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Sorption, desorption, and degradation of pesticides in biochar amended agricultural soils

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Abstract

In recent few years, extensive and inefficient utilization of pesticides prompted genuine soil and water contamination and impacting serious lethal impacts on living beings. To deal with the environmental issues, use of environment-friendly amendments for soil remediation is essential to counteract the presence of pesticides in soil. Biochar has a higher porosity, surface area, pH, abundant functional groups, and highly aromatic structure, mainly depending on the feedstock and pyrolysis temperature and thus, it has emerged as an efficient adsorbent, diminishing the pesticide bioavailability in treated soils. So, it’s important to recognize the effects of biochar and mechanisms on pesticide sorption and desorption in soils. High pyrolysis temperature increases biochar surface area and has a positive effect on pesticide sorption in soil, whereas a lower temperature during pyrolysis has a large number of functional groups attached to biochar thus exerting reducing the pesticide sorption. Thus, to design biochar modifications a rational understanding of effects and mechanisms of biochar action are necessary. This review primarily ascertains dominant properties of biochar including porosity and surface area, pH, surface functional groups, carbon content and aromatic structure, and mineralogical composition, and evaluates the effect of biochar on pesticide sorption, desorption, and degradation in agricultural soils. In addition, a vision for future research prospects has been anticipated by considering the pesticide bioavailability as residues in soil, influence of contaminants in biochar on pesticide removal, pesticide properties and its behavior in biochar amended soils, mutual effect of soil microorganisms and biochar on pesticide degradation and multifunctional use of large- scale application of biochar on agricultural soils.

Keywords: pesticides, soil remediation, biochar, biochar modifications, sorption, desorption, degradation

Introduction

In modern agriculture, the use of pesticides is inevitable because they are required to control weeds, insects and other pests which gradually deteriorate the soil quality. Accumulation of pesticide residues exceeding the self-purification capacity of the soil, which resulted in serious soil pollution and deteriorated soil quality, has been the result of extensive and inefficient use of pesticides over the last several decades. The potential impacts of pesticides on the environment and public health needs extensive attention. Thus use of sustainable and environment-friendly alternatives to counteract soil contamination for soil remediation appears to be one suitable approach (Cheng *et al.*, 2016) [9].

Biochar is porous carbon rich solid produced from biomass via pyrolysis in anoxygenic condition (Lehmann *et al.*, 2006) [20] and accrediting to its high cation exchange capacity (CEC), which is related to the biochar surface area, negative surface charge and surface charge density it can also act as a fertilizer depending on feedstock type and can retain nutrients. Biochar amendment and its effect on heavy metal behavior in soils have been well investigated (Inyanga *et al.*, 2016; Li *et al.*, 2017; Liu *et al.*, 2018) [14, 21, 24]. In recent times, the ability in sorption and immobilization of heavy metals and organic contaminants in the soil attracts attention towards biochar (Martin *et al.*, 2012; Mukherjee *et al.*, 2016) [26, 27] which is as a result of the presence of highly porous structure and various functional groups (e.g., carboxyl, hydroxyl, and phenolic groups). Biochar is most commonly applied as soil amendment for improving soil quality, increasing crop yield, and reducing irrigation and fertilizer requirements (Liu *et al.*, 2016) [24], and mitigating greenhouse gas emissions (Sohi, 2012; Xu *et al.*, 2012) [36-37, 47].

Investigation to understand sorption-desorption and degradation of pesticides as an impact of biochar application in agricultural soils has gained importance in past years. Soils incorporated with 1% biochar in soils decreased biodegradation of benzonitrile due to enhanced sorption

(Zhang *et al.*, 2005) [55], reduced herbicidal efficacy and microbial degradation of diuron on barnyard grass (Yang *et al.,* 2006) [48], and decreased uptake of chlorpyrifos by Chinese chives and Spring onion (Yu *et al.*, 2009; Yang *et al.*, 2010) [52, 49]. Yu *et al.* (2006) [52] reported an enhanced the sorption of diuron, and increased the non-linearity of the adsorption isotherm and the extent of sorption-desorption hysteresis in soils amended with biochar derived from pyrolysis of red gum chips.

