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Research article

Silver removal from aqueous solution by biochar produced from biosolids via microwave pyrolysis

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ABSTRACT

The contamination of water with silver has increased due to the widespread applications of products with silver employed as antimicrobial agent. Adsorption is a cost-effective method for silver removal from aqueous solution. In this study biochar, produced from the microwave assisted pyrolysis of biosolids, was used for silver removal from an aqueous solution. The adsorption kinetics, isotherms and thermodynamics were investigated to better understand the silver removal process by biochar. X-ray diffraction results demonstrated that silver removal was a combination two consecutive mechanisms, reduction and physical adsorption. The Langmuir model fitted the experimental data well, showing that silver removal was predominantly a surface mechanism. The thermodynamic investigation demonstrated that silver removal by biochar was an exothermic process. The final nanocomposite Ag-biochar (biochar plus silver) was used for methylene blue adsorption and photodegradation. This study showed the potential of using biochar produced from biosolids for silver removal as a promising solution to mitigate water pollution and an environmentally sustainable approach for biosolids management and re-use.

1. Introduction

The number of applications using nanosilver products has increased significantly due to its antimicrobial ability. As a consequence of the use and disposal of nanosilver products, the contamination of water with silver ions is inevitable. Several methods have been used for silver removal from aqueous solutions, but adsorption is one of the most efficient methods with low energy consumption (Zhou et al., 2014). Adsorption is a surface process, where ions, molecules or atoms adhere to a surface of the substrate by chemical or physical interactions (Ok et al., 2015). Recently, adsorption has gained even more attention due to the potential use of biochar, which is a low-cost adsorbent produced by pyrolysis from different types of biomass, such as agricultural waste, sewage sludge, wood chips, orange peel, saw dust and tea waste (Ahmad et al., 2014). The adsorption capacity of biochar depends mainly on biochar feedstock biomass, pyrolysis technologies and pyrolysis conditions, in particular pyrolysis temperature, which has a great impact on biochar surface area (Ok et al., 2015; Rajapaksha et al., 2016; Tan et al., 2016).

The adsorption capacity of pollutants by raw biochar is limited; however, biochar production has several advantages compared to other types of adsorbents. Biochar feedstocks are abundantly available at low-cost, and beneficially, biofuel and biogas are produced from biomass while producing biochar (Tan et al., 2016). Recently, different physical and chemical activation methods have been explored to increase the adsorption capacity of raw biochar. Chemical modification of biochar is one of the most used methods, which consists of impregnating chemicals onto biochar to enhance the adsorption capacity of a target contaminant. For example, MgO-biochar and AlOOH-biochar have demonstrated a higher phosphorus removal capacity from aqueous solution than unmodified biochar (Jung and Ahn, 2016; Zhang and Gao, 2013). Chemical activation through an acid/base treatment has been used to increase surface area, modify biochar pore structure and surface functional groups. The common activation chemicals are hydrogen peroxide, phosphoric acid, nitric acid, potassium hydroxide and metal chlorides (Qian et al., 2015; Rajapaksha et al., 2016). For example, hydrogen peroxide modified biochar demonstrated a lead

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adsorption capacity 20 times higher than unmodified biochar (Rajapaksha et al., 2016). The physical activation of biochar is a chemical-free process, occurring between 600 °C and 1200 °C in the presence of steam, air and carbon dioxide (Qian et al., 2015). These gases have been used to increase the surface area of biochar and to create and/or enhance porosity within biochar by removing remaining volatile organic compounds.

Biochar adsorption has been explored for removal and recovery of several types of pollutants, such as metals, dyes, antibiotics, pesticides and polynuclear aromatics (Mohan et al., 2014; Reddy et al., 2017). The adsorption mechanisms depend on pollutant characteristics and biochar properties, which vary with feedstock and pyrolysis conditions (Ahmad et al., 2014; Ding et al., 2014). In general, the main mechanisms for organic contaminant adsorption by biochar are electrostatic interaction, π-π interaction, repulsion and intermolecular hydrogen bonding (Rajapaksha et al., 2016). Heavy metal removal by biochar can be explained by electrostatic interaction, precipitation, ion exchange, and surface adsorption by biochar surface functional groups (chemisorption) (Rajapaksha et al., 2016; Tan et al., 2016). Precipitation of metals takes place when the biochar is negatively charged, in particular with carbonate and phosphate groups as their release from biochar increases solution pH and consequently metal precipitation (Inyang et al., 2012). Adsorption of metals by biochar depends on surface functional groups, surface area and pore size. Biochar with high surface area usually exhibits higher metal adsorption capacity (Zhang et al., 2013).

