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Review

Immobilization of Cd in soil by biochar and new emerging chemically produced carbon

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ABSTRACT

Utilization of industrial and household wastes as fertilizer while wastewater as irrigation are common practices in developing country's agriculture. These practices played an imperative role in the accumulation of heavy metals in soil. Among different heavy metals, cadmium (Cd) contamination in soils has been rising to an alarming level. The contribution of natural activities is relatively low over anthropogenic activities for Cd buildup in the soil. Its toxicity adversely affects human health, soil and plant productivity. Instead of chemicals remediation, a nature-friendly biochar is suggested as a promising remedy to reclaim Cd-contaminated soils. Owing to high stability, greater surface area, and exchange sites, biochar can adsorb heavy metals. Thus, significantly reducing metals mobility, bioavailability, and uptake of heavy metals by the plant. It has active functional groups like ketones, carboxylic, and diols that bind the Cd and other metals. Biochar can also mitigate the harmful effect of Cd by improving plant chlorophyll contents, photosynthesis activity, SOP, POD and CAT enzyme activity through better availability of essential. Furthermore, the application of acidified biochar into alkaline soil is also gaining attention. It plays a vital role in declining soil pH, sodium adsorption ratio (SAR), and improving the availability of immobilized nutrients. Scientists are also working on acidified carbon (AC) chemical production to investigate its potential benefits in high pH soils. This review will help to provide the basis for understanding the potential benefits of thermopyrolyzed biochar and chemically produced AC, especially in Cd-contaminated sites. However, more advanced and in-depth investigations are required to use chemically produced carbon as an amendment against Cd and other heavy metals toxicity.

Contents

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1. Introduction

Rice is cultivated worldwide in all continents of the world except Antarctica. It is a staple food of more than 50 million people and is considered the cultural identity of various countries like China, Oman, Korea, Pongal, Onam, Indonesia, India etc. (Prasad et al., 2017). Due to its high consumption rate and ease of cultivation on various soil types, its cultivation gains much attention. It is considered a foreign exchange source in different countries like India, Thailand, USA, China, Vietnam, Pakistan, Italy, Brazil, Uruguay and Australia (Workman, 2019). According to an estimation of the United States Department of Agriculture, worldwide production of rice is 501.96 metric tons. In Pakistan, its cultivation area increased timely. According to Statistics of Pakistan, in 2007–2008 production rate was 5563 thousand tons which increased up to 7449.80 thousand tons in 2017–18. The area under rice cultivation is 2724 thousand hectares providing an average yield of 7500 thousand tons. After wheat, rice is the second staple food for Pakistani people. Rice contributed about 2.1% in agriculture and 0.6% in GDP of Pakistan's economy (GOP, 2016), among which Punjab and Sindh contributed the most. It is cultivated on 1766.8 and 361.2 thousand hectares, respectively, in Punjab and Sindh. Widely cultivated rice varieties in Punjab and Sindh are Basmati, IRRI-9, IRRI-6, D-98 and Begghi (Chandio and Yuansheng, 2018).

Rice plants are annual grass that is about 4ft tall with a hollow stem and fibrous root systems. Grains are produced on spikelet's. However, its physical parameters like height, biological yield, stem width, number of spikes and grains vary varieties and growing medium. Various varieties of rice include Basmati 370, JP-5, Basmati Pak, IR6, Basmati 198, Kashmir Nafes, DR 82, KS 282, DR 83, Swat 1 and 2, Basmati 385, Shadab, Sada Hayat, DR 92, Shut 92, Pakhal, Rachna basmati, Super Basmati, Kushboo 95, Saheen basmati, Basmat 2000, NIAB-IR, Sarshar, Jhona-349, Muskan-7, Basmati-370, Muskan-41, Sathra-278, Mahlar-346, Palman-246, IRRI-8 and 6, NIAB-IR9, Shaheen Basmati and super basmati rice. In the case of the nutritional value of rice, it is enriched with various minerals like N, P, K, Ca, Fe, Zn, Na and many more. In 100 g milled white rice, it contains energy (349–373 kcal) proteins (6.3–7.1 g), lipids (0.3–0.5 g), carbohydrates (77–78 g), fibers (0.2–0.5 g), riboflavin (0.02–0.06 mg), niacin (1.3–2.4 mg), thiamine (0.02–0.11 mg) and vitamin E (0.075–0.30 mg) (FAO, 1993).

1.1. Cadmium origin

Cadmium is a non-essential heavy metal whose specific gravity is 8.65 times more than water. It is produced during the refining process of Zn, Pd and Cu ores as a by-product. On average, its concentration is 0.1 and 0.5 ppm. It is widely distributed but up to a very reduced extent. In the ocean, 5–110 ng/L Cd is found due to the presence of Cd-containing phosphate minerals. It is also used in various products like paints, Cd-Ni and electrolyte batteries. From these sources, Cd is released into the environment and causes contamination. World south and the southeast regions are currently facing the most problem of Cd-toxicity in soil (Luo et al., 2010). In Pakistan, Cd concentration in soil increases due to the increasing rate of green revolution, urbanization and industrialization. Another reason for Cd contamination is the contamination of irrigation water from industrial effluent discarded in the river and canals (Lu et al., 1992).

