Ranbir Chander Sobti
Naveen Kumar Arora · Richa Kothari
Editors

Environmental Biotechnology: For Sustainable Future

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About the Editors

Prof. (Dr.) Ranbir Chander Sobti is former Vice Chancellor of Babasaheb Bhimrao Ambedkar University, Lucknow (UP), India, and Panjab University, Chandigarh, India. He has been proactively involved in cancer biology, with a focus on finding out novel tumour markers for cancer detection, and is currently engaged in the development of whole organ by tissue/organ culture through custom designed decellularization protocol. His intense scientific contributions have resulted in around 300 high-impact research publications, more than 40 books and 23 sponsored research projects. He is fellow of leading national and international academies of science and is associated with many other academic associations and institutions in the domain of higher education and research in India and abroad and was General President of the Indian Science Congress Association in 2014. He has been bestowed with a large number of prestigious awards and medals including the INSA Young Scientist Medal (1978), UGC Career Research Award, Punjab Rattan Award and JC Bose Oration Award. The Government of India bestowed upon him the honour of “Padma Shri” in 2009 by way of rightfully acknowledging his great contributions to higher education in India. On 2 July 2016, he was also honoured with “Bharat Gaurav” Lifetime Achievement Award at the House of Commons, British Parliament, London, UK.

Prof. (Dr.) Naveen Kumar Arora, PhD in Microbiology Professor in the Department of Environmental Science, Babasaheb Bhimrao Ambedkar University (a Central University), Lucknow, Uttar Pradesh, India, is a renowned researcher in the field of Environmental Microbiology and Biotechnology. His specific area of research is rhizosphere biology and plant growth-promoting rhizobacteria (PGPR). He has more than 60 research papers published in premium international journals and several articles published in magazines and dailies. He is editor of 11 books, published by Springer, and member of several national and international societies, in editorial board of 4 journals, and reviewer of several international journals. He is also the Editor-in-Chief of the journal *Environmental Sustainability* published by Springer Nature. He has delivered lectures in conferences and seminars around the globe. He has been advisor to 118 postgraduate and 9 doctoral students. He has also received awards for excellence in research by the Honourable Governor of Uttar Pradesh and Asian PGPR Society. Although an academician and researcher by profession, he has a huge obsession for the wildlife and its conservation and has authored a book, *Splendid Wilds*. He is President of Society for Conservation of Wildlife and has a dedicated website www.naveenarora.co.in for the cause of wildlife and environment conservation. He is also General Secretary of the Society for Environmental Sustainability.

Dr. Richa Kothari, M.Phil. and Ph.D. in Energy and Environment, is working as an Associate Professor at the Department of Environmental Sciences, Central University of Jammu, Samba, Jammu (J&K), India. She is awarded by one of the prestigious Indo-US Science and Technology Forum (IUSSTF) for Water Advanced Research and Innovation Fellowship Program in the year 2016 at the Robert B. Daugherty Water for Food Institute, University of Nebraska-Lincoln, Lincoln, NE, USA. She has guided more than 30 MSc and MTech students and 2 doctoral students. She has more than 60 articles in reputed peer-reviewed international and national journals with high-impact factors and chapters in edited books. She is also a reviewer of well-reputed Scopus journals. She is part of editorial teams of many national and international journals. Her research interests are bioenergy production approaches and low-cost wastewater treatment technologies.

Part I
Biodegradation and Bioremediation

Chapter 1
Biochar for Effective Cleaning of Contaminated Dumpsite Soil: A Sustainable and Cost-Effective Remediation Technique for Developing Nations

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Abstract Several studies have reported that open municipal dumpsites in developing countries are acting as a major source for a wide variety of pollutants. In developing nations, many dumpsites are located in the urban centers or even within the residential boundaries. Contaminants released during incomplete combustion of municipal solid waste have profound adverse impact on human health and the environment. Hence there is an urgent need to identify a low-cost technique to decontaminate such heavily polluted sites. In this chapter, we have reviewed several papers and discussed how different types of engineered biochars can be effectively used to adsorb contaminants from dumpsite soil. Biochars are basically carbon-rich solids treated by high-temperature pyrolysis. Biochars are obtained by heating biomass in presence of less oxygen or in anaerobic conditon. Properly pyrolysed mixtures of organic and cellulosic wastes are capable of adsorbing a wide variety of organic contaminants from wastewater, sludge and soil prior to the release or disposal in engineered landfills. Biochar produced from waste organic material such as coconut shells, sugarcane bagasse and straw has been reported with high adsorption capacity. Because locally produced waste organic material can be utilized for production of these low-cost adsorbents, they are especially attractive for remediation and treatment systems in developing countries. Pyrolytic temperature is believed to be the most important factor affecting the sorption capacity of biochar, followed by grinding to increase the surface area. Holding and adsorption capacity of the biochar for treating contaminants in soil could be a limiting factor of these materials. Some studies have shown that less than 5–7% (m/m) mixing of biochar and soil resulted in higher water retention capacity leading to increased potential for biodegradation. We therefore suggest that improved low-cost processing methods should be investigated so that biochar can be exploited as an adsorptive medium for remediating and treating contaminated soils in these regions.