Van Zwieten *et al.* (2010) [43] testified an increase in radish biomass when biochar produced from papermill waste was used without any additional fertilizer in both calcrosol and ferrosol, whereas, wheat biomass decreased in the calcarosol, but not in the ferrosol and no significant differences were stated for soybean biomass on either soil as compared to the control. Van Zwieten *et al.* (2010) [43] reported that in calcarosol soil, the co-application of both biochar and fertilizer had a positive effect on biomass production in most plants studied, except wheat and radish as soil and biochar properties determines the response of the soil system to biochar. The increase in crop yields and productivity is dependent on the availability of these retained plant nutrients. However, contradictory reports are observed in some cases (Spokas *et al.*, 2012).

Recent researches focused on the processes involved and impact of biochar in pesticide fate, sorption and dissipation of pesticides such as atrazine, terbuthylazine, diuron, isoproturon, and pyrimethanil (Martin *et al.*, 2012; Spokas *et al.*, 2009; Wang *et al.*, 2010; Yu *et al.*, 2006, 2010) [38, 26, 8, 44, 52]. Reports indicated an increase in pesticide sorption and decrease in dissipation in soils amended with fresh biochar. Yet, Martin *et al.* (2012) [26] testified decrease in sorptive capability of biochar over time with aging/weathering in the soil environment. Present reports either focus on one or several specific pesticides (J.W. Jin *et al.*, 2016; Yu *et al.*, 2011) [16-17, 52, 54], or one aspect of pesticide behaviors like sorption (Yavari *et al.*, 2015) [50]. Thus, understanding of the impact of biochar amendment on the fate of pesticides in soil, systematic characterization of pesticides behavior in agricultural soils as an effect of biochar application would help in risk assessment and modeling the fate of pesticides in the environment by on the dominant characteristics of biochar (Acosta *et al.*, 2016) [1], the effects of biochar on pesticide sorption-desorption in the soil and the effects of biochar on pesticide degradation in the soil (Ahmedna *et al.*, 2004) [3].

Dominant characteristics of biochar

The specific physicochemical properties of biochar determined largely by its feedstock and the pyrolysis conditions influence the sorption capability for pesticides in the soil environment (Yavari *et al.*, 2015) [50]. Pesticide sorption-desorption by biochar is pre-dominantly affected by porosity, surface area, surface charge, pH, functional groups, carbon content, aromatic structure, and mineralogical composition.

The sorption capacity of biochar for organic pollutants including pesticides is affected by the primary properties, porosity and surface area by influencing the pore filling and surface sorption, respectively. Higher surface area and more porous structures will result in higher sorption capacities. Pore structure can be formed in biochar due to water loss in dehydration process, volatilization of organic matter, fracture, as well as collapse during the pyrolysis of biomass. According to the International Union of Pure and Applied Chemistry (IUPAC, 1972) [15] the pore size of biochar is highly variable, comprising micropores (< 2 nm), mesopores (2–50 nm) and macropores (>50 nm). In general, size of pores plays a vital role in pesticide sorption. Large pesticide molecules aren't trapped with small pore-sized biochar, regardless of their charges or polarity (Ahmedna *et al.,* 2004) [3]. Pyrolysis temperature substantially affected biochar porosity and surface. Increasing the pyrolysis temperature decreased the mean pore size of biochar, resulted in larger pore volumes and surface area and the pore size of rice straw biochar (59.2–151.3 nm) was lower than pig manure biochar (88.4–229.9 nm) produced at 300–700 °C (Liu *et al.,* 2017) [24]. Conversely, in some cases, when biochar is produced at a temperature of over 550 °C it has lower surface area and porosity. J. Jin *et al.* (2016) [16-17] testified lower surface area in biochar produced from biosolids at 600 °C (5.99 $m^2\ g^{-1}$) compared to that at 550 °C (8.45 $m^2\ g^{-1}$). The small surface area at higher temperature may be attributed to more macropores other than micropores or tar blockage in biochar porous structure (Li *et al.*, 2017) [21]. Besides pyrolysis temperature, the composition of biochar feed- stock also affects its properties. The surface area of plant biochar (112–642 $m^2\ g^{-1}$) such as oak wood, corn stover, and pine needle is generally much higher than that of swine manure (4.11 $m^2\ g^{-1}$), pig manure (3.32–20.5 $m^2\ g^{-1}$), and bio- solid biochar (50.9–94.2 $m^2\ g^{-1}$) such as poultry and turkey litter (Cantrell *et al.*, 2012; Li *et al.*, 2017; Liu *et al.*, 2017) [7, 21, 24]

