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GREEN REMEDIATION: A CRITICAL EXAMINATION OF BIOCHAR'S HEAVY METAL ADSORPTION ABILITIES

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ABSTRACT: Biochar can be used as an efficient and low-cost adsorbent for wastewater treatment as heavy metal pollution has become the serious issue for environmental pollution today. A number of studies have demonstrated effective removal of heavy metals from water by biochar. Several factors affecting the sorption tendency of biochar, feedstocks materials play a significant role. Depending on the biochar type, heavy metals can be removed by different methods such as complexation, physical sorption, precipitation and electrostatic interactions. In recent years, ample method for heavy metal removal from wastewater has been extensively studied. This paper reviews the recent methods that have been used to treat heavy metal removal from wastewater and evaluates these techniques. These techniques include ion-exchange capacity, adsorption, membrane filtration, coagulation-flocculation, flotation and electrochemical methods. From literature review it is evident that ion-exchange, adsorption and membrane filtration are the most recent studied for the treatment of heavy metal wastewater.

INTRODUCTION: Biochar can be defined as carbon rich product obtained from the raw materials, like forest, animal compost, and plant residues, is heated in a close container without air or limited supply of air [1]. The process through which the biochar obtained in absence of oxygen is termed as pyrolysis. As the organic matter is converted into biochar having the stable form of carbon that does not easily released into the environment due to its highly reoccurring aromatic ring structure [24].

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The physical appearance of biochar is black, highly pervious, light weight, fine- grained and has a large surface area and its composition has 70% carbon. The remaining composition percentage consists of hydrogen, nitrogen, and oxygen [2].

The first discovery of biochar was by a European geologist in 1870, observed areas in South America with bizarrely productive soils-compared to the typically facile, acidic soils capable of only short periods of efficiency. Studies have found that biochar enriched soils in Amazon Basin from 8000BC, and anthropological analysis has determined that biochar enriched soils might have been used to create regions of extremely high productivity to enhance successive cultures in areas of South America with high populations. A carbon rich soil mix referred to as "terra preta" still remains in mainly areas of the Amazon Bains. The carbon content present in soils has long been known to be a important factor in soils ability to hold water, improve microbial activity and fungal populations, increase nutrient availability.

Previously, the generation of biochar and charcoal was done in covered pits, large piles and beehive style kins, causing in mostly anaerobic situations intensive. These ingenuous systems were also largely unmanageable [3].

The biochar used in this work was derived from the *Lantana camara*. All material was cut into small pieces and then air dried for one week. This material was charred for 6 hours at distinct temperatures (from 300 to 600 °C [4].

Method of Preparation of Biochar: The biochar can be produced by different methods as well depending upon the nature of biochar required. For instance.

Pyrolysis: The process involves heating raw material in the absence of oxygen to produce biochar as the primary resultant. It is one of the most common methods used for biochar preparation. By this method, raw materials (kelp, apple pomace, biofilm, *etc*.) can be used to prepare biochar [5]. There are two types of pyrolysis which are slow and fast pyrolysis. Slow pyrolysis in which raw material undergoes decay at a low heating rate (0.1-0.8 °C/s) with sufficient retention time. In fast pyrolysis, biomass is heated at a higher rate (1000 °C) and is used to make bio-oil and syngas as the main product.

Gasification: It is a partial oxidation process that converts a solid fuel into a gas that contains hydrogen, carbon monoxide, carbon dioxide, methane, and nitrogen. It consists of four steps including drying, pyrolysis or dehydrogenation, oxidation or combustion and gasification or reduction to thermolysis gas and biochar in discharge port [6]. Gasification based biochar is different from pyrolysis-based biochar, in terms of its morphology and surface-functional group [7].

Torrefaction: It converts raw material at temperature (200-300°C) in absence of oxygen at a low heating rate (50°C/min) to generate bio-oils, or biochar.

Flash Carbonization: Another process that converts biomass into gaseous and solid products by igniting a flash fire under an arranged bed of biomass at higher pressure of 1-2 mPa and a temperature of 300-400°C for not more than half an hour [8].

Hydrothermal Carbonization: It refers as a process through which biomass material is carbonized *via* thermochemistry. It involves a water environment at a temperature of 180-300°C and a certain pressure [9].

Microwave Pyrolysis: It is a process which involves rapid heating and extensive pyrolysis decomposition of biomaterial by including rapid dipole rotation and between biomass particles with microwave radiation in the range of 100-250°C [10]. The optimal methods for preparing biochar are hydrothermal carbonization and microwave pyrolysis because these methods are convenient, give high yield, and do not produce secondary pollutants.

Modified Biochar: Sometimes, the remediation of heavy metal by pure biochar yields unwanted results. To enhance the effect of biochar, the preparation method of modified biochar loaded with different elements has gradually become a research hotspot. The main methods for the preparation of modified biochar are in situ synthesis method and impregnation method.

Impregnation Method: In the impregnation method, either commercially available or homemade biochar is saturated with specific elements by soaking it in a solution that includes a modifier. This approach enables the creation of diverse modified biochar’s.

***In-situ* Synthesis Method:** It involves directly introducing the desired modification reagent into the raw material. This is followed by processes such as pyrolysis, chemical precipitation, and activation to yield the modified biochar. For instance, in one study, pine shavings were immersed in a 0.5 mol/L Fe (NO3) 3 solution for 5 hours, then dried at 105°C, and subsequently carbonized at 500°C for 2 hours in a nitrogen-protected muffle furnace to produce iron-bearing-modified biochar.

