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Removal of Pesticides and Reclamation of Soil through Biochar Application as a Soil Amendment

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Abstract— The extensive use of pesticides and inorganic fertilizers has promoted soil contamination and also contaminated groundwater through the percolation of water and imparting lethal severe health effects on living beings and the environment. In modern agriculture, pesticides are inevitable as they are required to control pests, weeds, and other pests, which undoubtedly result in the gradual degradation of soil quality. Therefore, to deal with environmental as well as possible health effects, the contaminated soil has to be remediated by using environmental-friendly soil amendments. In this context, biochar could be a promising agent because biochar has high porosity, maintain soil alkalinity, have abundant functional group, and has an exceedingly aromatic structure, which makes biochar an efficient adsorbent; hence these properties of biochar make it a suitable agent to reduce pesticides in the soil and also prevent percolation of pesticides to the water. The mutual effects of soil organisms and biochar on pesticide reduction have received recent attention. In this review, we have highlighted the use of biochar as a soil amendment in the context of the removal and degradation of pesticides in the soil, along with the probable mechanism of biochar action on soil remediation.

Keywords—Biochar, Pesticides, soil toxicity, remediation, contaminated food grains

I. INTRODUCTION

Increasing food production for the rising population remains the primary goal and intention of all the countries, as the global human population is likely to reach nearly about 10 billion by 2050(Gill and Garg, 2014; Singh et al., 2020). As per the forecast of the FAO, food production must be raised by 70% to meet the expected demand of the evolving population. The escalating population and the demand for food have put pressure on the agricultural system to meet the demands under the same land, water, and other natural resources(Rajmohan et al., 2020). This increases the rate of application of pesticides, fungicides, nematicides, insecticides, weedicides, and fertilizer in the soil system. The detrimental effect of the pesticide and awareness was first published in the book "Silent Spring" written by Rachel Carson in 1962(Carson, 1962)where she explained how the indiscriminate use of pesticides kills the animals and the birds of a jungle by drinking the water of a lake which was contaminated by the pesticides. Now the use of pesticides is so extensive that it is included in our daily life as it is used in the Agric field, in the storage of grain, flower gardens, and preventing the spread of infectious diseases(Gill and Garg, 2014). Researchers are designing and formulating agro-pesticides to meet the demands of the agro-pesticides that are to be used in the agricultural sectors. The ideal pesticides should only be toxic to the target organism, must be degraded by biological processes and should be eco-friendly to some extent(e.g. use of biopesticides), but sadly, this is not the case because most of the pesticides are not specific and kill other microbes which are non-target or useful for the ecosystem (Gill and Garg, 2014; Pathy et al., 2020) it has been reported that only 1% or less than 1% of pesticides deliver to the organism that has targeted and the remaining of the pesticide contaminates the adjacent ecosystem and remain persisted in the soil which causes pollution to different components of the environment(Aktar et al., 2009; Meena et al., 2020; Rajmohan et al., 2020). The persisted pesticides have entered the food chain and bioaccumulated in higher trophic levels. Most human chronic and acute diseases and illnesses are associated with pesticide exposure and other non-targeted organisms like amphibians, fish, predators, pollinators, birds, earthworms, and animals. The residues of the pesticides, with time, leached to the groundwater and washed away to the source of the water reservoir and imparted deleterious effect to the aquatic life and to the organism which depends on that source of water. Therefore, the removal of pesticides from the soil, water, or the point source of pollution is one of the alternative ways to check the leading problems caused by pesticides; in this regard, biochar, with its great potential as a natural adsorbent and with different physical and chemical properties would help in removal and remediation of the heavily loaded soil pesticides residue either by chemical or physical process. In this review, we have discussed the methods of biochar production, factors affecting physical and chemical properties, the negative impact of pesticides on human health, soil microbes, and the role of biochar in the removal of pesticides. Biochar can bind to pesticides differently; some pesticides bind to biochar more strongly than others(Pathy et al., 2020; Yang et al., 2010). The capacity of binding on the surface of the biochar depends on many factors, which have been discussed in this article.

