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Review

Toxicity of Cadmium and nickel in the context of applied activated carbon biochar for improvement in soil fertility

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ABSTRACT

Toxicity induced by heavy metals deteriorates soil fertility status. It also adversely affects the growth and yield of crops. These heavy metals become part of the food chain when crops are cultivated in areas where heavy metals are beyond threshold limits. Cadmium (Cd) and nickel (Ni) are considered the most notorious ones among different heavy metals. The high water solubility of Cd made it a potential toxin for plants and their consumers. Accumulation of Ni in plants, leaves, and fruits also deteriorates their quality and causes cancer in humans when such a Ni-contaminated diet is used regularly. Both Cd and Ni also compete with essential nutrients of plants, making the fertility status of soil poor. To overcome this problem, the use of activated carbon biochar can play a milestone role. In the recent past application of activated carbon biochar is gaining more and more attention. Biochar sorb the Cd and Ni and releases essential micronutrients that are part of its structure. Many micropores and high cation exchange capacity make it the most acceptable organic amendment to improve soil fertility and immobilize Cd and Ni. In addition to improving water and nutrients, soil better microbial proliferation enhances the soil rhizosphere ecosystem and nutrient cycling. This review has covered Cd and Ni harmful effects on crop yield and their immobilization by activated carbon biochar. The focus was made to elaborate on the positive effects of biochar on crop yield and soil health.

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Contents

1. Introduction

Heavy metals disturb the natural ecosystem due to their toxic effects (Abid et al., 2017; Danish et al., 2019a; Fiaz et al., 2014; Younis et al., 2015; Zafar-ul-Hye et al., 2020a, 2020c). These heavy metals are continuously becoming a part of the ecosystem through anthropogenic activities such as industrialization mining, overuse of pesticides in agriculture, and sewage water irrigation. It is a well-documented fact that any compound's accumulation beyond the soil's threshold limit becomes a soil pollutant (Zafar-ul-Hye et al., 2020b, 2020). The soil pollutants caused toxic effects on the plants and animals and soil microorganisms (Adriano, 2001). This also can affect the diversity, viability, and physiology of microbes in rhizosphere area which play very important role for healthy plant growth (Basu et al., 2021).

Such problematic soil conditions adversely affect the growth of plants and cause deterioration of crop productivity and quality. Among different environmental pollution, heavy metals are notorious that induce abiotic stresses in the plants. These heavy metals disturb the plant metabolism and restrict growth due to their high accumulation in different plant parts. In addition to plants, heavy metals are also dangerous for human and animal health that consumes metal contaminated food (Shah and Nongkynrih, 2007).

2. Cadmium and nickel as a pollutant

Cd (Zafar-ul-Hye et al., 2020a) and Ni (Gill and Tuteja, 2011) are the most notorious among different heavy metals. Both heavy metals have accumulated in Pakistan's soils with time in significant quantities (Bhutto et al., 2009). Indifferent biogeochemical and environmental cycles Cd enter through anthropogenic sources such as electroplating, industrial waste, pigments, plastic accessories, paints and metal alloys (Nriagu, 1996). In addition to the above sources, Cd also becomes a part of our environment through wastewater irrigation, mining of zinc, overuse of phosphorus fertilizer, uses automobile smoke, burning of fossil fuels, higher application of pesticides and cement industries (Dixit et al., 2011; Rao et al., 2011).

On the other hand, Ni is also a heavy metal, which also induced toxic effects in the plants beyond the required amount. It shares 3% composition in the earth and the 24th essential nutrient in the earth's crust. Emission of smoke from vehicles, mining of metals, burning fossil fuels, organic manure, industrial and municipal waste is also a major contributor of Ni in our environment. The role of anthropogenic activities is also crucial in that regard (Alloway, 1995).

3. Cd, Ni, agricultural soil and living organism health

In agricultural systems, Cd accumulation due to human activities has become one of the major issues globally, protecting crop productivity and making food poor quality (Chen et al., 2007). Most diseases caused by the higher accumulation of Cd in humans and mammals are not detectable because they show no symptoms. Search characteristics of Cd make it a potential toxin (López-Millán et al., 2009). Untreated sewage water is a major source of Cd contamination in both plants, especially vegetable crops, and soils (Hossny et al., 2001; Satarug et al., 2003). It has been observed that 80% of Cd becomes part of the human body by consuming Cd-contaminated cereal crops and vegetables (Satarug et al., 2010). Cancer, renal tubular dysfunction, low bone density, heart failure, nephritis, and nephrosis are essential diseases caused by Cd toxicity (Nishijo et al., 2006; Nordberg et al., 2002). As Cd can persist in our environment for more than 20 years, it makes it a potential life-toxic element for humans' survival (Ruiz et al., 2009).

