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Review Paper

Biochar as a low-cost adsorbent for heavy metal removal: A review

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Abstract

Conversion of agricultural residues to biochar can be used as an alternative remediation of heavy metals from the environment used as a low-cost adsorbent. Ground water, originated from natural and anthropogenic sources, is contaminated by heavy metals. Removal of heavy metals from aqueous solutions has been examined by a number of studies using biochar as a sorbent. Generally, development of commercial biochar for reliable data on production of biochar technologies is required. For this purpose, peer-reviewed scientific articles on carbonization technologies (pyrolysis, gasification, flash carbonization and hydrothermal carbonization) have been analyzed. Different mechanisms such as ion exchange, electrostatic interactions, complexation, membrane filtration, physical sorption, and precipitation have been effective for removal of heavy metals. Mathematical sorption models can be used to evaluate the efficiency of biochar for removing heavy metals, and also promote in water treatment through the application of biochar technology in water treatment. Biochar used as a low-cost adsorbent for heavy metal removal from aqueous solution is promising and an emerging wastewater treatment technology. When the biochar was impregnated with chemicals, the effect was a little increased. Under optimum conditions, 99% Cd, Pb and Zn were removed from aqueous solution using biochar.

Keywords: Aqueous solutions, Adsorption, Biochar, Carbon sequestration, Water pollution

Introduction

Heavy metal toxicity is a major risk to public health and human-altered environments in all over the world. They mainly act as environmental pollutants and used as a severe threat to animal and human health by their long term perseverance in the environment^[27]. Usually most of the heavy metal pollutants are focused on non-essential heavy metals like Pb, Cu, As, Cd, Cr, Hg and essential heavy metals like Cu, Ni and Zn which are toxic and carcinogenic that could cause health problems in humans. Natural constituents of the earth's crust are heavy metals^[13,18]. Industrialization and technology have led to a rising use and pollution of heavy metal. Toxicity of heavy metals contrary to organic substances is nondegradable in nature which accumulates in the environment. Heavy metals are elements that contribute metallic properties such as cation stability, conductivity, ductility, ligand specificity, and malleability. The heavy metals that are available for plants uptake are those that are present as soluble components in the soil solution or those that are solubilized easily by root exudates^[2]. The capacity of plants to accumulate necessary metals equally enables them to acquire other unnecessary metals^[24]. Heavy metals are bioremediated using microorganisms, plants, or the combination of both. The industrial and agricultural effluent is the most toxicological relevance due to presence of heavy metals. Due to the disposal of heavy metals it has been increasing water pollution worldwide. Their presence in lakes, sand, stream has been responsible for serious health problems for plants, animals, and human beings. Metal toxicity compounds arising to the earth's surface not only contaminate earth's water (lakes, seas, reservoirs and ponds) but also causes ground water

contamination in trace amounts through leakage from the soil after snow and rain. Therefore, the earth's water may reserve various toxic metals. Thus, it is a vital role for removal of heavy metal ions from wastewaters, before they are arrived to the environment. This technological review considers biochar production, biochar properties, and advancement for removal of heavy metals, from inorganic, organic and other pollutants using biochar. Biochar is pyrogenic black carbon coming from thermal degradation (e.g., pyrolysis) of carbon-rich biomass in an environment which is an oxygen-limited technology. In recent years, biochar has gained increasing attention due to its multi-functionality including carbon sequestration and enhancement of soil fertility^[15] production of bio-energy^[8] and environmental remediation^[17]. Biochar mainly enhanced as an amendment of soil but it can also acts as a well adsorbent, which can employed as a low cost wastewater treatment. Activated carbon is already being used for this, but biochars may form a lower cost alternative. Adsorption on the other hand, mostly important processes such as physico-chemical treatment which is commonly applied and used to remove heavy metals from aqueous solutions and waste water mainly due to its large surface area, distributed pore size, distributed particle size and highly surface reactivity. Use of Biochar and its Production, produce renewable energy and releasing greenhouse gas emissions from soils and the decomposition of waste.

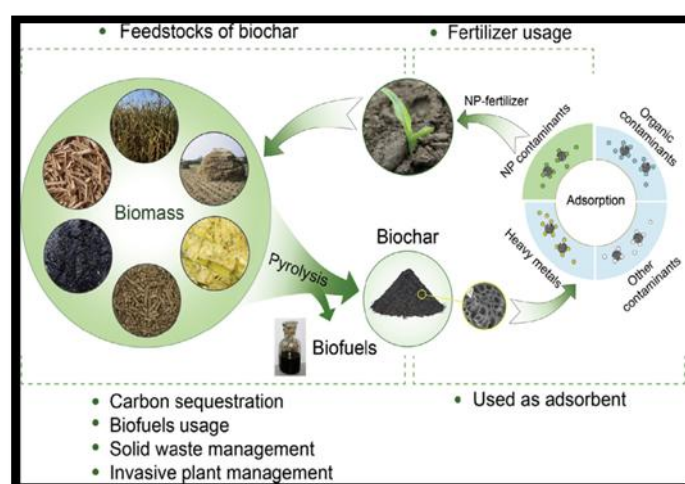


Figure 1: The benefits of biochar applied as an effective adsorbent for wastewater treatment