II. BIOCHAR PRODUCTION AND ITS PROPERTIES

"Biochar is a carbon-rich product obtained when biomass is heated in a close container in a limited source of air"(Nsamba et al., 2015). Recently the conversion of biomass and organic waste into biochar is targeted for bio-energy production (synthetic gas and bio-oils). Not only this the biochar is alternatively used in agriculture as a soil amendment(Pathak et al., 2020); moreover, biochar sequestrates carbon for 100-1000 years or more into the soil if added in the soil depending on the process of biochar production.

The process of biochar preparation depends on the objectives of biochar production (such as for agriculture, biogas, bio-oils, etc.). It has been established that biochar is typically obtained from a wide variety of biomasses by thermal degradation under different operating conditions. The process like pyrolysis and carbonization converts biomasses into bioenergy's. Economically biochar can be produced by employing three modes, i.e. Slow, intermediate, and fast (Panwar et al., 2019). It has been recognized that biochar yields are higher in slow pyrolysis methods than in other pyrolysis modes (Jyoti Rawat, 2019; Kung et al., 2015; Singh et al., 2022). The biochar production system can be classified as shown in the flow diagram below in figure-1.

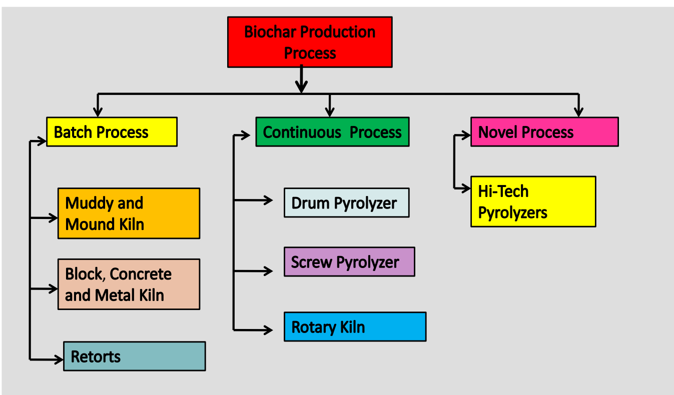

Figure-1 Classification of the biochar production process.

The most efficient, cost-effective, eco-friendly, and farmer-friendly method of biochar productions is drum pyrolizers' the common drum pyrolyzers is TLUD (Top Lit Up Draft) shown in figure-2. Though the production of biochar yields 10%-22% by traditionally employing the prevalent TLUD method, it is a simplified and widely used method because its cost of construction is very low compared to the other reactors and easy to make at home. However, TLUD biochar is inevitably varied in its properties for a considerable variety of reasons (see section 2.1 and figure-3) (Masís-Meléndez et al., 2020; Panwar et al., 2019).

2.1. Physiochemical properties of biochar.

The physiochemical characteristics of the biochar highly rely on the nature of the feedstocks used for the production; temperature and time are of great concern. The physicochemical nature of the biochar generally plays a fundamental role in remediating the soil contaminated byopesticides and other toxic substances. The most common physical properties of biochar are Bulk density, pores size, surface area, grindability, and Hydraulic conductivity, and chemical properties like EC, pH, half-life, absorptivity, paramagnetic property, proton activity, cation and anion exchange capacity, binding capacity, and solubility are considered if it is to be used in the soil for bioremediation of the soils as well as for pesticides removal.

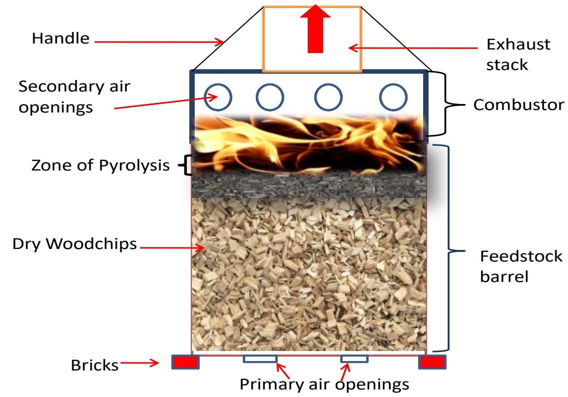

Figure-2 Schematic diagram of TLUD working and construction method using a barrel.