This modified biochar exhibited effective catalytic reduction capabilities for model dyes. In another example, Liu *et al.* employed the in-situ synthesis method to create Fe-rice-husk-derived biochar, which was used for remediating soil contaminated with hexavalent chromium, achieving an approximately 81% removal efficiency. Khan *et al.* also utilized the in-situ synthesis method to synthesize superparamagnetic nano-Fe3O4 biochar from *Acacia mearnsii*.

Mechanism of Heavy-Metal Contaminated Water Remediation by Biochar: With the development of industrial production and increment of human activities in China, the problem of soil pollution is becoming more concerned, as the decrement of soil area, and pollution by chemical compounds such as heavy metals, pesticides, acidic substance, undesirable organic matter [11].

The pollutants that mainly affect the soil include heavy metals and organic compounds such as Cd, Pb, Cr, fertilizers, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls [12], *etc*. These pollutants have carcinogenic affects, tetratogenic, mutagenic effects, and genotoxicity along with the degrades the quality and crop yield, causes deterioration of the atmospheric and water environment quality, which are harmful to human health through the food chain [13].

Biochar, being a complex carbon-rich substance, employs various mechanisms to adsorb heavy metals in aqueous solutions. Its surface is equipped with oxygen-containing functional groups and binding sites that facilitate complexation and ion exchange with heavy metal ions. Additionally, some insoluble inorganic salts formed during the biochar preparation process may coprecipitate with heavy metal ions on its surface. Furthermore, the electric charge on the biochar's surface allows for electrostatic adsorption of heavy metal ions.

Ion Exchange Adsorption: Biochar's surface binding sites readily engage in ion exchange with heavy metal ions. For example, Chen *et al.* investigated the adsorption of Cu2+ and Ag+ by biochar in aqueous solutions and observed a significant decrease in pH during the reaction. This indicates that exchange reactions occur with the acidic functional groups on the biochar surface.

Complexation: The oxygen-containing functional groups on biochar's surface can form complexes with heavy metal ions. Analyzing the infrared spectra of biochar before and after heavy metal adsorption, Adam *et al.* noted varying degrees of functional group involvement, highlighting the participation of oxygen-containing groups in the adsorption process. Additionally, [14], conducted scanning electron microscopy analysis, revealing the presence of insoluble complexes on the biochar surface before and after heavy metal adsorption. EDS analysis confirmed that these insoluble complexes comprised heavy metal ions from the solution.

Precipitation Sedimentation: Surface co-precipitation is a primary mechanism for removing heavy metals from aqueous solutions using biochar. Scanning electron microscopy (SEM) observations can directly identify insoluble substances on the biochar surface. Cao *et al.* determined the contribution of each functional group to heavy metal ion removal using the Beom Titration method, highlighting the significant role of hydroxyl groups in surface co-precipitation. Additionally, (Edmend *et al.*) used MINTEQ software analysis and found that, with cow dung biochar, 75-80% of Pb2+ ions in aqueous solution were removed through coprecipitation, whereas only 25-30% were removed through surface complexation.

Applications of Biochar in Soil Remediation:

Removal of Heavy Metals: Removal of heavy metals by biochar is mainly done by two aspects. One is the adsorption of heavy metals in the pores of biomass to decrease the residual amount in the soil; the other is the ion exchange or redox reaction between the effective components in biochar [15]. Boostani [16] investigated the effect of earthworm and sheep manure biochars on Pb immobilization in an adulterated calcareous soil. Addition of biochar causes an increment in the Pb content in the residual state, which decreases the Pb activity in the soil. Yang [17] *et al.* presented that straw and bamboo biochar are more effective than Zn in reducing extractable Cu and Pb.

Removal of (Pops) Persistent Organic Pollutatnts: Biochar has a strong capacity for organic pollutants, and the process can be understood as the extraction and collection of organic pollutants on biochar. The persistent organochlorine pesticides in land soil in are still seriously polluted, and the polycyclic aromatic hydrocarbon pollution caused by sewage irrigation can be ignored.

Dry Organic Dyes: Organic dyes are prevalent pollutants found in industries like textiles, coatings, paper manufacturing, and dyeing [18, 19]. The significant discharge of dyes into different ecosystems has garnered global concern. Many commercially used dyes, such as methyl orange, methylene blue, naphthol green, and yellow dyes, exhibit notable characteristics like strong chemical stability, water solubility, and intense colour."

Biochar Derived Catalyst: Materials rich in carbon, such as carbon black, carbon nanotubes, and graphene, have found widespread use as catalyst supports and direct catalysts in various applications [20]. Biochar, which is also a carbon-rich material with the ability to regulate porosity, holds promise as a potential substitute for existing carbon-based supports. This is due to its cost-effectiveness and environmental friendliness [21]. Furthermore, the presence of intrinsic heteroatoms (like N, O, S, P) and embedded metallic compounds in biochars enhances their catalytic capabilities [22]. Additionally, the surface properties of biochar can be tailored through additional physical or chemical activation processes [23].

CONCLUSION: The physical chemical and biological alter can increase the active sites, pore volumes and functional groups of biochar. It is of great significance to make a new altered biochar with environmental protection and strong sorption capacity. In the laboratory, biochar formed has demonstrated promising results, and it can be further explored for applications such as water treatment in river. It can also show effectiveness in desorption process.

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