THE INFLUENCE OF WETLAND MEDIA IN IMPROVING THE PERFORMANCE OF POLLUTANT REMOVAL DURING WATER TREATMENT: A REVIEW

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Abstract. Biochar is used for water treatment as a low-cost adsorbent with high efficiency. It has a large pore volume and is environmentally friendly. Recently, biochar has been a popular topic in the field of environmental management and wastewater treatment. There has been a rising interest in biochar due to its low-cost production, environmental stability and potential effects on several ecosystem functions. A high number of studies have shed light on the potential use of biochar as a sorbent as well as the application of biochar to adsorb pollutants in wastewater and enhance the efficiency of constructed wetlands. The removal of heavy metals from aqueous solutions was examined and biochar was found to efficiently remove more heavy metal ions from these solutions than activated carbon. This study has shed light on the role of biochar in water treatments and provided an updated review to produce biochar from different biomass feedstock around the world.

Keywords: *biochar, biomass feedstock, biochar preparation, water treatment, constructed wetlands, potentially toxic elements*

Introduction

A basic necessity of life is clean and safe drinking water. It is documented that water contamination with potentially toxic elements (PTEs) has been a critical problem since the last few decades, which risks the lives of humans, plants, and animals around the globe. Due to increasing amounts of waste and lack of waste management, water bodies have become polluted. In the 1990’s, a huge percentage of the world’s population was suffering from water scarcity. In 1990, it was reported that more than 2.7 billion people around the world lacked access to improved sanitation services such as garbage collection and wastewater disposal. Raising awareness for common people and waste management authorities brought a mere 7% improvement. In 2015, the number of people who lacked access to sanitation facilities decreased to 2.4 billion (WHO, 2015; Sanjrani et al., 2018). Waste management is a big issue. It is estimated that more than 80% of wastewater in developing countries is released into the environment without treatment. Most problems in regards to wastewater are faced by urban populations. Currently, 54% of the world’s population are living in urban areas and the percentage is expected to increase to 66% by 2050 (WHO, 2015). Thus, providing good quality sanitation and wastewater treatment facilities is required. Mining or chemical plants should be documented to deal with sewage, sludge storage and waste treatment, as an attampt to supply safe drinking water to people in affected areas. Several studies are being conducted for solid waste management plans (Sanjrani et al., 2019; WHO, 2015).

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A report has been issued by the United Nations World Water Assessment Programme (UNWWAP, 2017) which stated that in some developing countries, around 80% of sewage effluent and more than 70% of the industrial wastes are being discharged into surface water without proper treatments. This means water bodies contain several potentially toxic elements (PTEs) and the quantities of these pollutants have risen to over the year. These toxic elements include arsenic (As), chromium (Cr), cadmium (Cd), copper (Cu), nickel (Ni), mercury (Hg), lead (Pb), vanadium (V), selenium (Se), and zinc (Zn) (Sanjrani et al., 2018; Rakotondrabe et al., 2018). Recent studies have recommended that easy and low-cost water treatment techniques should be introduced to the public; especially in the affected areas where health is threatened due to water pollution. Alternative water supply options should be introduced and should consider the social, and economic status of the local population. Several options have been implemented for treatment, but wetlands technology has been found more efficient and low-cost. One of the best and valuable services given by wetlands is that they generally create a system where everything occurs naturally. Constructed wetlands are complex systems with large number of active chemical, physical, and biological processes that mutually influence each other and treat the water properly (Varga and Oirschot, 2017; Sanjrani et al., 2017).

Recently, the use of wetland media "biochar" to increase constructed wetland efficiency for treating wastewater has been demonstrated in several studies. Results from those studies have been highly appreciated by the organizations who work for the improvement of water quality. Biochar was first mainly studied as an amendment of soil but further studies found out it can also acts as a well-adsorbent; later, it was proved to be an easily available option for low-cost wastewater treatment. In addition, after activated carbon, biochars got more attraction for their new techniques as an effective low-cost alternative. Biochar is a generally carbon-rich solid material generated by the pyrolysis of bio-organic things at middle to low temperature approximately (<700_C) under anoxic conditions. The formation methods of biochar are: pyrolysis, hydrothermal carbonization, gasification, and so on. Moreover, some studies concluded that different bio-organic materials, modification methods, and pyrolysis temperatures may show different performances. In addition, many studies also demonstrated that biochar stimulates N transformation, due to its highly porous structure and DOM release (Gupta et al., 2015; Lehmann and Joseph, 2015). The present paper attempts to provide an overview on the role of Biochar in wetlands systems and its effect on removal efficiency. It also provides review about the materials from which biochar is being generated as well as its preparation methods.