2.2. Factors affecting biochar production.

Factors that affect the biochar production and physicochemical properties depend on the various parameters such as:

- Nature of feed stocks
- Operating temperature
- Method used
- Needs of the biochar
- Process of application
- Heating rate
- Pressure
- Pyrolysis (fast and slow)
- The moisture content of feedstocks.

The aforementioned factors should be seriously taken into account while preparing for the production of biochar, as these factors determine the use of biochar and the purpose of its use. The applications of the biochar and the key factors affecting biochar production are shown below (figure 3).

III. UNDERSTANDING SOIL TOXICITY DUE TO PESTICIDES

The mobility and bioavailability of pesticides depend on the absorption and desorption mechanism of soil particles (Rajmohan et al., 2020). Pesticides have detrimental effects on soil diversity, integrity among the soil components, and of course, on humankind directly or indirectly. The toxicity of the pesticides relies on the functional group, nature of the pesticides, mode of action, and chemical structures. Pesticides are complex in their structure and compositions and are categorized as organochlorines, organophosphorus, carbamates, pyrethrin, and Pyrethroids (Odukkathil& Vasudevan, 2013). The classification of the pesticides is generally sorted based on nature, toxic level, and target applications. The different class of pesticides, toxicity, and half-life, along with the common name, is shown in table 1.

The inputs of pesticides to soil constitute a substantial source of soil pollution and water pollution, 50% of the rivers and streams water gets contaminated due to agrochemicals (details in Section-3.3). Directly or indirectly, pesticides are drained off to the aquatic ecosystem by sprinkling drift (usually common in agricultural irrigation practices), an aerial sprinkling (dominant in hi-Tech farming), soil erosion (more common in the coastal regions), and in discriminated use of oleochemicals (basic source are industrial, medical and household)(Odukkathiland Vasudevan, 2013; Rajmohan et al., 2020). The residue of the pesticides causes toxicity to the soil microbial system (discussed in section-3.2) and adversely affects the soil's productivity, and is related to the soil carbon budgets, as the microbes help in nutrient recycling of the soil and balance the carbon and nitrogen ratios. The intense use of agrochemicals has led to a high degree of persistence level of these chemicals in the soil due to the lack of timely degradation.

Table 1: Pesticide common name, class, and their toxicity along with half-life

Pesticide Name	Chemical Formula	Class	Toxicity	Water Solubili-ty	Half-life in Surface soil (days)
Acephate	$C_4H_{10}NO_3PS$	Organophosphate	Moderate acute toxicity	79g/ml at 100ml	5-32
Atrazine	$C_8H_{14}ClN_5$	Organochlorine	Moderate acute toxicity	32mg/L	110
Bifenthrin	$C_{23}H_{22}ClF_3O_2$	Pyrethroid	Moderate acute toxicity	0.1mg/L	7-150
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	Organophosphate	Highly toxicity	1.39mg/L	60-120
Cypermethrin	$C_{22}H_{19}ClNO_3$	Pyrethroid	Highlytoxicity	Not Soluble	7-168
Deltamethrin	$C_{22}H_{19}Br_2NO_3$	Pyrethroid	Highly toxicity	Not Soluble	11-72
Endosulfun	$C_9H_6Cl_6O_3S$	Organochlorine	Highly toxicity	0.33mg/L	60-800
Fenlaverate	$C_{25}H_{22}ClNO_3$	Pyrethroid	Highly toxicity	Not Soluble	30-120
Carbofuran	$C_{12}H_{15}NO_3$	Carbamate	Extremely toxic	320mg/L	10-200
Diazinon	$C_{12}H_{21}N_2O_3PS$	Organophosphate	Slightly toxic	40mg/L	30-40
Dichlorovos	$C_4H_7Cl_2O_4P$	Organophosphate	Extremely toxic	10mg/L	50-60
Lindane	$C_6H_6Cl_6$	Organochlorine	Highly toxic	7.3-7.8 mg/L	100-126
Monocrotophos	$C_7H_{14}NO_5P$	Organophosphate	Extremely toxic	154 mg/L	20-30
Permethrin	$C_{21}H_{20}Cl_2O_3$	Pyrethroid	Highly toxic	0.07mg/L	30-38