Alike to porosity and surface area, biochar pH was also subjective of pyrolysis temperature and feedstock. Generally, biochar is alkaline and with increasing pyrolysis temperature the pH increases further (Cantrell *et al.*, 2012) [7]. Studies on of biochar produced from several other biomass, like biosolids, agricultural residues and livestock manure confirmed positive relationships between pH and pyrolysis temperature (J. Zhang *et al.*, 2015; Liu *et al.*, 2017) [24, 56]. Increasing temperature results in higher pH of biochar due to higher ash content (J. Jin *et al.*, 2016) [16-17]. Besides, at a higher temperature there is reduction of acidic functional groups such as –COOH on biochar contributing to higher pH (Li *et al.*, 2017) [21]. Higher pH of biochar can hasten the hydrolysis of organophosphorus and carbamate pesticides in the soil through alkali catalysis mechanism.

The sorption capacity of biochar is essentially affected by the surface functional groups including carboxylic (–COOH), hydroxyl (–OH), lactonic, amide and amine groups (Antón-Herrero *et al.*, 2018; Li *et al.*, 2017) [5, 21-24]. Generally, quantities of functional groups on biochar are influenced by two crucial factors, surface pyrolysis temperature and raw materials. Though, unlike the increasing tendency of surface area, porosity, and pH, higher temperature generally decreases the ratios of H/C, O/C, and N/C (Liu *et al.*, 2017) [56], indicative of reduction in abundance of functional groups on biochar.

Sorption capability of biochar for pesticides is also affected by carbon content and aromatic structure (Lian and Xing, 2017; Pignatello *et al.*, 2017) [22, 30]. Sustainability of biochar behavior in the soil is dependent on its aromatic structure (Martin *et al.*, 2012; Xiao and Chen, 2017) [26, 21, 46, 58]. As temperatures rise above 500 °C, biochar derived from lingo-cellulosic materials becomes increasingly carbonized (Allen-King *et al.*, 2002) [4], and accordingly carbon content of biochar increases with higher temperature (Liu *et al.*, 2017) [24]. For that reason, over the years, biochar can contribute towards pollution control in soils.

The mineralogical composition of biochar which determines the cation exchange capacity is also considered important for pesticide sorption from soil (Dias *et al.*, 2010) [10]. Surface chelation and/or surface acidity mechanisms can reduce the availability of pesticides (Wei *et al.*, 2001) [45]. The concentration of mineral component of biochar is influenced by pyrolysis temperature and raw material. Higher temperature enhances minerals content in biochar (Subedi *et al.*, 2016) [39]. Generally, biosolid biochar contains much higher P contents (1.82–3.60%) as compared to oak wood biochar (0.03–0.06%) (H. Zhang *et al.*, 2015) [56], while K content in higher in poultry litter and pig manure biochar (1.6–5.9%) than that in biochar from other feedstocks (Subedi *et al.*, 2016) [39].

Pesticide sorption-desorption in biochar amended soils

The processes of mobility and conversions as chemical transport, leaching, bioavailability in the soil, absorption, biotoxicity and utilization of pesticide by plants is affected by capability of biochar to adsorb pesticides (Khorram *et al.*, 2016) [18].