Biochar production around the world

The interest in biochar firstly grew in USA, nearly 17 million tons of organic waste was identified in Washington State. This waste mostly came from wood and straw, a situation where pyrolysis is an attractive option to recover energy and produce stable carbon, which can then benefit the soils and climate (Bio, 2018). The Center for Sustaining Agriculture and Natural Resources (CSANR) and the Washington Department of Ecology at Washington State University has produced a series of in-depth reports on biochar production, use, and economics. Later, it was innovated by Australia, China and Japan. Water treatment by biochar and constructed wetlands has been widely studied in temperate countries such as Canada, Belgium (Lesage et al., 2007), the Republic of Czech

(Vymazal, 2014), the United States of America (Kadlec et al., 2010) and the United Kingdom (Shutes, 2001). It has also been studied in tropical countries such as Thailand (Kantawanichkul et al., 2009), Kenya (Mburu et al., 2012), Malaysia (Sim et al., 2008) and in subtropical countries such as Australia (Greenway, 2005). Up-to-now, it is being used all around the world, especially; addition of biochar in constructed wetlands is an innovation and adopted by several countries. Recently, For biochar, different materials have been used in different countries, some of them are shown in *Table 2*.

Biochar preparation methods

Recently, the preparation of biochar requires some methods including the cleaning and drying of material, pyrolysis, hydrothermal-carbonization, gasification, as well as some other methods. The preparation of Biochar is not complicated; the basic process is known as pyrolysis. Pyrolysis releases gas as the material is broken down, a process (heating rate up to 1000 °C/s) of a decomposition reaction under high temperature and anoxic-conditions. Before material transferred into high temperature resistance furnace for pre-oxidation, carbonization and activation treatment, the material (mostly less than <2 cm in size) is washed with HCL plus water solution for a few hours and then is baked in a vacuum oven at about 65-105 °C for 12 h depending on the type of material (Li et al., 2018). After pyrolysis, major changes can be found in the material. Finally, the obtained product is immersed in a 1 M hydrochloric acid solution for 2 h to remove impurities, such as ash, from the product, it is washed with deionized water until at a considerable pH level, and then it is baked in an oven (105 °C) for 1-2 h, until the product is ready. It can be further divided into slow-pyrolysis, rapid-pyrolysis, and flash-pyrolysis which are based on temperature, time, and the heating rate of pyrolysis process. Slow-pyrolysis is considered as a main preparation of biochar (Shaheen et al, 2018; Li et al., 2018; Patra et al., 2017; Kambo and Dutta, 2015).

Another method for the preparation of biochar is hydrothermal-carbonization. From studies (Berge et al., 2015; Tan et al., 2015; Kambo and Dutta, 2015) the hydrothermal-carbonization is a process under heating conditions and high pressure, which uses water as the reaction medium. In addition, the reaction of biomass is undertaken in a system (an underwater stagnant system), which has a relatively low temperature (<350 °C) and pressure of 2–6 MPa for 5 min to 16 h. It was concluded in the study (Breulmann et al., 2017), that pyrolysis is more effective than hydrothermal-carbonization. The capacity of cat-ion exchange for sewage sludge was successfully reduced by hydrothermal-carbonization but stayed on a higher-level than after pyrolysis, because it failed to increase the chars' resin-extractable phosphorus contents. In addition, slow pyrolysis is recommended as the comparison was studied, chars were made from same feedstock material (corn, C4) while using hydrothermal-carbonization and slow pyrolysis. Results showed differed chemical properties and decomposition behavior, even different physical appearance. Although both chars were produced from the same feedstock, results by pyrolysis had a higher potential for carbon sequestration than hydrothermal-carbonization. In addition, this method is limited by the preparation conditions; there is a high preparation cost, and a high need for high pressure and high temperature of the expensive reactor (Berge, 2015; Tan et al., 2015; Kambo and Dutta, 2015; Malghani et al., 2013).