Due to their less solubility and high stability, the hydrophobic pesticides limit their degradation via physiochemical processes. Therefore, most of the hydrophobic agrochemicals(pesticides) adsorb to the soil surface or the organic matter and get into the pore matrix of the soil particles, and thereby becoming less bioavailable, and so degradation by the microbes also decline proportionally (Odukkathiland Vasudevan, 2013). Slowly and gradually, accumulation of the pesticidal residue in the soil resulted in soil pollution, destruction of soil quality, reduction of soil microbes, causes water pollution, loss of biodiversity, biomagnifications, and interference with primary metabolites of the non-targeted organism (Aktaret al., 22009; Meenaet al., 2020).

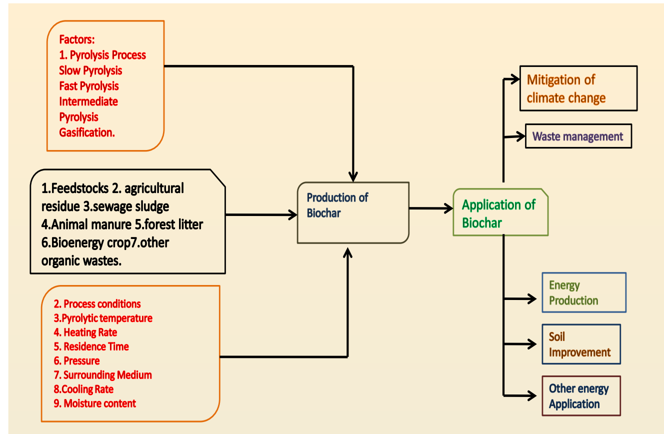

Figure-3 Schematic process of factors affecting biochar production and applications.

3.1. Resistance of pesticides by the organisms:

Resistance is the heritable changes or adaption in pest population that is reflected in the constant failure of products to achieve the expected self-control when used according to the label recommendation for the pestspecies(Gill and Garg, 2014). Due to this, the resistant individual tends to be a normal population, but the susceptibleness's eliminated by the chemicals, and therefore the resistant individuals thrive and reproduce their numbers without any competition resulting in more havoc to the crops as the pesticides no longer effective, which create pull for more additions of pesticides indiscriminatingly (Gill and Garg, 2014). Resistance is the major drawback or threat in the successful implementation and use of pesticides these days. Excessive use of pesticides has led many targeted pest species to develop resistance to pesticides around (Tabashnik et al., 2009). Now, the conditions are such that important crop pests, the parasite in livestock, and disease vectors have developed such resistance against the pesticides that it becomes more challenging to control the pest population.

3.2. Effects of pesticides on soil microbes:

Even though the goal behind the use of pesticides is to drive away from the targeted pests, their extensive use of them has resulted in numerous toxicological effects on non-targeted species that were supposed to be playing an important role in the soil dynamics. The applied pesticide, when it gets contaminated with the soil, it shows detrimental effects on beneficial microbes. It has been stated, "that 1gm of soil in a country is an index of the agricultural prosperity of that country"(Kalia and Gosal,2011).