Cadmium is found with Zn ores like zinc sulfate. However, its minor concentration is found in all kinds of minerals that are in less toxic amounts. However, lake sediments and marine black shales are enriched with Cd, which is found in lower concentrations in agricultural soils, but in paddy rice fields, its contamination increased. Now, anthropogenic activities are contributing a major part to Cd contamination. Various studies highlighted the role of the phosphatic fertilizer in Cd-contamination as it contains trace elements. It becomes a major concern because of continuous Cd-containing P fertilizer addition, e.g., rock phosphate, single super phosphate (SSP) and triple superphosphate (TSP) (Loganathan et al., 2008). But contents of Cd vary in fertilizers such as Cd with SSP have high water solubilizing ability, whereas TSP contains very little concentration of Cd. The effect of three different P fertilizers in paddy fields was studied by Jiaka et al. (2009). They observed that Cd uptake is directly and highly correlated with ammonium present in phosphatic fertilizers. Ammonium-containing two fertilizers [$(NH_4)_2HPO_4$ > $NH_4H_2PO_4$] increased the Cd uptake by plants as compared with Ca-hydrogen phosphate.

The utilization of industrial and household wastes in agricultural lands as fertilizer is common in various developing countries like Pakistan. Wastes and sewage sludge are enriched with heavy metals when disposing of rivers, or lakes cause water contamination. Pollution of heavy metals is gaining researcher attention nowadays. Heavy metal uptake adversely affects humans, soil, plant productivity and the combined effect caused severe environmental problems (Bolan and Duraisamy, 2003). The term biosolids/sewage sludge was used for the final product of municipal waste. Combined with other organic waste and animal manures, it connotates into a more precise term green waste compost. Traditionally, biosolids are considered the major sources of metal pollution in the soil. There is no regulatory measure or threshold level formulated for Cd safe limit in biosolids used as fertilizer (Bolan et al., 2013). Although biosolids are enriched with C, continuous addition causes its accumulation and toxicity of Cd in agricultural lands.

Malik et al. (2010) conducted a study on heavy metal contamination measurement in soils of the urban area. They reported that metal concentration in the soil exceeds their permissible limits (3 mg/kg). The industry's effluent caused Cd contamination in the river of Shah Alam, more than WHO prescribed limits. Similarly, in another survey, Rauf et al. (2009), also reported a high concentration of metals in Ravi river sediments. The concentration of Cd exceeds from 0.99 to 3.17 μg/gram dry matter. These metals provide a source of pollution in the environment. Kashif et al. (2009) analyzed the metal pollution in the Hudiara drain, in the district of Lahore. Index of metal pollution continuously increased due to contamination of Cd and other metals from polluted waste in drains. From there, metals get a chance to become a part of our food chain.

Anthropogenic activities like mining and smelting of ores containing heavy metals increased the contamination of water and soil. Millions of tons of tailing sulfide are produced from open casting mining activities. Generally, Cd toxicity is more observed in areas near the mining site than in other areas (Ok et al., 2011). A huge quantity of tailings was leftover without proper treatment, which became a major source of arsenic, Zn, Cd, Cu and Pd. These tailings are spreading by soil erosion, wind and water actions. Also, discharged wastewater from coating and paint industries, metal plating factories, home appliance and electronic manufacturing units (Matsuzaki et al., 1987) when mixed with drinking and irrigation water resources, heavy metals get a chance to enter in the food chain.

Cd occurs in various forms in soil, including free ionic species, organometallic complexes (can be soluble or insoluble), adsorbed on other nutrient minerals, especially on riebeckite and biotite (Adriano, 2001). Furthermore, in low land paddy soil, alteration in flooded conditions modifies the soil conditions into aerobic and anaerobic. Modification in oxygen contents alters the soil pH and redox potential significantly and alters Cd speciation in paddy fields. Zheng and Zhang (2011) studied the behaviour of Cd and OM in waterlogged soils. They reported that Cd at high pH and lower value of Eh, favours the formation of the organometallic layer on OM. Organic matter Cd bound or microbially immobilized fraction of Cd is thus not available for plants use.

Sarwar et al. (2019) evaluated the impact of wastewater irrigation on agricultural lands in the Vehari district. From 15-peri urban sites, they collected wastewater, soil and plant samples for quantifying the heavy metals concentration in them. Results reported that Cd, Fe, and manganese (Mn) concentration in applied wastewater was more than the threshold concentration. Similarly, lands receiving that wastewater had Cd, Fe and Mn beyond the permissible concentration. Continuous wastewater application leads to raising the accumulation of these metals in plants and humans (from consumption of contaminated plants), which causes a health risk.