Other methods are mainly used to generate gaseous materials or bio-oil, such as gasification, drying, rapid pyrolysis, and "flash" pyrolysis (Tan et al., 2015). Different techniques to prepare biochar require different temperature and time, it is shown in *Table 1.*

Table 1. *Different techniques to make biochar. (Modified from Tan et al., 2015; Oliveira et al., 2013; Deng et al., 2017)*

Main products	Material size	Mode	Temp °C	Heating rate	Residence time
Oil, gas, char ~1/3 each	1-200 mm	Slow pyrolysis	400-650	Slow 1-20 °C/m	Minutes to days
Bio-oil, 75% Char, 10-20%	<1 mm	Fast pyrolysis	700	Very fast >300 °C/s	Second
Gas, 80% Char, 10-20%	5-20 mm	Gasification	>800	2-100 °C/m	5-30 ins

Characterization of media

Biochar prepared from different biomass, has different physic-chemical properties: the size of particle of the feedstock, the temperature and pyrolysis, the time of pyrolysis, and the conditions of modification. It is recommended to know the characterization of media so one can recognize if it is prepared well or not. Characterizing the biochar is mostly done by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) (Li et al., 2018; Tan et al., 2015). Many factors affect the structure of biochar; in addition, biochar has an abundant surface of functional groups (carbonyl, carboxyl, hydroxyl and methyl). In addition, the high specific surface area, the natural and developed pore structures, and the stable molecular structure, allowbiochar to have good adsorption performance. Hence several studies have concluded that biochar is favorable for waste water treatment (Tan et al., 2015; Li et al., 2018; Berge, 2015; Tan et al., 2015; Kambo and Dutta, 2015; Malghani et al., 2013).

Biochar from different sorbent materials

Different types of sorbent materials were studied and used in the previous studies because media influences numerous processes. Media controls the retention time, rate of water infiltration, provides surface biofilms, provides sorption surfaces so nutrients can absorb heavy metals, filters sediments and particulates, and provides a nutrient source for macrophytes and microbes (bacteria, fungi, protozoan, algae) (Greenway, 2008). Recently, the following sorbent materials are being used: hydrous zirconium oxide (Kumar et al., 2018), clay minerals (Uddin, 2017), brick dust (Allahdin et al., 2017), activated alumina (Millar et al., 2017), nano-materials (Yazdani et al., 2017; Gunti et al., 2018), hematite and feldspar (Yazdani et al., 2017), Zeolite (Visa, 2016), activated carbon (Saleh et al., 2017; Shaheen et al., 2015), and limestone (Iakovleva et al., 2015). Five to ten years ago, coal fly ash (Hizal et al., 2013), Zeolite (Shaheen et al., 2012), and red mud (Gupta and Sharma, 2002) were used in removal of PTEs from waste-water. Though they are effective for water treatment, the most of these sorbents keep some demerits, such as low stability, production of waste products, difficulties in recyclability, high operational cost, use of hazardous chemicals in the synthesis of some sorbents and high operational cost (Gunti et al., 2018; Barakat, 2010). Several studies around the world have different media commonly used in constructed wetlands, which are given in *Table 2*. In addition, studies found that wood-based biochar is more effective with no demerits or less demerits.

Table 2. *Media commonly used in constructed wetlands around the world*

Composition of media	Study area/location	References
• Combination of turf sand, Krasnozem and coir peat • Combination of turf sand, red mud and coir peat • Combination of turf sand, Water treatment residual and coir peat	Australia Logan, Queensland	Lucas and Greenway, 2011a
• Gravel • Wood mulch • Gravel and mulch	Australia Melbourne	Saeed and Sun, 2011
• Pinewood • Rice husk	China Beijing	Liu and Zhang, 2009
• Wood	China Beijing	Sun et al., 2011
• Cinder 25%, rubble 25% and furnace slag 50%	China Guangzhou	Cui et al., 2015
• Gravel (diameter 10-40 mm) and (30-50 mm)	China Huazhong	Peng et al., 2014
• Macrophytearundodonax	China Shandong	Li et al., 2018
• Zeolite • Caremsite • Quartz granules	China Shanghai	Zhong et al., 2015
• Rice husk • Dairy manure	China Shanghai	Cao et al., 2009
• Corn straw	China Shanghai	Xu et al., 2013
• Luffa	China Qingdao	Zhai et al., 2017
• Gravel	China Wuhan	Chang et al., 2012
• Natural zeolite • Volcanic rocks	China Xiamen	Huang et al., 2013
• Gravel and sand	China Cuihua Xi’an	Wang et al., 2016
• Iron rich soil and gravel	Cuba	Perez et al., 2014
• Crushed rock • Sand	Czech Republic Trebon	Vymazal and Kropfelova, 2011
• Gravel	Egypt Giza	Abou-Elela et al., 2013
• Soil	Egypt Manzala Lake	El-Sheikh et al., 2010
• Light weight aggregate (LWA)	Estonia Paistu	Oovel et al., 2007
• Medium from quarry • Fine gravel from river sand	Greece	Akratos and Tsihrintzis, 2007
• Gravel • Coarse sand	Greece Buyukdolluk, Edirne	Cakir et al., 2015