It has been estimated that the total biomass of micro and macroflora underneath is about 20times that of the earth's human population (Torsvik et al., 1990). One gram of healthy soil contains nearly 1 million to 100 million bacteria which participate in the breakdown of organic matter, 0.15-0.5 mg of fungal hyphae,10000-100000 protozoa, a few to several hundred microarthropods, 15- 500 nematodes, and a few earthworms are also present (Coleman, 1994; Kalia and Gosal, 2011). Microbes play an important role in soil fertility and in maintaining the soil system's food web and facilitate the recycling of nutrients and the retention of the basic structure of the soil. Hence when agrochemicals are applied to the soil and their persistence in the soil for long periods kills a certain specific group of microorganisms, as a consequence, decreases the number of microbes and disrupts that particular process in the food web that an individual or group performs.

The metabolites secreted by the soil microbes execute the biochemical process that helps bind pesticides to metabolites and, as a result, reduce the bioavailability of pesticides; by these activities, microbe numbers in the soil indicate the quantities of freely available pesticides in the soil. Moreover, the soil types also affect the binding of pesticides to soil particles as the pesticides interact differently with different types of soil particles (Odukkathiland Vasudevan, 2013). Several pesticides alter the symbiotic relationship between legume crops and Rhizobium and hinder the N-fixation process (Meena et al., 2020). AM fungi play an important role in symbiotic association with higher root plantain uptake of phosphate and nitrogen, but the pesticide residue imparts deleterious effects on the population of the AM fungi(Meena et al., 2020).

3.3. Pesticide residue and its relation to water pollutions:

Pesticides can contaminate the surface and groundwater through runoff and leaching from the treated soil and chemicals industries; water contamination by agrochemicals is widespread (Aktar et al., 2009). The broad use of these pesticides is more common in developed countries than in developing countries. Different surveys and sampling of water samples from urban and agricultural sources of water bodies show the presence of the pesticide residue, and it has been increasing slowly and gradually year by year (Rajmohan et al., 2020). The applied agrochemicals tend to move in the environment and to groundwater by various means. The pesticides persist in the soil and seep into the groundwater; heavy rain and showers of water carry away the pesticides to the source of surface water and creates health issues for the organism present in the water, as well as those who consume the contaminated water (see figure 4) (Srivastava et al., 2018). The residual pesticides once contaminate groundwater; it takes many years to clean up the contamination. The pesticide compound mostly detected in the water sampling are "atrazine, simazine, alachlor, metolachlor, and trifluralin of the herbicides, diazinon, parathion methyl of the, and Lindane, endozoan, and aldrin of the organochlorine pesticides" (Srivastava et al., 2018).

3.4. Effect of pesticides on human physiology:

The hazardous effects of pesticides on human physiology have started growing day by day due to the pesticidal toxicity and their persistence in the environment. Pesticides enter the food chain and become an integral part of human life; pesticides enter the human body by direct contact with chemicals through consuming contaminated food, contaminated water, or air(Gill and Garg, 2014).When accumulated in the human body above the permissible limit, pesticides are linked to causing both acute and chronic diseases. Poisoning of pesticides to humans, intentional or unintentional, may cause death. When inhaled or entered in a low amount in the body, it causes body pain, headache, eye irritation, raise body temperature, skin rashes, nausea, cramps, etc. Long-term exposure to pesticides could damage DNA. It may cause mutation of important bases of DNA, the exposure to pesticides linked with the heart attack, cancer, Parkinson's disease, Alzheimer's disease, reproductive disorders, and hormonal disbalance (Gill and Garg, 2014; Odukkathil and Vasudevan, 2013; Rajmohan et al., 2020). Pesticides of any class, when accumulated and persisted in the food and potable water, increase the risk of the deformation of the fetus development and may affect such an extent that offspring born with permanent disabilities as pesticides at a certain ppm amount passes to the placental wall, moreover, the infant after during breastfeeding get intoxicant by the pesticides if the mother had consumed repeatedly foods or water which have an accumulation of pesticides beyond the permissible limits(Youssouf et al., 2018). The exposure of pesticides to a fetus triggers neurological disorders and remains a congenital disorder; therefore, it is a severe concern for human health &hygiene and for the next generations. The concentration of pesticides is increasing gradually in the soil and water; however, biopesticides have been introduced to check the use of synthetic pesticides. But biopesticides have their limitations. Therefore, many technologies have been adopted to remove pesticides or reduce their use in agriculture using different management strategies. A sustainable management method has discussed below.