2. Cadmium contamination and crops

Cadmium contamination in soils leads to an alarming level, as reported by various studies (Liu et al., 2013). In the terrestrial ecosystem, soil act as a major source of transferring heavy metals in the food chain through plants. Naturally, Cd concentration is 0.1–16.5 ppm in soil. Its concentration starts rising due to various anthropogenic (e.g., mining, smelting, sewage sludge and paints, plastic stabilization and metal processing) and natural activities (e.g. weathering, sea sprays and wind dust) (Bi et al., 2007). Natural activities contributed 10% to Cd pollution and anthropogenic activity has 90% contribution. Despite regulatory measures, pollution in the environment started rising. A significant concentration of Cd was also observed in agricultural lands found near the industries where it started accumulation in the surface layer of soil and concentration reduced with depth. The surface layer can easily be taken up by plant roots and translocated in various parts of plants where it accumulates. Among anthropogenic activities, 12% of contamination occurs due to agricultural activities like fertilizer application, irrigation with wastewater and pesticides, or insecticides. Impurities in phosphatic fertilizers seem to contaminate the soil with Cd (Nziguheba and Smolders, 2008).

Cadmium uptake by plants depends upon its bio-availability and concentration. Its entry in the roots of plants followed the same pathway/ membrane carriers used in calcium (Ca), magnesium (Mg), zinc (Zn), iron (Fe) and copper (Cu) uptake (Clemens, 2006; Roth et al., 2006). From roots, it easily gets entered into the plant system, where it negatively influences plant physiochemical processes and reduced yield (Uraguchi et al., 2009). Plants have a certain level of Cd tolerance (0.01% of plant dry weight), but the rise in Cd concentration from that level can cause phytotoxicity in plants. Studies reported that plants grow on Cd polluted soils usually had low productivity and yield. It negatively affects plant metabolism, vegetative and reproductive growth and thus declines the productivity rate. In severe toxicity cases, plant growth becomes restricted and cells are deformed. Bolan et al. (2013) reported that Asian people uptake 30–35% Cd derived from rice (Fig. 1).

The fate of cadmium in plants was studied by Zhang et al. (2009) by using rice cultivars of sensitive and Cd-resistant cultivar. Application of 0.1–0.5 μM Cd on rice grown in hydroponic culture significantly increased the Cd accumulation in plants up to 108% Cd in susceptible rice cultivar and 55% in Cd-tolerant cultivars. High Cd supply also increased the Cd concentration in the roots of rice. Cd starts localization in the plant cells as Cd concentration increases in the growing medium (vacuoles and cell walls). In Cd-resistant rice, excess Cd also detoxifies in the root cell wall, polysaccharides, organic acids and proteins by forming bonds with them. Thus, translocation of Cd from shoot to root decreased.

Seeds that are sown in the Cd polluted environment usually accumulate Cd, which negatively affects seed physiological processes, thus hindering seed germination (Ahsan et al., 2007). Cadmium inhibitory effect on seed germination rate was studied in rice crop. A wide range of Cd concentration from 0.2 to

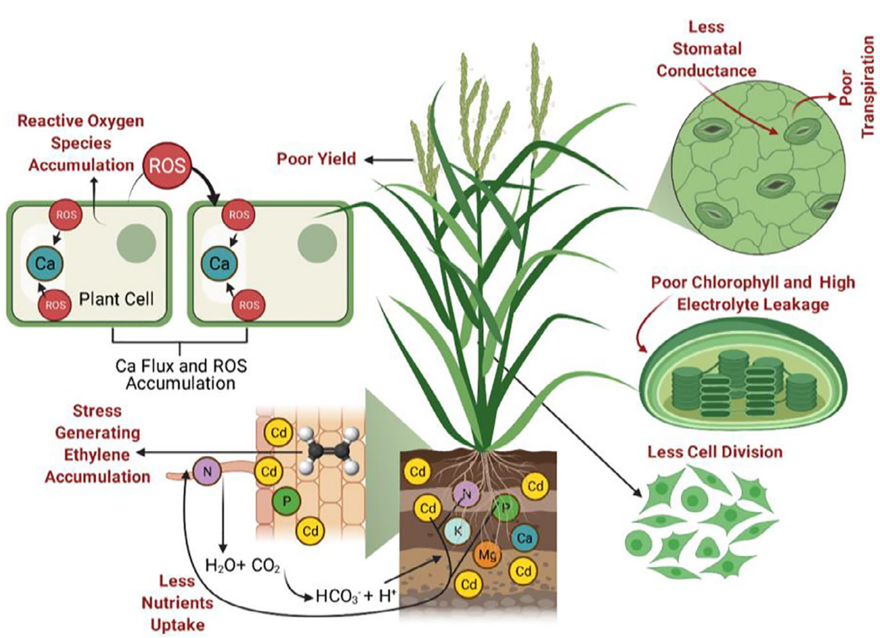

Fig. 1. Major negative effects of Cd in crops.