Similarly, Ni becomes part of biota by involving precipitation, adsorption, and complexions with clay. It has been observed that a decrease in the soil pH significantly increases the bioavailability of Ni, especially in rural areas where crops are cultivated (Bencko, 1983). The distribution of Ni in the soil is mostly uniform. However, most Ni toxic effects are observed in the soil's upper layer with 3–100 ppm Ni concentrations (Bencko, 1983). The existence of Ni in the soil can be in several forms such as crystalline minerals (inorganic), on cations exchange surfaces which are inorganic, cations surfaces that are organic, as a free ion, water-soluble and chelated compounds (Scott-Fordsmand, 1997) which cause harmful impacts on plants (Chen et al., 2009). It is necessary to dispose of Cd contaminated waste materials with proper treatment to avoid its contamination in the environment. In 2010 Cd generated pollution was 21,000 tons; however, in 2011, it was up to 21,500 tons. Such conditions create alarming situations for crops cultivation in soils where Cd toxicity presents in dangerous concentrations (Pinto et al., 2004).

4. Cadmium as an essential nutrient vs pollutant

Cadmium is also required in small quantities to develop plants properly; however, its higher uptake in plants causes injuries (Reeves and Baker, 2000). So far, all the mechanism of poisoning caused by Cd is not well understood. Scientists are exploring the major mechanisms that Cd adopted two induced adverse effects in the plants (Fig. 1; Table 1). It also restricted physiological and metabolic activities, which decreased the growth attributes of crops. The higher Cd level in plants reduces transpiration (Inouhe, 2005) and photosynthesis rate (Bazzaz et al., 1974).

Less uptake of carbon dioxide due to Cd higher composition played an imperative role in disturbing the rate of photosynthesis in the plants (Larbi et al., 2002). It also decreases the germination of seeds when present in threshold limits in the soil. Low plant population due to poor germination causes a significant decrease in the yield (Larbi et al., 2002; Lozano-Rodríguez et al., 1997). Cd toxicity tolerance is different from different crops according to