• Soil	Greece Pompia	Tsihrintzis et al., 2007
• Soil	Israel Kiryat	Ran et al., 2004
• Combination of marble and gravel • Combination of sand and gravel • Marble chip • Sand	India Nagpur	Kadaverugu et al., 2016
• Gravel and coarse sand	India Patancheru	Datta et al., 2016
• Gravel (diameter 8-16 mm) and river sand	Indonesia Bandung	Kurniadie, 2011
• Fine grain	Iran Isfahan	Haghshenas-Adarmanabadi et al., 2016
• Iraqi Luffa	Iraq	Saleh et al., 2014
• Alum sludge	Ireland Dublin	Babatunde et al., 2010
• Gravel • Sand and gravel	Italy Florence	Masi and Martinuzzi, 2007
• Gravel	Italy Trento	Foladori et al., 2015
• HumicGleyed Andosol	Japan Mito	Abe et al., 2014
• peanut straw • canola straw	Korea	Tong et al., 2011
• Palm kernel shell	Malaysia Sarawak	Jong and Tang, 2015
• Tezontle gravel	Mexico Ocotlan, Jalisco	Zurita et al., 2009
• Sand • Gravel	Nigeria Akure	Akinbile et al., 2016
• Carbonate-silica rock (opoka)	Poland Chrzanow	Jozwiakowski et al., 2017
• Pig manure	Poland Lublin	Kołodyńska et al., 2012
• Gravel	Singapore Nanyang	Zhang et al., 2012
• Sand • Grain • Fine gravel	Spain Barcelona	Avila et al., 2016
• Gravel • Lapilli	Spain Canary Islands	Melian et al., 2010
• Gravel	Spain Galicia, Boimorto	Jacome et al., 2016
• Granitic gravel	Spain Santiago of Compostela	Vazquez et al., 2013
• Gravel • Sand • Iron oxide	Spain Valencia	Martin et al., 2013a

• Soil	Spain Valencia	Martin et al., 2013b
• Gravel	Srilanka Peradeniya	Weerakoon et al., 2016
• Fine gravel • Medium gravel	Thailand Bangkok	Konnerup et al., 2009
• Soil	Thailand Chiang Mai	Kantawanichkul and Duangjaisak, 2011
• Gravel	Tunisia Joogar	Kouki et al., 2009
• Soil	Turkey Garip	Gunes et al., 2012
• Gravel • Marble stone • Iron slag • Zeolite	Turkey Kocaeli	Ayaz et al., 2012
• Sand	Uganda Kampala	Bateganya et al., 2016
• Rice straw • Corn straw	USA	Chen et al., 2007
• River sand	Vietnam Cao Tho	Trang et al., 2010

Wood-based biochar

Up-to-now, Wood-based biochar has been recommended for the removal of potentially toxic elements in water and wastewater such as such as bioenergy crops (willows, miscanthus, and switchgrass) and forest residues (sawdust, grain crops, and nut shells). Biochar is generally produced from the pyrolysis of different low-cost starting materials. In recent studies (Shaheen et al., 2018; Li et al., 2018; Patra et al., 2017), biochars were originated from different wood feed-stock, i.e. luffa, water-melon, saw dust, pine cone, softwood, hardwood, and bark as they have major chemical and physical properties and their efficiency in removing potentially toxic elements in water. Studies (Shaheen et al., 2018; Li et al., 2018; Patra et al., 2017) demonstrated the biochar and discussed the (i) preparation, characterization and removal efficiency of wood-based biochar; as well as removal mechanisms of potentially toxic elements by wood-based biochar; therefore, it was concluded that wood-based biochar is effective for enhancement of wetlands systems. This particular study (Li et al., 2018) concluded that by-products from forests and agriculture may not be easily available. Furthermore, most of them are seasonal, but the “arundodonax” is a wetland plant which can be easily accessible anytime from many parts of the world. A study from Malaysia (Jong and Tang, 2015) used palm kernel shell and got promising results. Further studies are being conducted to find out the material for biochar which is easily available and effective.