Table 1
Decrease in yield of different crops due to the toxicity of Cd.

Crop	Decrease in Yield (%)	Cadmium Toxicity	References
Rice	63.90	150 ppm	(Kanu et al., 2017)
Wheat	30.00	250 µM	(Idrees et al., 2015)
Maize	20.00	375 µM	(Anjum et al., 2015)
Barley	11.00	200 ppm	(Kherbani et al., 2015)
Tomato	25.50	50 ppm	(Kumar et al., 2015)
Oat	40.00	40 ppm	(Rolka and Rolka, 2015)
Pepper	20.00	500 µM	(Mozafariyan et al., 2014)

1.0 mM was used with the rice test crops. Cd high supply increased the accumulation of Cd in rice seeds and caused an inhibitory effect on seed germination. It also reduced the plant growth, water contents and biomass of rice plants (Kanu et al., 2019). When plants faced the toxicity of Cd, their defence system activates. It binds Cd with protein's sulfhydryl group, which caused distortion in the protein structure and increases the production of reactive oxygen and free radicals. Hydrogen peroxide, malondialdehyde and leaf electrolyte contents increase with high Cd uptake (Kanu et al., 2019). Cadmium accumulation in rice at a higher level, decrease antioxidant enzymes (superoxide dismutase, peroxidase and catalase) activity and yield components, e.g., panicles, spikelet/panicle, grains number, 1000-grain weight, and total yield of grain (Ahsan et al., 2007; Kanu et al., 2019) (Table 1).

3. Biochar and crops growth

The most critical parameter for determining the fertility and productivity of any soil is organic carbon contents. Pakistan soils usually have less organic matter content (2% only). In such a scenario, the application of biochar significantly increases the organic carbon contents in soil (Abid et al., 2017). Biochar is a high carbon-containing solid product of biomass/ residues pyrolysis. Biochar is heterogeneous material that consists of both kinds, e.g., stable and labile materials (Lehmann et al., 2011). Its major component is carbon, followed by volatile matter, ash, and moisture. Its properties vary with the conditions and procedure adopted during the pyrolysis process and substrates used (Lehmann et al., 2011) (Fig. 2).

Although it is enriched with minerals due to heating at high temperature, volatile components like nitrate and ammonium are lost (Deluca et al., 2009). In a study of wood biochar preparation, as the pyrolysis process starts, N becomes volatile as the temperature reaches 200 °C, at 375 °C S volatile and at 700–800 °C K and P volatilization started. As the temperature reaches above 1000 °C, Ca, Mg and Mn become volatile. Therefore, nitrogen is sensitive to heat and is only 0.18–5.60% is present in biochar. Carbon is the major structural component of biochar which is 17–96% in biochar concentration. Phosphorous is present in 0.27–48% and K is of 0.1–5.8%. A minor quantity of S, H, O and other basic cations are also present (Preston and Schmidt, 2006). Biochar is the nutrient-enriched and environmentally friendly product of pyrolysis. It is prepared from straw residues, crop residues, manures, grains and grasses (Demirbas, 2004).

Different methods are used for the preparation of biochar e.g. gasification (Sánchez et al., 2009), carbonization and pyrolysis. Muffle furnace is one of the most used method in testing laboratories (Sánchez et al., 2009). Pyrolysis was performed in inert conditions. Nitrogen or helium gas was used it reactor. It is also prepared in Kilns. Kiln is a very simple, cost-effective and easy method (Zhang et al., 2010). This type of production is usually suitable for large-scale biochar production as it yields only 35% and cost-effective (Van Zwieten et al., 2010).

Maroušek et al. (2019) reported that biochar incorporation in the soil significantly enhances the carbon sequestration in the soil, improving soil fertility and aggregate stability. Poor aggregate stability of soil is one reason behind the low quality of soil, which is caused by lower organic carbon contents in soil. Biochar can increase soil aggregation, leading to improved soil properties due to increased aeration, bulk density, water-holding capacity, and ion exchange capacity. Properties of biochar vary with feedstock, pyrolysis temperature and conditions (Freddo et al., 2012).

