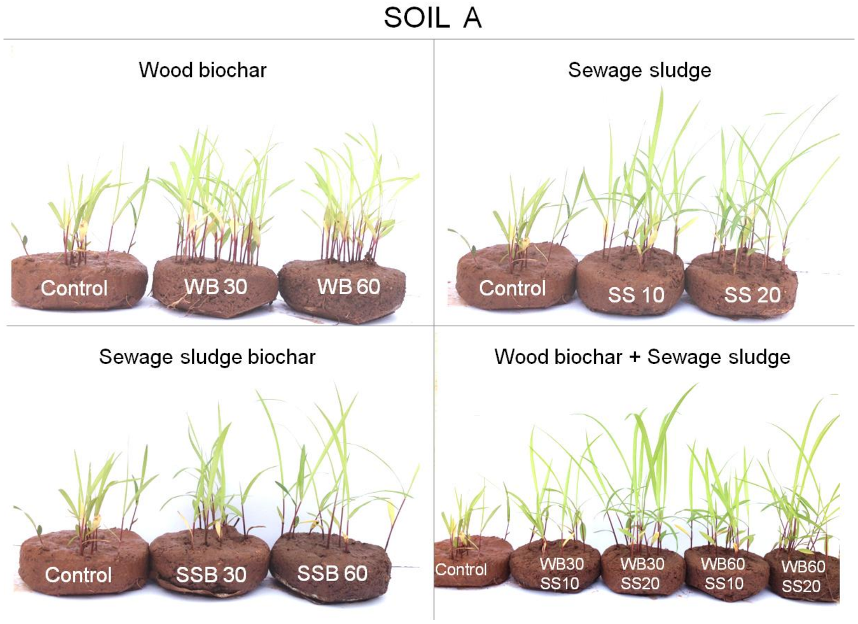


Fig. 10. Photographs of plants after 45 days since seeds were sowed according to the amendment, for Soil A and Soil B.

Rees et al. (2016) found that biochar can favor root growth both by decreasing the phytotoxicity of metal-contaminated soils and by immobilizing specific nutrients in the soils.

Overall, results from the greenhouse experiments demonstrated significant biochar benefits to plant growth. Our results agree with previous research demonstrating that the contributions of mineral nutrients in the biochar ash component play an important role in remediating soils and promoting plant growth (Basta et al. 2015; Rees et al., 2016).

Conclusion

The pyrolytic conversion of sewage sludge into biochar is a potential alternative to reuse and aggregate value to the residue. Applying sewage sludge biochar into soils were beneficial for plant development and lowered bioavailable levels of Cd, Pb and Zn in both soils and leachate. Blending wood biochar and sewage for soil application also improved soil quality.

So far, most studies using biochar as an amendment were performed under greenhouse or laboratory conditions. But, study in field conditions confirmed the reduction of Cd and Pb availability and transfer to rice plants up to three years after a single application (Bian et al., 2014). Future study should focus on field trials in order to evaluate the effectiveness of the amendments herein investigated. Furthermore, long-term effects on soil ought to be carried on.

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