Use of biochar in constructed wetlands for waste water treatment

Use of biochar and wetlands technology has received great interest because they are helpful to treat wastewater at low-cost. The untreated wastewater released in the environment increases the concentrations of suspended solids, nitrogen (N), phosphorus

(P), and organic matter (Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)) in water bodies. These chemicals are easily treated by the combination of wetlands and its media (biochar).

Up to now, only a few studies have focused on integrating biochar into constructed wetlands when treating wastewaters. Combining both of these technologies can play a vital role in pollutant removal performance; when compared in the studies as shown in *Figure 1* (Li et al., 2018; Gupta et al., 2015), it was concluded that the wetlands with biochar were more efficient as compared to the wetland with gravels alone (Li et al., 2018; Gupta et al., 2015). Constructed wetlands (CWs) are an effective option to be applied around the world due to their lower cost. Plants and media are the main factors; they determine the effectiveness of the CWs in removing pollutants. Biochar is a potential media amendment for pollutant removal, which can be used in subsurface CWs (De Rozari, 2017).

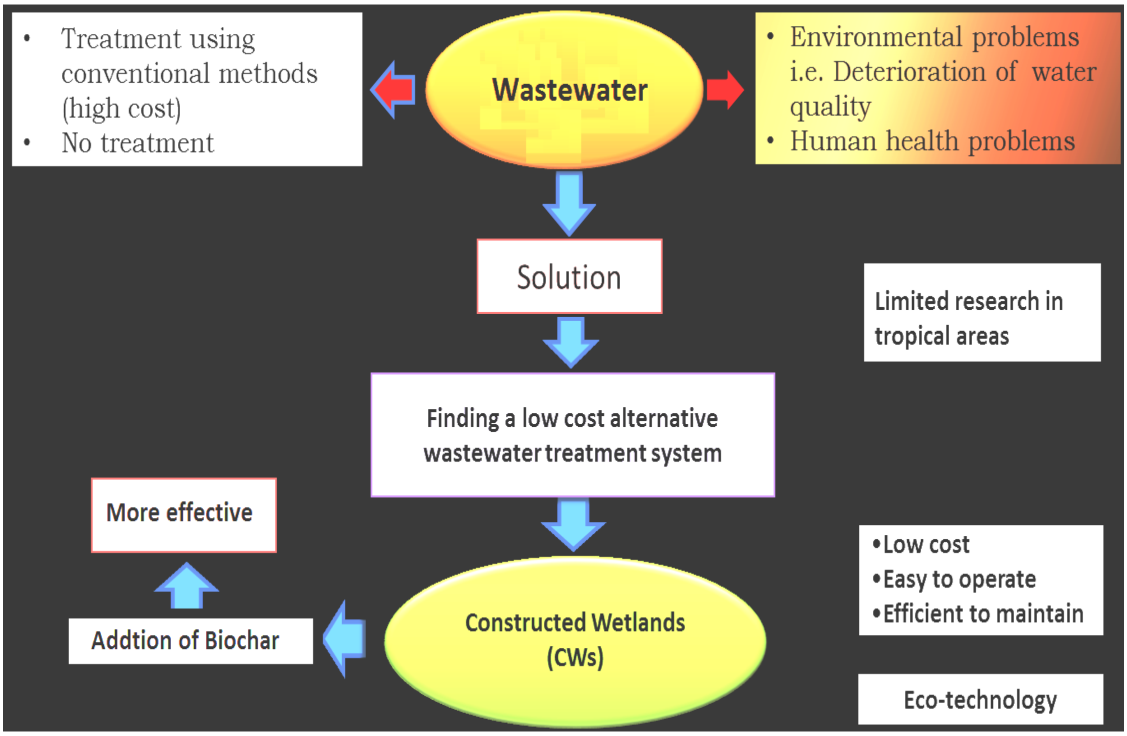

Figure 1. *Combination of constructed wetlands and biochar as an alternative and low-cost technology for wastewater treatment. (Modified from De Rozari, 2017)*

Effect of biochar on contaminants produced from different feedstocks

The removal of the pollutants by biochar depends on various factors such as adsorption, precipitation, filtration, sedimentation, microbial degradation, and plant uptake. The application of biochar produced from different feedstocks and techniques in aqueous solutions has been studied and it has been concluded that biochar isa more effective and better option. For Chromium, the biomass feedstock from Coconut coir goes under slow pyrolysis; the pyrolytic temperature ranges from 250 to 600 °C and has been effective (Shen et al., 2012). For Copper and zinc, the biomass feedstock from Corn straw under slow pyrolysis the pyrolytic temperature 600 °C has been effective (Chen and Chen, 2009; Chen et al., 2007). Comparison of rice husk-and dairy manure-derived biochars for simultaneously removing heavy metals (Pb, Cu, Zn, and Cd) from aqueous solutions was studied; biochar was formed from from rice husk and dairy manure under slow pyrolysis the pyrolytic temperature 350 °C (Xu et al., 2013). The biomass feedstock from Sugarcane bagasse was studied for removal of Sulfamethoxazole. Biochar was formed under slow pyrolysis; the pyrolytic temperature (°C) ranges 450 (Subhashini et al., 2013).