In three years of field research, biochar effect on the bioavailability of Cd and Pd was analyzed by Bian et al. (2014) using rice as a test crop. Biochar was prepared by wheat straw through pyrolysis at 550 °C. Extractable concentration (through $CaCl_2$) of Cd and Pd was significantly decreased in all years by 70.9, 64.8, and 60.9% during three years and 33.3, 59.1 and 79.6% Pd availability respectively. Excess available Pd and Cd was immobilized by sorption on

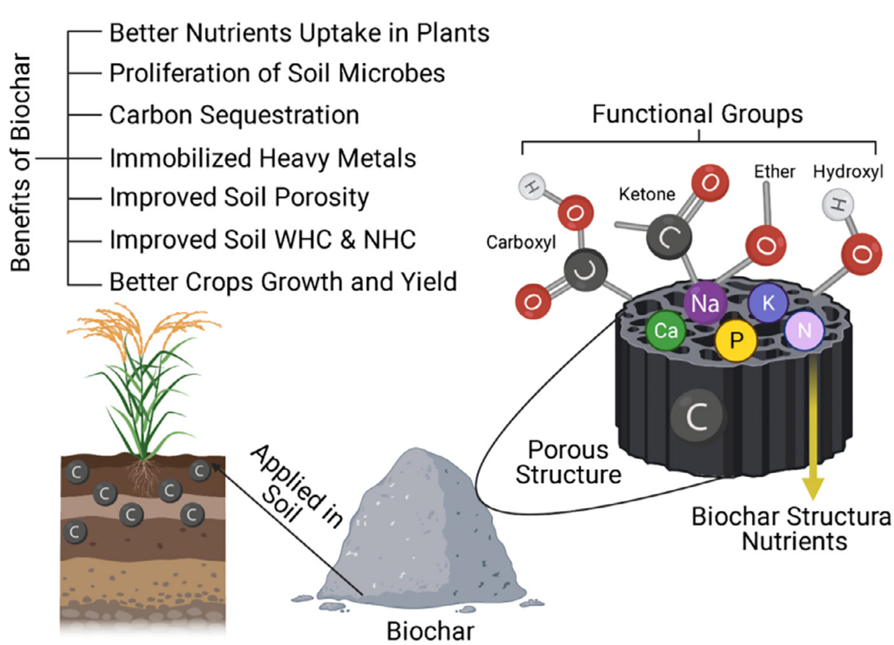

Fig. 2. Some major benefits associated with biochar application in soil.

clay minerals, precipitate with carbonates due to reduction in soil pH. Except for this, ion exchange and functional groups of biochar form complexes. Furthermore, mineral-organic layers were formed on surfaces of biochar, which was thickened over time. That result proved that immobilization of metals with biochar application increased with the time passage.

Biochar was first produced by Amonette and Joseph (2009), through the oxygen-free burning of crop residues at high temperature (700 °C). It is comprised of inorganic carbon, Mg, Ca and sodium and various other minerals. It can protect the nutrient leaching, reduce greenhouse emission and their detrimental effect on the environment, increased carbon sequestration and agriculture productivity (Oni et al., 2019). Biochar can increase the CEC and anion exchange capacity (AEC) of soil, mediate soil pH, increase N and P availability, boost up plant above and below ground growth, and increase moisture contents, leading to a reduced risk of soil erosion. Biochar has pores in its structure, among which micropores are responsible for its high-water holding capacity and macropores are responsible for aggregation, aeration and ease in root penetration (Freddo et al., 2012). Micropores also allowed the sorption of OM, which is beneficial for high microbial activity and their inhabitation. Microbes are involved in soil remediation from various kinds of soil and environmental pollutants (Hameed et al., 2017). The ability of biochar to degrade pollutants and heavy metals is utilized in removing pollutants from soil, especially for heavy metal remediation.

Improved physical soil properties were reported by Herath et al. (2013) due to biochar application. Corn residues are pyrolyzed at different temperature (350^{o}C and 550^{o}C) and its effect on soil properties, e.g., bulk density, hydraulic conductivity, aggregate stability and hydraulic conductivity was analyzed. Results showed that biochar amendment improves the aggregate stability, which varies with soil type and other parameters were improved significantly. Reduced agricultural productivity is directed towards soil degradation. Soil degradation leads to reduced agricultural productivity. To lower the soil's degradation rate, biochar application is an effective measure reported by Vinh et al. (2014). In an experiment, biochar, compost and inorganic fertilizer application, biochar addition provides a significantly positive result. It increases micronutrient accumulation in rice plants and increases the yield of rice up to 22.3% (Table 2).

Only soil reduced the nitrogen losses and protected underground water from contamination (Dong et al., 2014). Nitrogen has a high mobility rate and N-fertilizers can caused contamination of groundwater through leaching. In such a scenario, two years of consecutive field experiments showed that the application of biochar could significantly absorb nitrogen on its surface. Increased retention of nitrogen in surface soil significantly increased the productivity of rice plants grown in paddy fields. Biochar can replace inorganic fertilizers, as reported by Lakitan et al. (2018). In a paddy field experiment, 0, 0.4, 0.8, and 1.2 Mg ha^{-1} biochar was applied. Its application positively affects agronomical rice parameters. Root elongation and shoot length were not much affected, but during the vegetative growth period of rice, biochar addition significantly increased the tillering capacity of rice along with its grain's quality and quantity.

Table 2
Improvement in crops yield by application of biochar.