Mechanism of interaction between biochar and heavy metals

Various mechanisms may play role in controlling heavy metals removal from aqueous solutions using biochar, including precipitation, complexation, ion exchange, electrostatic interaction (chemisorption), and physical sorption. Biochars having high surface area and pore volumes have a greater affinity for metals because metallic ions can be physically sorbed onto the char surface and retained within the pores^[18]. Many biochars surfaces have negatively charged and can sorb metals positively charged through electrostatic attractions, ligands Specificity and various functional groups on biochars can also interact with various heavy metals by forming complexities^[6,7,30] or precipitates of their solid mineral phases^[11]. Compared with activated carbon, biochar appears to be a new potential low-cost and effective adsorbent. The activated production of carbon needs higher temperature and additional activation process. Ultimately, the biochar production is cheaper with lower energy requirements^[3,34,15]. Physical or surface sorption describes the heavy metals removal by diffusional movement of metal ions into sorbent pores without formation of chemical bonds. For both plant and animal biochars, temperature increases of carbonization ($=300^{\circ}\text{C}$) will favor surface areas high and pore volumes in biochars. Heavy metals Sorption through exchange of ionizable cations/ protons on biochar surfaces with dissolved metal species is another mechanism. Electrostatic interaction between surface charged biochars and metal ions is another mechanism for the heavy metals immobilization. Mechanism of biochar depends upon biochar-metal sorption process which depends on pH solution and point of zero charge (PZC) of biochar^[6,22]. High temperatures ($>400^{\circ}\text{C}$) of carbonization also promote the formation of grapheme structures in the chars to favor electrostatic attractions sorption mechanisms^[16]. At the time of sorption process Precipitation is the formation of solid(s), either in solution or on a surface. Precipitation has been commonly cited as important mechanism responsible for the immobilization of heavy metals using biochar sorbents. Due to the optimization of adsorption process pH of the solution is the most vital parameters. It affects on charge

surface area, degree of ionization and speciation of adsorbent. Biochar carried various surface functional groups (mainly oxygen containing groups, e.g. hydroxyl, AOH and carboxylate, ACOOH);. Change of these functional group acts with the increase of the pH solution. At low pH, functional groups on biochars present in the form of positively charged [13,17,33] report that the pyrolytic temperature significantly influence the structural, morphological, elemental and properties of biochars.

Table 1: Review of adsorption capacity of biochars from literature

Metal (mg/g)	Adsorption capacity	Adsorption pH	Biochar feedstock	References
Cd	1.5	5	Alamo switch	[25]
Cu	4	5	grass	
Cd	16.6	5	Pig manure	[17]
Cu	6.3	6		
Pb	19.8	5		
Zn	4.2			
Pb	4.1	5	pinewood	[20]
Pb	2.4	5	residues	
			rice husk residues	
Cr (VI)	3.0	2	Oak wood	[17]
Cr (VI)	4.6	2	Oak bark	
Cu	0.04	5	peanut straw	[29]
Cu	0.09	5	canola straw	

Application of biochar for water treatment:

Due to the large specific surface, highly porous structure, functional groups of biochars have more important features and they are highly contaminant removal and more effective application of biochar for aqueous solution. According to the literatures studies for waste water treatment, the biochar application is nearly 45% for heavy metals, 40% for organic pollutants, 13% for NP, and 2% for other pollutants. Toxic metal contamination in aqueous solutions has become a great problem throughout the all over world. Thus, heavy metal removal has become one of the main focuses of research on the water treatment using biochar application. The concerned heavy metals include nickel (Ni), aluminum (Al), mercury (Hg), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), uranium (U), and zinc (Zn). Adsorption isotherm emphasize as an optimizing adsorbents which describes interaction between adsorbates and adsorbents. Adsorption characteristics of biochars focused to different heavy metals are presented in Table 2.

Table 2: The application of biochar produced from different feedstocks and techniques in aqueous solutions

Biomass feedstock	Pyrolytic temperature (°C)	Pyrolysis techniques	Contaminants	References
Coconut coir	250–600	Slow pyrolysis	Chromium	[26]
Corn straw	600	Slow pyrolysis	Copper and zinc	[4]
Dairy manure	350	Slow pyrolysis	Pb, Cu, Zn, and Cd	[31]
Rice straw	100–700	Slow pyrolysis	Aluminum	[5]
Sludge	400–700	Slow pyrolysis	Fluoride	[9]
Sugar beet tailings	600	Slow pyrolysis	Phosphate	[32]
Sugarcane bagasse	450	Slow pyrolysis	Sulfamethoxazole	[27]
Wood	200–600	Slow pyrolysis	Fluorinated herbicides	[28]
Rice husk	350	Slow pyrolysis	Pb, Cu, Zn, and Cd	[31]
Corn straw	600	Slow pyrolysis	Copper and zinc	[5]

