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Effect of dried olive pomace – derived biochar on the mobility of cadmium and nickel in soil

Frantseska-Maria Pellera, Evangelos Gidarakos *

School of Environmental Engineering, Technical University of Crete, Politechnioupolis, 73100 Chania, Greece

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ABSTRACT

This study aims to evaluate dried olive pomace derived biochar as a potential soil amendment for cadmium and nickel immobilization. Biochar was produced through pyrolysis under oxygen-limited conditions, at 400 °C (BC400) and 700 °C (BC700). Batch sorption/desorption experiments were conducted, investigating different agitation times (30–1440 min), initial metal concentration in the solution (100–3000 μM) and desorption pH (2–7). Results showed that by amending soil with biochar at increasing rates, enhanced sorption and decreased desorption of both metals were observed. In fact, biochar addition resulted in increased soil pH, possibly enhancing not only metal adsorption on soil surfaces (minerals or oxides), but also metal precipitation. Modeling results concerning sorption equilibrium corroborated this statement. Amended samples showed higher metal retention even at low pH values. Both biochars enhanced the ability of soil to immobilize cadmium and nickel, however in most cases BC700 was proven to be more efficient.

Introduction

Soil contamination by metals has been an issue of global concern for the last decades, since it represents a serious threat to the environment. In fact, under certain circumstances metal mobility may increase, possibly causing metal leaching through soil, which in turn may lead to groundwater contamination [1]. This would have deleterious effects not only on humans, but also on animals, due to the fact that metals are non-biodegradable, thus they tend to bioaccumulate in living organisms [2,3].

Cadmium is a considerably environmentally mobile and bioavailable metal. It is used mainly in alloys, pigments and Ni–Cd batteries, as a protective plating on steel as well as a stabilizer in plastic materials. It is highly toxic to plants and animals and has no essential biological function. Nevertheless, the levels at which it is naturally found in the environment are low enough not to cause acute toxicity. Within soil horizons, the surface layer is where cadmium is mostly encountered and its concentration in the majority of non contaminated soils is not expected to exceed 1 mg/kg, unless they are developed on parent materials of higher cadmium content [4,5]. It is an element of long biological half-life (15–30 years), which leads to chronic toxicity. In fact, its accumulation in the body often results in kidney damage and fractures, osteoporosis, lung and prostate cancer and endocrine disruption [5,6]. Nickel can be extracted from sulphide and oxide ores, such as lateritic oxides and pentlandite and is included among the most dangerous chemical elements [7]. Because of its anticorrosion and electrochemical properties it is commonly used in various industrial activities, such as stainless steel manufacture, electroplating, alloys, Ni–Cd batteries, electronic equipment and catalysts. Nickel may significantly contribute to metabolic processes of higher plants, animals and humans, while it plays an essential role in the development of microorganisms. Reduced nickel intake could eventually disrupt liver metabolism and reduce iron absorption and enzyme activity. On the other hand, toxic effects may appear if organisms are exposed to high doses of nickel [4,8]. The main factors affecting cadmium and nickel levels in soils, eventually leading to site contamination, are the type of soil parent materials, long term application of fertilizers, manures and sewage sludge, mining and smelting activities, as well as waste disposal and combustion of coal and oil [4,7–9].

There are numerous techniques that can be used for the remediation of metal contaminated soils, including isolation, immobilization, toxicity reduction, physical separation and extraction technologies [2,12]. Despite the effectiveness of the majority of these methods, their application is often limited by their high cost. This results in the development of more economically feasible techniques, among which is metal immobilization/stabilization with the use of amendments [3]. Different

* Corresponding author. Tel.: +30 2821037790; fax: +30 2821037850.
E-mail addresses: fpellera@isc.tuc.gr (F.-M. Pellera), gidarako@mred.tuc.gr (E. Gidarakos).

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types of amendments can be used for this purpose, including inorganic and organic materials. Lately, there has been an increasing interest regarding the use of biochar as an amendment for the remediation of metal contaminated soils [11].