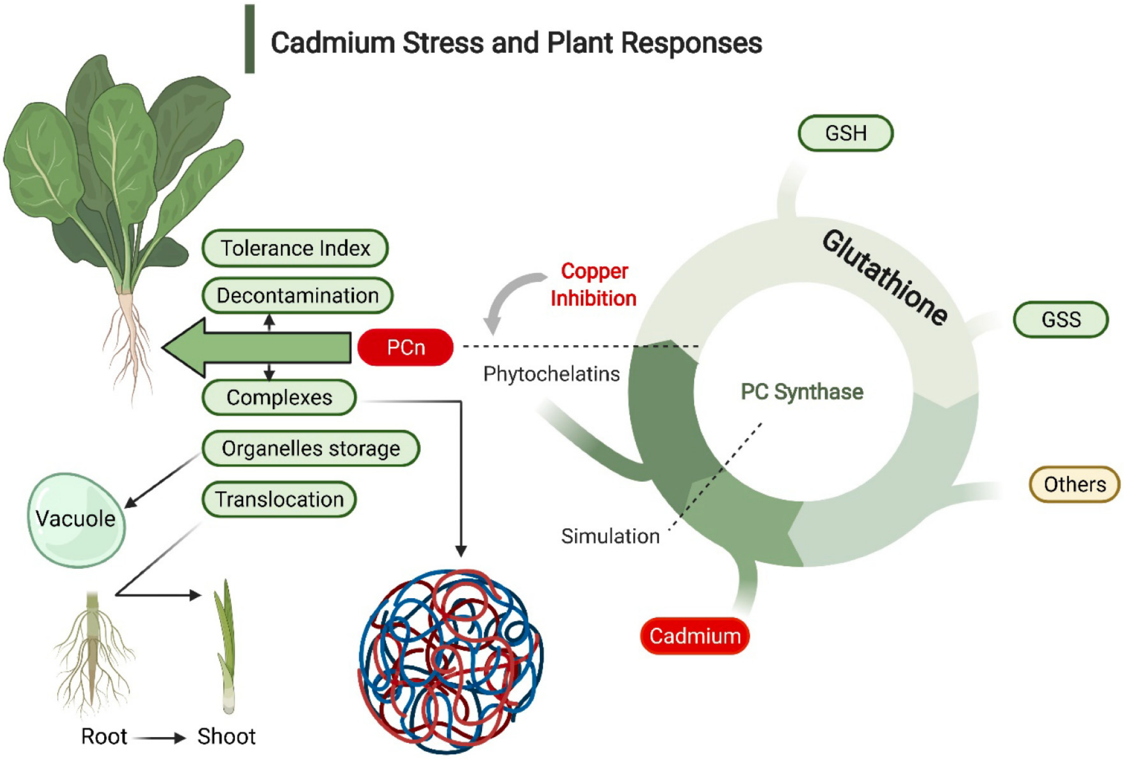

Fig. 1. Cadmium stress and plant responses to mitigate the adverse effects of Cd.

Table 1
Decrease in yield of different crops due to the toxicity of cadmium and nickel.

Crop	Decrease in yield (%)	Heavy metal toxicity	References
Wheat	72.0	Ni	(Ouzounidou et al., 2006)
Barley	27.2	Ni	(Kumar et al., 2018)
Maize	30.0	Cd	(Dresler et al., 2015)
Bean	36.5	Ni	(Al-Qurainy, 2009)
Chickpea	28.9	Cd	(Hasan et al., 2008)
Sunflower	50.0	Ni	(Ahmad et al., 2011)
Radish	52.0	Ni	(Yadav et al., 2009)
Mustard	43.8	Cd	(Irfan et al., 2013)
Tomato	80.0	Ni	(Palacios et al., 1998)
Alfalfa	33.2	Cd	(Dražić et al., 2006)

their stages; however, sitting stages are more susceptible to Cd toxicity (Sharma et al., 2010).

4.1. Antagonistic effects of cadmium

Cadmium also showed antagonistic relationships with the different essential nutrient elements that are required for the optimum growth of plants (Fig. 2). Higher intake and mobility of cadmium in the plants significantly decreased the iron uptake resulting in chlorosis (Genchi et al., 2020; Larbi et al., 2002). It also disturbs the optimum uptake of magnesium, potassium, and calcium; thus, plants suffer from nutritional deficiency stress (Dong et al., 2006; Greger et al., 1991; Larbi et al., 2002). In plants, Cd uptake beyond the threshold limit induces oxidative stress and restricts the electron transport chain activity, directly affecting the plant's nucleic acid-associated mechanisms (Cuypers et al., 2010). Low uptake of zinc, iron, and manganese also disturb the plant cell's proper functioning (Lasat, 2002), which played an essential role in decreasing the yield (Dong et al., 2006).

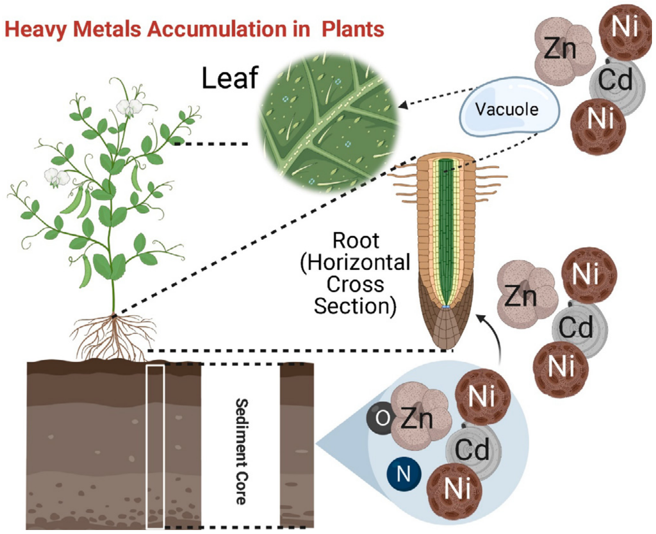

Fig. 2. Heavy metals uptake and accumulation in the plants leaves vacuole.