Crop	Increase in Yield (%)	Biochar Application Rate (t/ha)	References
Wheat	17	20	(Sun et al., 2020)
Rice	10.00	20	(Huang et al., 2019)
Barley	39.5	10	(Agegnehu et al., 2016)
Maize	22.50	15	(Omara et al., 2020)
Cotton	22.00	20	(Tian et al., 2018)
Tomato	23.00	10	(Almaroai and Eissa, 2020)

Silicon (Si) is considered beneficial for plants, especially under stress conditions. It is thought to alleviate nutrient stress. Biochar incorporation in soil provides Si and other macro and micronutrients and increased the mobility of these nutrients in agricultural lands (Li et al., 2019). Different feedstock biochar was prepared and analyzed in field conditions. Analysis of biochar showed that rice husk biochar was enriched with Si and on average, its concentration varies from 3 to 20% in biochar. Other than Si, biochar also had 1.23% N, 0.6% S, 0.3% P, 2.7% K, 1.2% Ca and 0.54% magnesium. The addition of crop residues biochar significantly contributes to nutrient cycling in croplands.

4. Immobilization of heavy metals

Once a site is contaminated with metalloid or metal, it can't be reversed or removed easily from the soil. Metal is only transformed from more available or more toxic to less bioavailable or less toxic forms (Wu et al., 2015). Otherwise, the remediation process can only be performed by plant uptake of these metals. The metal transformation from toxic to less toxic form is practised more. Biochar is a highly stable product that contains a negative charge on its surface. Due to this negative charge, biochar can retain the metal on its surface. Sorption of metal on biochar surface reduced the risk of metal availability for a longer extent due to the high stability of biochar (El-Naggar et al., 2018). Biochar has ketones, carboxylic and diols groups which are chemically active and bind the Cd and other metals. Instead of this, the high aeration capacity of biochar caused an increased flow rate of oxygen which enhanced microbial activity and aids in the immobilization of these metals (Freddo et al., 2012).

Biochar application reduced the vertical leaching of Cd significantly (Sun et al., 2020). A pot experiment was conducted on Cd-polluted saline-alkaline nature soil. Biochar addition not only lowers the Cd accumulation in plant tissues but also reduced residual Cd concentration. Moreover, biochar reduced the mobility and availability of residual Cd for a longer time. It also protects Cd from vertical leaching, which saves underground water from Cd contamination. But the rate of immobilization was directly related to soil properties and adopted practices. Reduced Cd availability due to biochar addition was also reported by Abbas et al. (2017). Soil was incubated with rice residues biochar, applied at different rate (0, 1%, 1.5%, 3% and 5% w/w). Results reported that the biochar amendment increases the solution pH and silicon (Si) contents and reduces Cd accumulation in plant tissues. In comparison which control plants, biochar amended plants showed more plant height, tillers, biomass and yield of grains. That improved growth was due to reduced oxidative stress, increased antioxidant enzyme activity and photosynthesis rate in biochar amended plants. Biochar application at 1.5%, 3% and 5% reduced 26%, 42% and 57% accumulation of Cd in plant tissues respectively. Except for this, it also reduced the Cd translocation towards grains which was the desired result.

Cadmium translocation and its deleterious effect on rice growth were analyzed by Rizwan et al. (2018). Applied biochar at 1.5, 3.0, and 5.0% w/w significantly reduced the Cd toxicity effect on rice. The harmful effect of Cd was mitigated by increased chlorophyll contents, photosynthesis activity, SOP, POD and CAT enzyme activity. Increased antioxidant enzyme activity helped reduce Cd accumulation in rice tissues. Results demonstrated that 24.4, 36.6, and 57.5% Cd concentration was decreased by 1.5, 3.0, and 5.0% biochar application. However, the duration of reduced mobility of Cd in soil solution was still unknown (Table 3).

Biochar application in Cd polluted soil significantly reduced the bioavailability of Cd in soil solution (Qiao et al., 2018). Reduced

Table 3
Immobilization of heavy metals by different feedstock produced biochar in different crops.

Heavy Metals Immobilized (%)	Type of Biochar	Crops	References
59.50	Wood	Wheat	(Ali et al., 2019)
49.00	Bamboo	Maize	(Xu et al., 2016)
39.00	Wheat straw	Mung bean	(Ramzani et al., 2017)
44.00	Wheat straw	Ryegrass	(Jiang et al., 2020)
97.00	Rice hull	Lettuce	(Kim et al., 2015)
88.50	Wheat straw	Green pepper	(Sun et al., 2020)

bioavailability leads to reduced uptake of Cd by rice roots. Lower uptake of Cd leads to 93% reduced accumulation of Cd in rice grains. Analysis indicated that iron (Fe) concentration was more in biochar amended treatments. High Fe availability increased the immobility of Cd in soil. The study proved that biochar application is a promising strategy for the utilization of Cd polluted sites. The same results were also observed by Bashir et al. (2018) in their pot experiment. Among rice straw biochar and rock phosphate addition, biochar addition increased in situ immobilization of Cd in soil up to 22.91%. Biochar raised the soil pH significantly, which played a key role in Cd immobilization and its transformation/ precipitation into unavailable forms. Reduced uptake and translocation of Cd were reflected from lowering the antioxidant enzyme activity during Cd stress and even no deleterious effect was reported on plant growth and productivity (Fig. 3).