Biochar is characterized as a carbonaceous material, generated through thermal processing (i.e., pyrolysis) of biomass under oxygen-limited or inert conditions [13–16]. Biochar materials are mainly used as amendments, in order to improve soil quality and fertility [17,18] through a variety of mechanisms, such as retention of water and nutrients [19]. Furthermore, biochar is known for its ability to sequester atmospheric carbon [20,21] and store it in soil for long periods of time, thus reducing emissions. Research concerning the use of biochar for soil remediation from organic [22] and inorganic [15,23] contaminants is in its infancy; however, the interest about this subject is increasing day by day. Especially regarding metal-contaminated soil remediation, the use of biochar seems promising, since recent studies have provided quite positive results [24,25]. In fact, several researchers have mentioned that the application of biochar to soil can reduce metal mobility and bioavailability. Uchimiya et al. [15], in a research of theirs found that Ni(II) and Cd(II) immobilization was enhanced when broiler litter-derived biochars were added to soil and linked this phenomenon to the positive effect of chars on pH. In a later study [16], by investigating a wider range of pyrolysis temperatures for char production, the authors assessed that biochar selection is case-specific and depends on biochar and soil characteristics as well as on amendment purposes. Beesley et al. [20] compared biochar with greenwaste compost regarding their effect on mobility and bioavailability of several organic and inorganic contaminants. The results obtained with biochar were particularly encouraging, especially for what concerned water-soluble Cd and Zn reduction. In a study conducted by Jiang et al. [26] enhanced adsorption of Pb(II) was observed when using biochar derived from rice straw as a soil amendment. Oak wood-biochar prevailed other amendments in reducing Pb availability and phytotoxicity in a military shooting range soil, in a study performed by Ahmad et al. [27]. Xu et al. [28] found that biochars generated from peanut and canola straws induced electrostatic and non-electrostatic mechanisms, which contributed to the increase in Cu(II), Pb(II) and Cd(II) adsorption by an Oxisol. The application of biochar to a contaminated soil reduced metal mobility and bioavailability in the study of Houben et al. [29]. The authors attributed their results to the biochar liming effect. Ehsan et al. [30] successfully used biochar derived from unfertilized dates to reduce the extractability and immobilize Ni and Cd in soil, while Hmid et al. [31] used olive mill waste biochar to obtain lower mobility, bioavailability and toxicity of metals in soil. In their study, Venegas et al. [32] determined that biochars obtained from tree barks and vine shoots are promising materials to be used for the remediation of metal-contaminated soils.

As shown in literature, biochar can be generated from various types of feedstock materials, as well as through different thermal processes, involving a wide range of process temperature and duration, pre- and post-treatment (e.g., chemical activation), equipment types, etc. [19,33,34]. Therefore, further studies are needed in order to gain a better understanding of the mechanisms that take place in the soil system after the incorporation of such materials, as well as the identification of the processes responsible for the remediation properties that they manifest. This will improve research concerning the optimization of biochar production conditions (type of feedstock and pyrolysis conditions), thus making it possible to produce materials suitable for different purposes.

Olive oil industry is one of the most important agroindustrial activities in the Mediterranean basin, with European countries accounting for 69.6% of the world's total production of olive oil in 2013. In fact, the top 5 producers of virgin olive oil, in descending order, are Spain (1.11×10^6 t), Italy (442×10^3 t), Greece (305.9×10^3 t), Tunisia (191.8×10^3 t) and Turkey (187.9×10^3 t) [35]. High olive oil production however, implies accordingly elevated amounts of solid waste and wastewater originating from olive mills. Management of these types of waste constitutes a major issue, which is often connected to environmental problems [36]. Olive mill solid waste, otherwise known as olive pomace, is usually subjected to further processing in order to produce a residual oil, known as olive pomace oil. This processing yields a type of by-product called dried olive pomace [37,38] which is mainly used for heating purposes.

The main objective of this study is the production of biochar through pyrolysis of dried olive pomace (DOP) and its evaluation as an amendment for metal immobilization/stabilization in soil. Specifically, two types of biochar were produced at two different temperatures, 400 and 700 °C, respectively. These materials were then added to soil at four amendment rates (i.e., 5, 10, 15 and 20%) and their effect on the mobility of two metals, specifically cadmium and nickel, was studied by conducting batch sorption–desorption experiments.

This study provides information regarding the possible mechanisms responsible for the variation in cadmium and nickel mobility in soil after biochar addition. Given the potential toxicity of these metals, it is important to find amendments, able to increase their retention in soil. This paper makes a significant contribution to this regard. In addition, the application of multiple kinetic and equilibrium models to sorption processes involving amended and non-amended soil samples has not been extensively studied before. Furthermore, the conversion of dried olive pomace to biochar and its use as a soil amendment for metal immobilization is provided as a possible alternative management option for this material.

Materials and methods

Soil and biochar preparation

The soil used in this study was obtained from an agricultural area in Chania, Crete. At first, the sample was air-dried and subsequently the soil lumps were manually ground and sieved (<2 mm).

Dried olive pomace (DOP) was obtained from an olive mill, situated in the Akrotiri area of Chania, Crete. As soon as DOP was brought to the laboratory, it was initially oven dried (100 °C) and ground (Pulverisette 19, Fritsch) to obtain a particle size lower than 500 μm. Subsequently, the material was pyrolyzed under oxygen-limited conditions in order to produce the two biochar materials. Briefly, porcelain crucibles were filled to capacity with the ground DOP, covered with a fitting lid and introduced in a muffle furnace. For both biochar types the target temperature (400 and 700 °C) for their production was achieved within 1 h and the duration of the pyrolysis process was of 2 h. The resulting materials were then washed with deionized water in a solid:liquid ratio of 1:15 (g:mL), in order to remove excess ash. Then, the residues were separated by vacuum filtration, rinsed once again with deionized water and dried in an oven. Following this procedure two types of biochar were produced, which are hereafter referred to as BC400 and BC700, where 400 and 700 represent the pyrolysis temperatures.

Characterization

The properties which were determined for soil include pH, point of zero charge (pH_{PZC}), pseudo-total metal concentration, texture, moisture, ash and organic matter contents, specific surface area (SSA_{BET}) and mineralogical composition. DOP was characterized regarding pH, pseudo-total metal concentration, moisture,