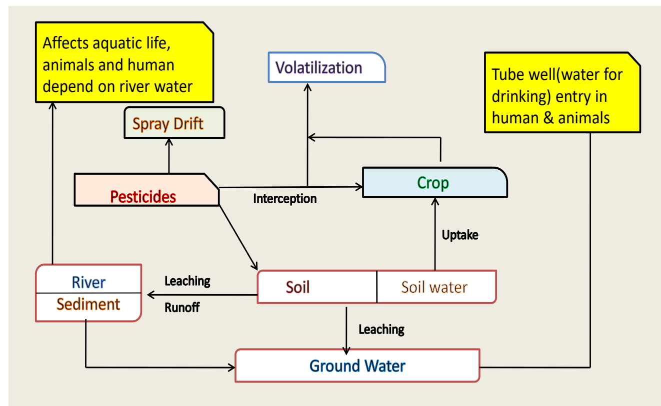

Figure-4 The pathways of different water sources contaminated by the pesticides and their entry to the non-targeted organism, including humans.

IV. RECLAMATIONS OF SOIL AND REMOVAL OF PESTICIDES BY BIOCHAR

Soil contaminated by pesticides threatens agricultural products, soil microbial diversity, and human well-being, so it is necessary to choose economical and sustainable effective remediation techniques to remove or mitigate the pesticides' deleterious effect, which we have discussed in the above sections. As we have already discussed the physicochemical properties of biochar and the factor that affects the characteristics of biochar, therefore based on the chemical and physical properties, it has been reported by various studies that biochar could remediate soil contaminated by agrochemicals. In a study, Atrzine based pesticides were found to be absorbed by the biochar significantly (Zheng et al., 2010). Another similar study was done using the biochar obtained from burning cotton straw chips under two different temperatures and amended to the soil to achieve 0,0.1,0.5, and 1% by soil dry weight to investigate the dissipation of insecticides (chlorpyrifos and fipronil) applied in Chinese chives and reported the loss of both pesticides in the soil considerably with the increasing amount of biochar in the soil (Yang et al., 2010). In the same study, it was established that the soil amended with the biochar reduces pesticide uptake by the plants markedly compared to control (Yang et al., 2010); it was also suggested that biochar produced at quite high temperature 850^0C is likely to be more effective than those produced at lower temperatures, primarily due to its higher surface area and microporosity and greater ability to sequester pesticides in soil. Biochar has a high adsorbent capacity, and this potency of biochar makes them competent to absorb organic contamination of the soil (Hayyat et al., 2016). Biochar could be used as an alternative to inorganic fertilizer by proper activation (Pathak et al.,2020). Biochar provides residence to the soil microorganisms and helps in the improvement of soil inhibiting microbes populations (Pathy et al., 2020). The properties of the biochar determine its adsorption capacity to any heavy metals or pesticide residue from soil or water (Hayyat et al., 2016; Wang et al., 2018). The mechanism of adsorption by biochar greatly depends on the following properties:

- Aromaticity.
- pH.
- Ion exchange capacity.
- Surface area.
- Porosity.
- Functional group.
- Material used for biochar preparation.
- The temperature at which biochar is prepared.
- The methods of applications of biochar.

The replacement adsorption of biochar surface is one of the key parameters for the adsorption of the pesticide residue. The greater the number of cation exchanges, the stronger the retention of pesticides by the biochar (Lehmann, 2007). The ion exchange is based on the electrostatic interaction between negative charge groups on the biochar surface and positive charge in the soil (Wang et al., 2018). The aromatization of the biochar controls the cationic π functions; the more the π conjugate aromatic structure exits, the greater the negative charge in π-orbital changes so, therefore, the ability to lose electron of the functional group increases, which significantly increases the adsorption effects (Li et al., 2017).