5. Antagonistic effects of Ni on plant

In plants, the edible part of vegetables is a significant Ni accumulator that humans consume and other living organisms (Gupta et al., 2010; Olowoyo et al., 2012). Plants that suffer from Ni toxicity mostly show chlorosis and necrosis symptoms (Ahmad and Rasool, 2014). Likewise, Cd also decreases the uptake of iron, which adversely affects crop productivity (Kabata-Pendias, 2011). Ni also shows the antagonistic relationship between magnesium and calcium. Less uptake of magnesium deteriorates the structure of chlorophyll in the leaves. Low chlorophyll content in leaves ultimately resulted in the poor rate of photosynthesis in the plants (Piccini and Malavolta, 1992).

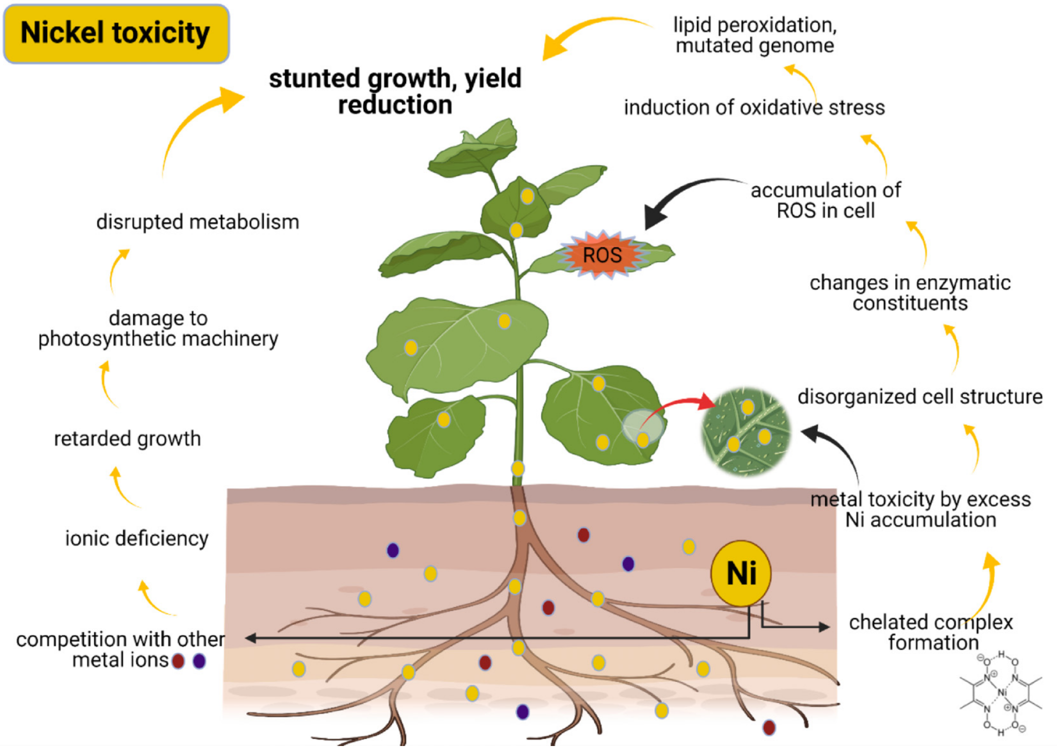

Fig. 3. Adverse effects of nickel on plant (Chen et al., 2009).

Seregin and Ivanov (2001) noted that mainly Ni is accumulated in the plant's laminar region and adversely affected photosystem II, which played a significant role in low photosynthesis (Maksymiec, 1998; Veeranjaneyulu and Das, 1982). It causes plastoquinone QA and Fe to plastoquinone QB and change the structure of the electron carrier (Krupa and Baszynski, 1995; Mohanty et al., 1989). Sheoran et al. (1990) observed restriction of Calvin cycle in the lives of *Cajanus cajan*. They argued that in 1 mM NiCl2, the Ni inhibits the activities of Rubisco, 3-phosphoglycerate kinase, fructose-1, 6-bisphosphatase, aldolase, and NAD. Search conditions decrease the rate of photosynthesis and result in the development of toxicity of Ni. Molas (1998) observed a significant reduction in the photosynthesis of *Brassica oleracea* in the presence of 10–20 g/m^3 $NiSO_4$–$\cdot 7H_2O$. They suggested that the cell's moisture contents were decreased when plants were cultivated in Ni toxicity and induced a condition of stress, which results in low photosynthetic activity of leaves.