A number of empirical models have been engaged to analyze experimental data and describe the heavy metal equilibrium adsorption using biochars. From aqueous solution removing of ammonium, nitrate, and phosphate using biochar has helped in pollutant mitigation from aquatic ecosystems and

soil^[28]. The efficiency of biochar adsorption tends to be impacted by biochar properties, like adsorbent dosage, deashing treatment, competitive anions, pH and temperature^[17]. It has been reported that the pyrolytic temperature influence the structural, morphological and elemental properties of biochars. Knowledge's about the effects of deashing treatment and de-mineralization of biochars on their adsorption of water contaminants are limited. The influence of pH on adsorption was dependent on the target contaminants and various types of biochars. It influenced the adsorbent surface charge, speciation of the adsorbate and degree of ionization. Removal of contaminant is a very cost effective application applying an optimum dosage of biochar, reported that decreasing of the adsorption efficiencies and rising of the concentration of biochar^[10].

How biochar spent management

Since biochar application for pollutants removal from aqueous solutions is mainly dealing with various toxic pollutants, the disposal process of the spent biochar is an important issue to consider.

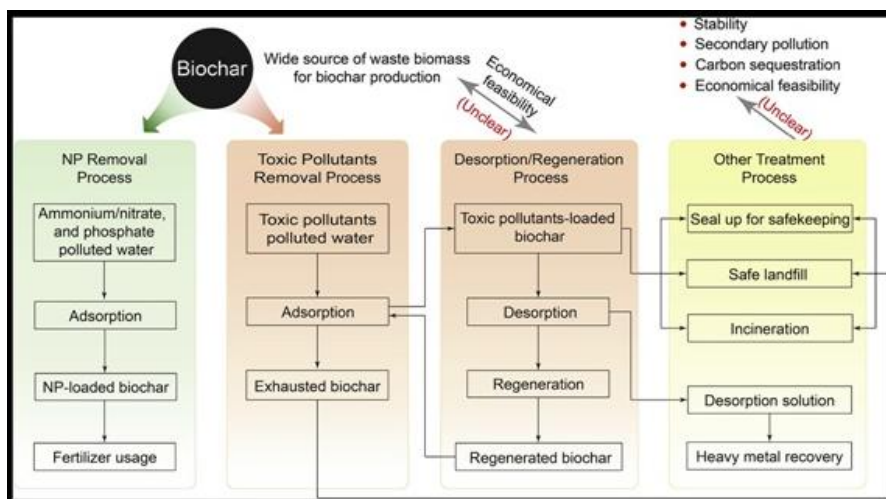


Figure 2: The schematic diagram of the system using biochar pollutants removal from water, desorption/regeneration of biochars, and other ailments processes

Problems, sustainability, and potential application of biochar

It is focused on removal of various contaminants (i.e. heavy metals, organic pollutants, and other inorganic pollutants) from water using biochar. Biochars plays an efficient role on potential toxic elements, heavy metals, metalloids and polycyclic aromatic hydrocarbons (PAHs) inevitably form and associates with biochar. Some researchers have detected the concentrations of extractable toxic elements contained within the biochar and regarding some recommendations regarding to minimizing the risk of potential toxic element. For a significant development of biochar and safety use as a soil amendment, the International Biochar Initiative (IBI) has established standards (Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil) to identify certain qualities and biochar materials characteristics, This further imitatates of biochar application used in water treatment for which biochar guidelines are also needed. Availability of information regarding biochar application in the treatment of contaminated sediment is very less. For its excellent adsorption ability in water pollutants, it can have a tremendous use as in-situ amendments sorbent for contaminated sediment management^[5].

Conclusion

This review has focused the effect of biomass on the removal of aqueous heavy metals by biochar. A literature survey on the reveals of biochars production a wide variety of biomass materials have been used as the feedstocks and pyrolyzed by different processes to reduce water pollution. Adsorption mechanisms analysis reveals that different kinds of interactions including chemical bonding, chemical interaction, (complexation and/or precipitation), physical adsorption, ion-exchange, and electrostatic attraction are predominantly responsible for binding waste water pollutants. About the biochar application pointed on aqueous solution, can be a novel and feasible adsorbent by all researches. This is because of the biochars' excellent adsorption ability, and their economic and environmental

benefits. Due to its high surface area, charged surface, and functional groups, influencing depth, Control density, Biochar is of great potential to adsorb heavy metal and organic contaminants. Addition of Biochar should decrease the Leachability, bioavailability, toxicity, and mobility of organic and inorganic pollutants. This has the potential to be beneficial for immobilization of contaminants with high concentrations. However, the amending of BC also has side effect on the efficacy of toxicides and herbicides, the degradation rate of organics and some sediment, and soil organisms.

Future Perspective

Due to the paucity of thermodynamic sorption studies on biochar, it is unclear whether these values can be applied to all heavy metals or not. Mathematical models can accurately describe the interaction of heavy metals with biochar. Furthermore, if pre-loading of biochar with nutrients can have benefits compared to adding both separately; this would further strengthen the case for biochar integrating into the wastewater management system. However, filtration studies for heavy metal removal by biochars are lacking. Experimental and modeling studies on heavy metals filtration in packed columns are highly recommended for future studies.

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