Heavy metal adsorption by biochar is one most studied contaminant type removal from aqueous solution because it is hazardous for the environment and human health, even at low concentrations (Mohan et al., 2014). Activated carbon has been used for heavy metals removal, but its adsorption capacity is low (a few milligrams per g). Furthermore, using activated carbon has some disadvantages; it is an expensive material, the metal desorption step is very costly and has several environmental issues (Mohan et al., 2014). Heavy metal adsorption by biochar may be an alternative approach to activated carbon because it has higher adsorption capacity, low-cost production and lower greenhouse gas emissions (Alhashimi and Aktas, 2017). In general, lead, copper and cadmium have the highest biochar adsorption capacity while zinc, arsenic and nickel have the lowest adsorption capacity; however, the adsorption capacity depends on biochar properties (Sparks, 2012). The high lead and copper removal capacity by biochar explains the extensive number of studies in copper and lead adsorption by biochar.

Silver adsorption by biochar is not well explored. However, the use of silver has been adopted across in a wide range of applications, such as jewellery, dentistry, clothing and the food industry has increased its concentration in wastewater effluents (Yao et al., 2015). Finding a sustainable removal and recovery technology for silver is therefore urgent. Silver is an expensive material and just a few ppm are hazardous for the environment; for example, the limit of silver in drinking water was fixed at a maximum of 100 ppb (Zhou et al., 2014). Biochar adsorption of silver seems to be one of the most advantageous processes over other treatment methods, such as precipitation and ion-exchange (Zhou et al., 2014). The regeneration of the adsorbent is usually done by chemical leaching, which is an expensive process and can negatively impact on the environment. Therefore, finding applications for the final material (Ag-biochar) after adsorption is fundamental to mitigate the environmental impacts. The final material has been used successfully as an antimicrobial composite, but more research should be done to find new applications and optimise the recycling cycle of materials and minimise the economic and environmental costs (Yao et al., 2015; Zhou et al., 2014). Finally, recycling resources should be prioritised to avoid future natural resources depletion.

Using biochar for heavy metal removal from aqueous solution has been studied and well reported in the literature. However, the regeneration of the biochar or the reuse of the metal-biochar composite should be investigated to better understand the economic and environmental viability of using biochar for contaminant removal and recovery. Therefore, this work has three main objectives: first, assess the impact of pyrolysis conditions on biochar specific surface area; second, study the adsorption kinetics, isotherms and thermodynamics mechanisms of silver removal by biochar; and third, test the final composite (Ag-biochar) for methylene blue adsorption and degradation, which is a significant environmental problem due to its impact on plants and animals.

2. Materials and methods

This study was performed in three steps. The objective of the first step was to understand the impact of pyrolysis conditions (temperature, time, percentage and size of activated charcoal) on physical properties of biochar (BET, pore size and total pore volume) and assess the impact of these properties on silver removal. In this first step, the Taguchi method was used to study the major effects. Then the biochar with the highest silver removal capacity was selected for the second step. The objective of the second step was to study the adsorption kinetics, isotherms and thermodynamics of silver removal using the biochar sample selected in the previous step. In the last step, the final nanocomposite (Ag-biochar), after silver removal, was tested for methylene blue adsorption and photodegradation. The principal aim of the third step was to find a potential value-added application for the final composite, instead of pursuing silver recovery from the biochar and subsequent reuse of the biochar.

Using Minitab 17 for statistical analysis, the Taguchi method was employed to find the major effects of pyrolysis conditions on biochar physical properties. Four factors (temperature, residence time, activated charcoal load and size) were considered at three levels, the nine combinations of these factors considered, as represented in Table 1. The silver removal by biochar tests were analysed with one-way analysis of variance (ANOVA) where differences were considered significant if $p < 0.05$.

2.1. Biochar preparation

Experimental pyrolysis tests were carried out with biosolids from Euroa Wastewater Treatment facility in Victoria, Australia. A complete characterisation of biosolids used in this study was previously reported (Antunes et al., 2017). Activated charcoal (AC) was used as a microwave absorber (Sigma Aldrich C2889). Three different activated charcoal sizes were used in this work: the material less than 0.425 mm (fine) was obtained by grinding and sieving the original material, and the other two fractions were obtained by sieving the activated charcoal sample. The particle size of medium AC was between 0.425 and 1.0 mm, and the particles of large AC ranged between 1.0 and 2.0 mm. The specific surface area of these three fractions was similar (710 ± 22 m^2/g), which allowed us to ignore the impact of this variable on the final response.

Biosolids with approximately 50% moisture content were sieved to obtain a sample with a particle size less than 5.2 mm then blended manually with activated charcoal to obtain a uniformly distribution of AC throughout the biosolids, ensuring that charcoal particles did not break during the blending process. Mixture samples (60 g) were used for microwave pyrolysis according to the process parameters exhibited in Table 1. Duplicate runs were carried out and the final presented values are the average of these two