Biochar sorption, is mostly through two processes involving surface adsorption and partitioning (Qiu *et al.*, 2009) [39]. Surface adsorption may be due to stable chemical bonds formed by the functional groups on biochar surface with ions or organic compounds. Biochar properties (e.g. surface area, porous structure, and aromaticity), pesticide characteristics (e.g. molecular dimensions, hydrophobicity), soil properties (e.g. soil pH, mineral content) and environmental factors affect pesticide sorption of biochar in soils (Qiu *et al.*, 2009) [39]. The abundance of aliphatic double bonds and variety in aromatization structure increases aromaticity of biochar increases the sorption capacity of biochar for hydrophobic pesticides. Sorption-desorption processes in soil are significantly influenced by the clay mineral interaction with biochar. Wang *et al.* (2010) [8] found that pine wood biochar produced at 700 °C had higher porosity and surface area and thus had higher sorption capability for terbuthylazine in the soil as compared with those produced at 350 °C. Soil amended with 2% biochar from Eucalyptus wood chips had higher surface area and had 5 times higher sorption capacity for isoproturon than the unamended soil (Sopeña *et al.*, 2012) [37]. J.W. Jin *et al.* (2016) [16-17] testified that with increasing biochar amounts (1–20%), the sorption capacity of biochar for imidacloprid, isoproturon, and atrazine in the soil increased, which was attributed to the increased organic carbon content, surface area, as well as the decreased hydrophobicity. Additionally, as compared to some other amendments biochar displayed higher efficiency in improving sorption capacity of the soil to pesticides. Wang *et al.* (2010) [8] reported that soil sorption of terbuthylazine was higher with biochar treatment than treatment with biosolids (both thermally dried anaerobically digested granule biosolid and thermally dried undigested granule biosolid). Cabrera *et al.* (2014) [6] pointed out that in silty soils amended with wood pellet biochar which had high surface area and low dissolved organic carbon content the herbicides, aminocyclopyrachlor, and bentazone were almost completely adsorbed. However, the sorption of herbicide in the soil decreased in soils amended with biochars with lower surface area and higher dissolved organic carbon contents. Desorption or the release behavior of pesticides adsorbed onto biochar is affected by sorption capability of biochar and environmental behavior of pesticides in the soil, is associated with the pesticide bioavailability and pollution of surface and groundwater. (Khorram *et al.*, 2016) [18].

Hysteresis is also a common phenomenon in soil-pesticide interactions. Sorption effect is partially reversible, desorption is much more difficult than sorption as all pesticides absorbed into biochar cannot be desorbed. Reversible sorption of pesticide on biochar in amended soils occurs through two mechanisms: (Acosta *et al.*, 2016) [1] the swelling of a sorbent during sorption, leadingto micro-/macro-pore network deformation (Sopeña *et al.*, 2012) [37], and (Agrafioti *et al.*, 2014) [2] weak binding between the pesticides and biochar components (Tatarková *et al.*, 2013) [41]. Sopeña *et al.* (2012) [37] reported higher hysteresis coefficient value of the biochar-amended soil compared with that of the unamended soil as micropore deformation led to reversible sorption of isoproturon 2% biochar amended soil. Irreversible sorption of a pesticide to biochar occurs due to several action mechanisms including surface- specific adsorption, entrapment into micropores, and partitioning into condensed structures (Yu *et al.*, 2010; Sopeña *et al.*, 2012; Wang *et al.*, 2010) [44, 37, 8].

Pesticide persistence in agricultural soil is influenced by biochar application (Sopeña *et al.*, 2012) [37]. A significant quantity of biochar or some of its components change with time, this may be referred to as “ageing” (Kong *et al.*, 2014) [19]. This process of biochar ageing affects pesticide sorption-desorption in the soil due to the changes in its physicochemical properties. Zhang *et al.* (2016) [9, 12, 17, 18, 33, 57] presented that the potential sorption capacity of biochar is negatively affected with biochar ageing due to decrease in biochar specific surface area. Hence, it’s essential to protect biochar from ageing and to utilize aged biochar to achieve a better effect on pesticide sorption-desorption in the soil.