Barsukova and Gamzikova (1999) noted that the reduction in the intake of Mg, Fe and Zn due to a higher intake of Ni (Calzado et al., 2005) resulted in the chlorosis (Khalid and Tinsley, 1980; Piccini and Malavolta, 1992). Pandolfini et al. (1992) noted a significant decrease in wheat's calcium and magnesium concentration when cultivated under 0.1–1 mM Ni concentration. Also, Ni shows an iron antagonistic relationship with potassium in the soil (Pulford and Watson, 2003).

Furthermore, pigeon pea's mitotic activity is significantly decreased due to Ni higher concentration (Madhava Rao and Sresty, 2000). The toxicity of Ni also reduces the germination of plants (Madhava Rao and Sresty, 2000). In the case of cereals, mostly the wheat plants (Fig. 3), it retards the growth of shoot (Gajewska et al., 2006) and also decreased productivity due to low pods in seed formation (Tripathy et al., 1981). Therefore, the necessity of time is to introduce such an organic amendment that - can detoxify these toxins from the soil on a long-term basis.

Table 2
Increase in yield of different crops by variable application rate of biochar.

Crop	Biochar (t/ha)	Yield increase (%)	References
Wheat	25	21.5	(Ali et al., 2019)
Barley	10	39.5	(Agegnehu et al., 2016)
Maize	25	20.0	(Arif et al., 2016)
Rice	10.5	10.0	(Liu et al., 2016)
Sorghum	22	22.0	(Laghari et al., 2015)
Winter rye	20	14.5	(Kraska et al., 2016)
Cotton	20	21.9	(Tian et al., 2018)
Soybean	10	45.4	(Van Zwieten et al., 2010)
Bean	30	30.0	(Rondon et al., 2004)
Radish	10	33.5	(Van Zwieten et al., 2010)
Carrot	30	100	(Rondon et al., 2004)
peanut	8.5	45.6	(Tando et al., 2017)
Tomato	10	70.0	(Hossain et al., 2010)

6. Biochar as remediation

Activated black carbon fiber is one of such organic amendments that immobilizes heavy metals in the soil and decreases their bioavailability to the plants (Danish and Zafar-ul-Hye, 2020; Major, 2011; Radziemska et al., 2021; Sultan et al., 2020; Verheijen et al., 2010; Zafar-ul-Hye et al., 2020c). It is a fine black powder, a highly porous carbon structure that can be used as a fertilizer and soil conditioner. It can modify the physical, chemical, and biological attributes of the soil. Most physical properties of soil such as texture, structure, pore size distribution, and density with implications for soil aeration, water holding capacity (Danish et al., 2020, 2015a, 2015b; Danish and Zafar-ul-Hye, 2020, 2019; Fiaz et al., 2014; Zafar-ul-Hye et al., 2020c) and soil workability are positively and directly affected biochar's application in the soil as an amendment (Danish et al., 2019b, 2015b; Downie et al., 2012; Hashmi et al., 2019; Zafar-ul-Hye et al., 2019).

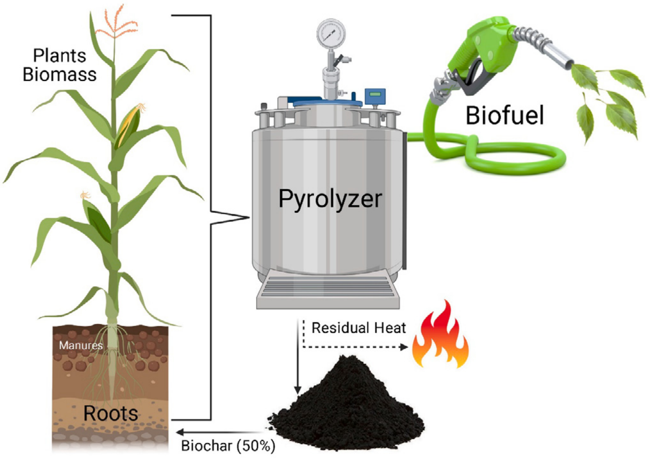

Fig. 4. Preparation of Biochar.

The history of biochar starts from the "Terra Preta de Indio" oxisols in Brazil which are suggested as Amazonian Dark Earth (ADE) developed about 7000 years ago. Most anthropogenic activities were involved in the establishment of these soils (Glaser, 2007). It has been observed that the fertility status of the soils was excellent due to the presence of significant amounts of char and organic debris, which act as natural soil fertilizers in the soil (Woods and Denevan, 2009). A significant increase in the yield of crops (Table 2) was observed in these soils compared to other soils where char was not applied as an amendment (Renner, 2007).