5. Alkaline soils and acidified carbon (AC)

Pakistan soil is alkaline, having high soil pH and high calcium carbonate contents in various regions' soil. The application of biochar significantly raises the soil pH. Alkaline nature of biochar sometimes imparts adverse effect on soil health, especially when soil is already alkaline. In such a scenario, acidified biochar application proves an effective measure for declining soil pH (Sultan et al., 2020). Doydora et al. (2011) explained the production of acidified biochar and its effect on soil properties. Pine chips and peanut hull was pyrolyzed by N_2 gas at 400 °C. After one hour's residence time, this biochar was grinded and sieved and then treated with 0.5 N HCl for half an hour and shake continuously. It was then allowed to stand for 24 h and then filtered through 0.45 μm sieve. Sieved biochar then dried in an oven for about 48 h at 65 °C. Experimental results showed that it reduced the N leaching losses but did not affect P and K leaching.

Acidified compost and AC results were compared by Ramzani et al. (2017). Three soils were used in the experiment and quinoa was the test plant. AC provided better results than acidified compost under various kind of stress conditions. Production of reactive oxygen species was reduced in AC amended treatments than control or acidified compost treatment. Moreover, AC addition reduced the pH of the soil and improved soil chemical properties. AC application in saline-sodic soil improves the soil quality. AC prepared by rice straw and dicer wood biochar was washed with HCl thrice (Sadegh-Zadeh et al., 2018). AC incorporated in the soil column at 50 g/kg rate and column leachate was analyzed. The analysis showed that AC reduced the EC and sodium adsorption ratio (SAR). Due to the ability to lower the SAR, it was used in the reclamation of saline-sodic soils. Rice straw AC was enriched with Ca and Mg. After incorporating AC in soil, it releases Ca2 + and H + in soil solution that replaced with Na^+. Except this, AC started dissolution of $CaCO_3$ which release Ca^{2+} and H^+ and played role in the remediation of saline sodic-sodic soil.

In calcareous soil, AC improves nutrients bioavailability and positively affects maize plant growth (Sahin et al., 2017). Acid-modified biochar (AB) was prepared by treating poultry manure biochar with phosphoric acid and nitric acid and their combination. Modified biochar was applied at 0.5% w/w rate and their effect on mineral nutrient availability, plant nutrition and plant yield were analyzed. Results demonstrated that AB produced from both acid combinations was enriched with both P and nitrate radicals. That modified biochar also improved the mineral nutrient availability like P, Ca, K, Mg, Fe, Mn, Zn and Cu, and accumulation of these minerals in plant tissues was also enhanced. It also increased the dry weight and yield of maize significantly.

Comparison of different methods of AC production was analyzed by Peiris et al. (2019). Tea-waste was pyrolyzed at different temperatures and produced biochar modified with three acids, e.g. HNO_3, HCl and H_2SO_4. Results denoted that increased pyrolysis temperature decreased the acidic functionalities of biochar and

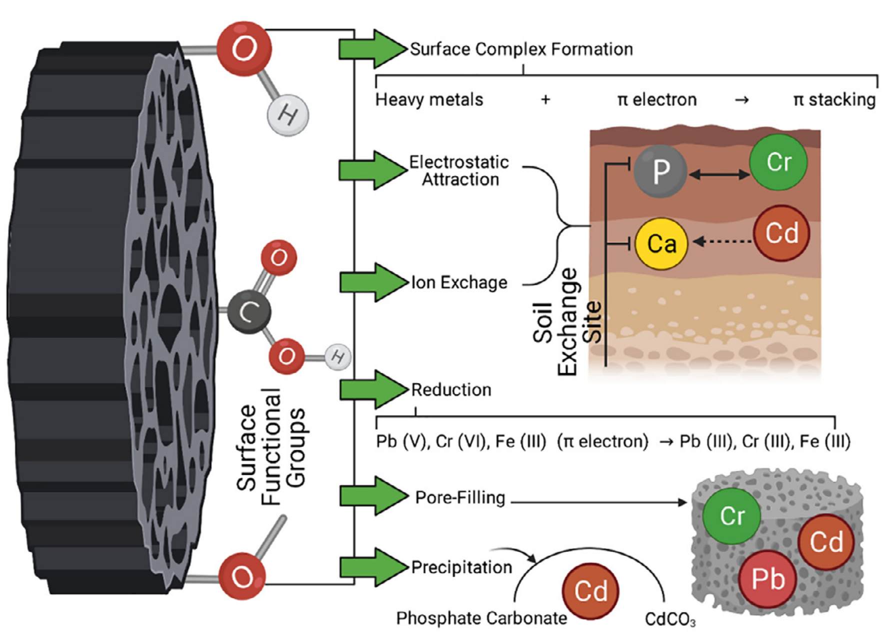

Fig. 3. Process involved in Immobilization of heavy metals by biochar in soil.