Pesticide sorption capacity in soils of biochar is comparatively lower other types of sorbents, such as clays (e.g. stevensite, smectite), and activated carbon (Acosta *et al.*, 2016; Antón-Herrero *et al.*, 2018) [1, 5]. Thus, biochar modification to increase the surface area, porosity, and/or functional groups, to enhance its sorption capacity has gained attention in the recent past. Biochar modification is possible by loading with organic functional groups, nanoparticles, and activation with alkali (Rajapaksha *et al.*, 2016; Tan *et al.*, 2016) [33, 40], loading with different minerals such as hematite, magnetite, zerovalent Fe, hydrous Mn oxide, calcium oxide, and birnessite (Agrafioti *et al.*, 2014; Van Vinh *et al.*, 2015) [2, 42] and by grafting exogenous functional groups, like amino and hydroxyl groups via polyethylenimine and chitosan modification (Huang *et al.*, 2016) [9, 12].

Even though, modification methods used for soil remediation provide higher sorption efficiency for pesticides but while considering modified biochar as a soil amendment, economic viability and potential problem of the element needs to be considered.

Pesticide degradation in biochar amended soil

Pesticide degradation in soil generally includes biodegradation, hydrolysis, photolysis, and oxidation. The principal pathway of dissipation and decomposition for most of the pesticides, as isoproturon in the soil is biodegradation (Si *et al.*, 2011; Sopeña *et al.*, 2012) [34, 37]. So, this review concerns mostly around the biodegradation of pesticides although several studies have reported the effect of biochar on other degradation pathways, such as the mechanism of persistent free radicals (Qin *et al.*, 2018) [31]. Biochar is an effective amendment for pesticides for decreasing pesticide biodegradation in soils due to sorption effect (Khorram *et al.*, 2016; Tatarková *et al.*, 2013) [18, 41]. In contrast, higher microbial stimulation with addition of biochar can lead to higher microbial degradation of pesticides (Qiu *et al.*, 2009a;

Zhang *et al.*, 2005) [32, 55]. However, biochar affects the pesticide biodegradation in soils depending on combination of both aspects, favoring the dominant one. In biochar-amended soil because of the increase of sorption and reduced desorption from biochar surface, decreased pesticide biodegradation resulting in lower pesticide availability for soil microorganisms (Muter *et al.*, 2014; Nag *et al.*, 2011; Spokas *et al.*, 2009; Yang *et al.*, 2006; Yu *et al.*, 2006) [28, 29, 48, 52]. Sopeña *et al.* (2012) [37] testified that soils amended with 1% and 2% red gum wood biochar showed reduction in biodegradation of the herbicide isoproturon due to enhanced sorption, slower desorption. The degradation of chlorpyrifos and carbofuran decreased significantly with increasing amounts of biochar in the soil as red gumwood biochar affected the bioavailability of pesticides (Yu *et al.*, 2009) [52].

Pesticide biodegradation is essentially dependent on soil microbes, their abundance and structure of the pesticide to be affected by the biochar in soils (Gul *et al.*, 2015; Zhu *et al.*, 2017). Microbial stimulation by the nutrients present in biochar attributes to the increased pesticide degradation in biochar-amended soil (Zhang *et al.*, 2005) [55]. Plant growth especially the root growth, the uptake and degradation of the pesticides may be enhanced by use of biochar. Thus pesticides degradation in the biochar-soil-root systems demands scientific attention.