Recently, Arundo donax, a wetland plant was used to prepare biochar; biochar was prepared for enhancing the performance in SFCWs nitrogen removal. Studies demonstrated that biochar significantly promoted plant growth in SFCWs (Li et al., 2018). Gupta et al.'s study (2015) was conducted for the removal of phosphorus, nitrogen and organic matter. An oak tree (Quercus sp) was used as a porous media to enhance constructed wetland performances in wastewater reclamation. This study reveals that the wetlands with biochar were more efficient as compared to the wetland with gravels alone with average removal rate of 58.3% TN, 79.5% TP, 91.3% COD, 58.3% NH_3, 92% NO_3-N, and 67.7% PO_4 (Gupta et al., 2015). In SFCWs with 20% (v/v) biochar addition enhanced the average removal efficiencies of TN and NO_3^--N as 85.62% and 81.16%. In the study (Li et al., 2018), it was concluded that the introduction of biochar has played an effective role to strengthen N removal efficiency in SFCWs. As comparisons were made, higher TN removal efficiency was offered by biochar added in SFCWs (Li et al., 2018).

In addition, a study was conducted to examine the treatment of wastewater; an evaluation of the efficiency of twotypes of pyrolysis chars (rice husk biochar and refuse derived fuel char) was done. Results of the study show that the efficiency of biochar in treating wastewater is much better compared to char. Hence, biochar could be the best option as a sorbent for wastewater remediation; moreover, biochar has a strong adsorption effect for organic pollutants such as antibiotics, phenols, herbicides, etc. (Rasheed et al., 2017; Deng et al., 2017). Biochar also has an adsorption effect for pollutants in liquid phase. Tan's (2015) study summarized the applications of biochar for water pollutants adsorption, it was concluded that 39% adsorption of organic-pollutants, 46% adsorption treatment for heavy metal, 13% for the adsorption of phosphorus and nitrogen (Tan et al., 2015). Studies (Zheng et al., 2013) were conducted for biochar preparation from donax to adsorb sulfamethoxazole (hazardous material), an antibiotic which is used for curing acute and chronic urinary tract diseases caused by proteus escherichia coli. Furthermore, the raw material has some inorganic components, which weaken the adsorption capacity of sulfamethoxazole in the high-temperature pyrolysis biochar and enhanced the adsorption capacity of sulfamethoxazolein low-temperature pyrolysis bochar. It varies from material to material; De Rozari et al.'s (2016) was conducted for the preparation of the sand media amended with biochar to develop its effectiveness. Two plant species (Cymbopogoncitratus and Melaleuca quinquenervia) were planted to remove phosphorus from sewage effluent in CWs. Removal efficiencies of TP in the mesocosms loaded with SCW, and septage ranged from 42 to 91%; 30 to 83% were recorded. The results revealed that the sand media performed better than the biochar-amended media (De Rozari et al., 2016). Overall, the application of biochar to enhance water treatment has concluded that biochar produced from different feedstocks and techniques is a more effective and better option.

Conclusion and recommendation

This review has focused on the effect of biochar in water treatment. A literature survey is conducted on the biochars production from the different feedstocks and pyrolyzed by different processes to reduce water pollution. Several researches confirmed that biochar is a good adsorbent with high efficiency and it has enhanced the efficiency of constructed wetlands for water treatment.

Biochar is efficient, but after the adsorption of heavy metal or organic pollutants, it may lead to secondary pollution if it is not properly treated. There is little research done on biochar recycling or regeneration after adsorption of pollutants. However, more research is needed to understand feedstock material for biochar, preparation parameters, biochar pore structures and the relationship between biochar adsorption performances. Studies for preparation biochar from different materials are recommended as future avenues for research. Experimental and modeling studies need to explore further in depth, especially on heavy metals, nitrogen and phosphorus adsorption, and whether biochar can be used as bio-fertilizers or soil conditioners after adsorption of nitrogen and phosphorus.

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