Current assessments elaborated that biotech application in soil significantly increased the carbon pool of soil through pyrolysis and unlimited oxygen availability. Biochar is produced using the organic waste materials collected from agricultural fields (Danish and Zafar-ul-Hye, 2020; Lehmann et al., 2006; Woolf et al., 2010). When carbon-containing biomass is heated in the absence of oxygen at 450–6500C, a significant amount of volatile matter is admitted in gases. These gases can be collected in condensed to get bio-oils, which help decrease environmental pollution and provide an alternative energy source (Sohi et al., 2010). The biochar is mainly prepared by pyrolysis, which is divided into three major stages. In the first one, biomass having carbon is converted into unreacted water and residue (Fig. 4). In the second step, most of the volatile gases are emitted and left the biochar behind. In the last step, the structural and chemical modifications occur in this biochar (Demirbas, 2004).

Table 3
Different functional group in different waste material produced biochar which can immobilize Ni and Cd.

Waste material for biochar	Functional groups	Heavy metal which is absorbed	References
Rice straw	Carboxyl	Ni	(Ali et al., 2020)
Wood and bark chars	Hydroxyl	Cd	(Mohan et al., 2007)
Cotton seed hull char	Carbonyl, Carboxyl	Ni, Cd	(Uchimiya et al., 2011)
Green waste	Aromatic	Cd	(Park et al., 2011)
Wheat straw	Carbonyl	Cd	(Cui et al., 2012)
Rice straw	Carboxyl, Hydroxyl	Cd	(Jiang et al., 2012)
Rice straw	Carboxyl, Hydroxyl	Ni, Cd	(Deng et al., 2019)

Scientists nowadays are developing different biochar using different organic waste Biomass through pyrolysis (Park et al., 2011; Sohi et al., 2010). The application of biochar saved our environment from polluted gases and played an essential role in decreasing fertilizers' volatilization losses (Woolf et al., 2010), also use of biostimulant and foliar application of fertilizer reduses the direct application of fertilizer to the soil (Abbas et al., 2020; Izhar Shafi et al., 2020; Rafiullah et al., 2020; Ullah et al., 2020). Micropores of biochar significantly increased the soil's water holding capacity and decreased the soil infiltration rate. It also plays a crucial role in increasing the soil's surface area (Downie et al., 2012). It has been observed that chemical properties of soil such as pH, electrical conductivity, cation exchange capacity, nutrients holding capacity, and water holding capacity of soil become improved when biochar is applied as an amendment. A significant improvement in the microbial growth and soil population through biochar application validated its effectiveness as a soil amendment (Amonette and Joseph, 2009; Verheijen et al., 2010; Warnock, 2009). Furthermore, micro aggregates' stability is also enhanced due to activated carbon biochar's high binding ability (Lu et al., 2014).

Small pore spaces in biochar provide shelter to the microorganism present in the rhizosphere. Such conditions provide a chance for microbes to better floor acceleration and growth (Quilliam et al., 2013). As compared to organic matter, the shelf life of activated carbon is high. It remains in the soil for an extended period compared to the organic matter due to its high resistance against the composition process (Downie et al., 2012; Pathan et al., 2018; Thies and Rillig, 2009; Woods and Denevan, 2009). Activated carbon biochar has many functional groups that act as binding sites for heavy metals (Table 3).

When biochar is applied in the soil, the heavy metals become bound on the biochar's active sites, significantly decreasing their mobility in soil and bioavailability to the plants (Machida et al., 2005). The above mineral nutrition, an integral part of the biochar structure, is also released in the soil and on the exchange sites that become readily available to the plants. Such conditions improve soil fertility and decrease the chances of heavy metals uptake, potentially toxins for plants, humans, and animals (Quilliam et al., 2013).

7. Conclusion and future perspective

Biochar is an effective organic amendment that can improve soil fertility status. Besides improving soil health by ameliorating the physio-chemical and biological properties of soil, it can mitigate Cd and Ni toxicity in different crops. The different scientist has done much work for manufacturing of thermo-pyrolyzed biochar. However, the need for time is to convert the production technology to chemically pyrolyzed biochar manufacturing. It decreases the potential hazards and can be easy for the industry to produce activated carbon on a large scale.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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