Interaction of pesticides to the functional groups like hydroxyl group (-OH), carboxyl group (-COOH), and amino-group (-NH2) on biochar surface could make great contributions to the adsorption of pesticides from the soil and the water contaminated by extensive pesticides. It has been reported that higher surface area and higher surface energy are helpful for biochar to strongly absorb the heavy metal and probably pesticide residue (Wang et al., 2018). The absorption rate of the biochar affects by many factors that have been mentioned above. There are many types of biochar, and many factors affect the structure, and how it works in the soil, this may affect whether a specific ingredient would bind to it.

Biochar can bind diverse pesticide ingredients in soil and water, and the best adsorption happens when biochar and soil are mixed thoroughly. Once the pesticide ingredients bind to biochar, how long pesticides may stay sticking is unknown. Over time pesticide residue desorbs or unstuck and may become mobile again in the soil. Absorption capacity and removal of pesticides depend greatly on the methods of application of biochar. In one of the studies carried out by Herath et al. (2016) where they evaluated the effects of pH, reaction time, and glyphosate(herbicide) loading on the rice husk biochar (RHBC) adsorption process from an aqueous solution, they reported 82% of adsorption of the herbicide from the aqueous solution, it was also reported that the adsorption capacity of the RHBC decreases considerably with increasing pH, they postulated that pore diffusion,π-πelectron-acceptor interaction and H-bonding was involved in physisorption of the glyphosate and suggested that the activated RHBC could be promising tools of glyphosate removal from the aqueous solutions.

To remove the inorganic and organic pollutants from the water source and wastewater treatment, the use of activated granulated carbon and pulverized carbon are being used as the adsorbent material(Alves Pimenta et al., 2020); therefore, using biochar would be a sustainable approach and economically viable as the biochar could be generated by using agricultural crop residues, which will prevent the burning of crop residues in the open field after harvesting and hence could contribute in mitigating the emission of carbon by burnings, it has also been reported that biochar, when used as a soil conditioner promotes plants growth and reside in the soil more than 100 years as a carbon, hence helps in sequestrating the carbon while fertilizing soil and reclamation of the degraded soil by different toxicants and heavy metals. Therefore, more research on biochar as a remediation tool in the soil and water needed to be done on a large scale to establish the proper utilization and application of biochar in this regard.

4.1. Future suggestions related to biochar in removal of the pesticides:

Charcoal is one of the important materials used since the ancient period in the preparation of water filters by country methods and still in the interior of the rural area where the mud pot is filled with sand, small pieces of stones, and Charcoal made of wood and used to filter the drinking water. The advancement of scientific technologies and their integration in the development of a precise protocol for the removal of pesticides using biochar will reflect a new dimension in reducing pesticide toxicity in the soil and water system. Some of the suggested work needed to be done are:

- Investigating the potential of biochar in water treatment at the community level.
- Mechanism of pesticide removal from soil system using biochar.
- Investigation of different pH range for the suitable adsorption of toxic compounds by the biochar.
- Establishment of the activation method for the Char produced from the agricultural crop residue.
- Enactment of regulation in the utilization of biochar which is to be used in the filtration of drinking water.
- Cost management in the preparation of water treatment plants using biochar as adsorbent.
- A comparative study needs to be carried out with already commercialized adsorbents with biochar.
- Investigation of pesticide's fate after binding to the biochar surface

V. Conclusion

In this review, we have considered the inductions of biochar for the removal of pesticides from the soil and water system, the methods of biochar production and factors affecting its production have been considered along with the physicochemical properties, the impact of pesticides on soil toxicity, microbes, and human health have been summarized. Several researchers have addressed the grave issue of pesticides in the environment, and many remediation technologies have been adopted, but every method includes certain limitations; therefore, a holistic approach should be considered. Biochar for this purpose may be investigated in a long-term field experiment. The application of biochar in the removal of pesticides is culminating and thought to be a promising sustainable method. Regulation regarding the application and remediating technology must be made as such that its implementation can be carried out at each level of society.

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