effects on pH and CEC of the biochar. Modified biochar had lower ash contents as compared with simple biochar. Sulfuric acid-modified biochar had higher CEC and then nitric acid modified. The cation exchange capacity of applied biochar is of significant importance because nutrient retention is directly related to CEC. Due to AC incorporation in soil, cationic species become part of soil solution, especially in high pH soils.

5.1. Chemically produced acidified carbon and plant Cd uptake

Another method for acidified biochar production was adopted by Sultan et al. (2020). Syrup waste was taken in a reactor and concentrated sulfuric acid (H_2SO_4 conc.) was added at 2:1 v/v rate. In a vigorous reaction, water evaporates and AC formed and further treated. Soil incubation with that AC and simple biochar showed that 2% AC was more effective in reducing soil pH and EC from 3.52 to 4.71% and 45.2–71.4%, respectively. Availability of other mineral nutrients like P, Zn, Fe and boron (B). Results reflected that AC was far more effective than simple biochar for maintaining soil health and quality.

Irrigating agricultural land with wastewater is becoming a common strategy in various regions of the world. That wastewater is enriched with several types of heavy metals, among which Cd is also included. This increasing trend put our agricultural lands at risk due to continuously increasing metal contamination. The high concentration of Cd negatively affects all kind of plants like rice. Despite strategies utilizing chemicals for remediation, a nature-friendly product should be used for remediation, which not only aids in remediation but also improves soil quality and plant productivity (Rehman et al., 2019). Adsorption behaviour of Cd^{2+} due to AC was studied by Chen et al. (2019). Phosphoric acid-modified biochar had a higher adsorption capacity of Cd^{2+} as compared with non-modified biochar. The adsorption rate of AC was 1.38 times higher than non-modified biochar. Cadmium adsorption forces are electrostatic interaction, O–H bonds and precipitation.

Keeping in view the issues mentioned above, Rehman et al. (2020) experimented on a modified form of biochar effect on rice growth. AC was prepared with H_3PO_4, HCl and HNO_3, applied at 2.5 and 5 N concentration. Results reported that maximum results were obtained with 5 N H_3PO_4 AC addition as it increased the agronomical parameters, e.g., root length 58.8%, plant length 48.8%, spike length 36.4% and 132% straw yield than control contaminated treatments. Inclusive of this, Cd concentration was also lowered in 5 N H_3PO_4 AC treatment. AC application reduced the Cd bioavailability in soil up to 87%.

AB (acidified biochar) effect was analyzed on soil and plant productivity (Abd El-Mageed et al., 2020). Citrus wood biochar was prepared with citric acid at 3:100 w/w and applied on faba bean grown on saline soil (EC 0.76 dS/m) at 0, 5 and 10 t/ha rate in two consecutive years 2016–17. The field was irrigated with wastewater which contains a high amount of heavy metals. Results reported that due to high CEC values of AC, it greatly modified the soil properties and reduced SAR of soil. AB bind the Na^+ present in soil solution with its surface and reduced the bioavailability and accumulation of Na^+ in plants. Reduced accumulation of Na^+ positively affects on growth and agronomical parameters of plants, even with metal-polluted irrigation water. AC not only bind Na but also increased immobilization of heavy metals like Cd, lead (Pd), nickel (Ni) and chromium (Cr).

6. Conclusion and future perspective

Heavy metals concentration in the soil exceeds their permissible limits (3 mg kg^{-1}) throughout the world due to the increasing rate of green revolution, urbanization and industrialization. Their toxicity and high uptake by plants adversely affect human health, soil and plant productivity and cause serious environmental concerns. Biochar is a stable C enrich pyrolytic product used as an echo-friendly remedy to remediation of heavy metals (Cd) contaminated soils. Owing to its high stability and negative charge, it adsorbs metals, thus significantly reducing metals mobility, bioavailability, and uptake by the plant. It also has active functional groups like ketones, carboxylic, and diols that bind the Cd and other metals. Biochar can also mitigate the harmful effect of Cd by increasing plant chlorophyll contents, photosynthesis activity, SOP, POD and CAT enzyme activity. Biochar can increase the CEC and anion exchange capacity (AEC) of soil, mediate soil pH, and increase N and P availability, boosting plant growth. Its highly porous structure improves soil water and nutrient holding capacity, aggregation, aeration, and ease in root penetration. Researchers claim that biochar should be used as amendments that aid in the remediation of heavy metals contaminated soils and improve C sequestration, soil health, and plant productivity.

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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