According to previous studies the decline of pesticide mobility can be found in soil amended with biochar in comparison with the control (Cabrera *et al.*, 2014) [6]. Cabrera *et al.* (2014) [6] revealed that pyraclostrobin has higher absorption in soil, and biochar amendment did not further increase its sorption, which advocated that addition of biochar doesn't necessarily increase the retention of low mobility pesticides in soil. However, the sorption of pesticides with high mobility in the soil can be increased with addition of biochar with higher surface area and lower dissolved organic carbon contents. Yang *et al.* (2006) [48] stated that wheat biochar amended soil exhibited reduction in the bioavailability of diuron as evidenced by the decreased microbial degradation and its herbicidal efficacy due to enhanced sorption of diuron on barnyard grass. In biochar-amended soils, despite the longer persistence of the pesticide residues, the plant uptake of pesticides is decreased with the increasing application ratio of biochar in the soil. In soils, amended with 1% biochar, the plant uptake of chlorpyrifos and carbofuran decreased to 10% and 25%, respectively, in comparison with the soil without biochar amendment (Yu *et al.*, 2009) [52]. Several factors ranging from soil composition and physicochemical properties, pesticide properties and biochar physic-chemical properties determines the bioavailability of pesticide residues in the soil. To understand the mechanism involved in a specific process need further studies.

Reports suggested biochar as the prominent adsorption phase for organic contaminants in soils (Singh and Kookana, 2009). Though, the interaction of biochar with the soil organic substances and/or soil mineral fraction (Singh and Kookana, 2009) was anticipated to significantly affect the sorption process. Thus, the decreasing sorption capacity of biochar may be due to these interactions that lead to the adsorption site competition and/or pore blockage of biochar. Likewise, when other contaminants including organic and inorganic compounds, such as heavy metals appear simultaneously with biochar in the soil, biochar may have negative effects on pesticide removal. Further investigations regarding the action of biochar in pesticide removal and degradation in multi-contaminated soils are necessary.

Future line of work

The sorption, desorption, and degradation of them in the soils amended with biochar is largely affected by the properties of pesticides including types, molecular size, molecular polarity, and functional groups. Based on the polarity and ionizability of the chemical the same biochar may exhibit differential sorption abilities for different kinds of pesticides. Suitability of biochar to improve the sorption efficiency of biochar by immobilization of specific pesticide group is to be scrutinized. Pesticide biodegradation can be decreased by biochar as a soil amendment due to sorption. However, reports suggest that biochar can be used by microorganisms to increase microbial abundance and change microbial community composition, which would enhance biodegradation of pesticides. Thus, there's a need of further work to explore the interactions that occur among biochar, microorganisms, and pesticides, and their combined effects on pesticide biodegradation in the soil.

Biochar is considered to have dual function as a remedial measure for pesticide degradation as well as a soil amendment due to its high surface area and strong adsorption ability, which is dependent on different raw materials and pyrolysis conditions. Specificity of biochar suitable for remediation purposes should be checked before-hand and its application rate and frequency of biochar amendments to reach an optimal remediation can be assessed. Besides, for agricultural soil, enhancing plant growth is the primary function of the amendment thus the physicochemical properties of the soil should be maintained or improved. In view of the reported research on effects of biochar as carbon sequestration, nutrient retention and crop yield improvement in agricultural soils (Hussain *et al.*, 2017; Sohi, 2012; Xu *et al.*, 2012) [36-37, 47], biochar application for pesticide removal, would be multifunction, demanding further systematic study. Moreover, Large-scale field trials are needed for implementation of operational scale remediation projects as mostly the applications of biochar for remediation of pesticide-contaminated soil have mainly been conducted in laboratory, greenhouse or plot experiments.

Conclusion

Biochar is a carbon rich derivative from the pyrolysis of biomass. Applying biochar as an amendment to treat contaminated soils, improve soil quality and increase the crop yield has been receiving increasing attention, due to its specific physicochemical properties which largely depend on pyrolysis temperature and feedstock. Although biochar usually provide higher sorption efficiency for pesticides, while, considering modified biochar as soil amendment, balance should be maintained that the modification methods are economically viable for soil remediation. Additionally, due to sorption effect, biochar is considered to be an effective amendment for pesticides and decreases pesticide biodegradation in soils. Nevertheless, the addition of biochar may results in higher microbial degradation of pesticides due to high microbial stimulation. So, the effect of biochar on pesticide biodegradation in soils is largely dependent on the dominant action.

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