Keywords Open municipal dumpsites · Biochar · Pyrolytic temperature · Cost-effective · Adsorption capacity · Incomplete combustion · Organic content

Introduction

Urbanization and economic development have increased municipal solid waste (MSW) generation across the globe. In the twenty-first century, the treatment of MSW has become a serious environmental issue, and MSW management continues to be an important environmental challenge. As shown in Fig. 1.1, East Asia and Pacific regions lead in the generation of waste followed by Latin America and Caribbean region, Eastern and Central Asian countries, South Asia, Middle East and

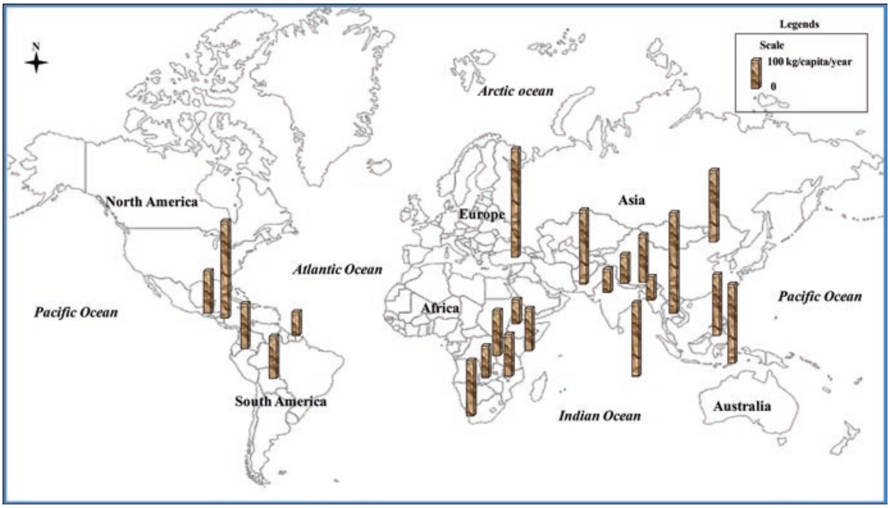

Fig. 1.1 Global map showing the quantity of annual solid waste generation (in kg/capita/year)

North African nations and finally the sub-Saharan African nations. It is projected that the global MSW generation levels will increase from 1.3 billion tons per year to 2.2 billion tons per year (World Bank 2012). The global waste generation rate is estimated to increase by about one million tons/day due to the current trend in economic growth (Inanc et al. 2004). The current situation is very serious in developing economies, as wastes have been poorly managed for many years. Even if waste is properly collected, often it does not reach legal disposal sites and is instead discarded in scattered, unregulated dumps. In addition to the existing large number of unregulated dumpsites, industrial, municipal and hazardous wastes are often mixed and disposed together, creating dangerous, toxic conditions because of the mixing of many different types of wastes. Improper location of disposal sites and the scarcity of modern engineering designs (liners and collection systems for leachate) threaten groundwater supplies and are a serious issue for those regions depending almost solely on groundwater sources. Simple waste management practices, such as covering wastes, weighing garbage and fences around dumps, are often not practiced in the developing countries.

A crucial, but often missing aspect, for MSW handling in developing countries is the establishment of sustainable approaches for treating these wastes in place. Waste tariffs only cover 30–40% of operating costs, leaving no funds available for capital investment. The shortfall is covered with money from the central or local budgets. Unless measures are taken, problems with waste disposal will only get worse. This problem is particularly serious in cities with limited capacity for dumpsite expansion. According to the United Nations (UN) Centre for Human Settlements (UNCHS), management of solid waste in developing and under developed nations is one of the most poorly treated services. Waste management systems are non-technical, obsolescent and inefficient resulting in indiscriminate open dumping of solid wastes (UNCHS; Habitat Refuse Collection Vehicles for Developing Countries; Nairobi 1991). Increasing imports of electronic waste (e-waste) for recycling by many Asian and African countries are contributing to improper handling of waste and haphazard dumping of refuse into low-lying areas of open land. To reduce the quantity of wastes in dumpsites, open burning is widely practised in landfills and dump yards particularly in the developing nations leading to the release of toxic pollutants such as dioxins, furans and heavy metals to the environment, thereby affecting human health (Chakraborty et al. 2018; Frazzoli et al. 2010; Robinson 2009; Thanh and Matsui 2011; Shih et al. 2016). For example, high concentrations of dioxin-like polychlorinated biphenyls (dl-PCBs) have been reported in human milk from mothers residing in and around the dumpsite of Kolkata due to the impact of fish diet (Someya et al. 2010).

Various technologies may be employed to remediate soil contaminated with mobile pollutants, including vitrification, mechanical separation, pyrometallurgic separation, phytoremediation, chemical treatment, electrokinetics, biochemical processes, soil flushing and soil washing (Mulligan et al. 2001). However, all these techniques have several drawbacks and point towards finding alternative techniques with lesser demerits for dumpsite soil remediation. Emission of toxic gases during vitrification process, pretreatment requirements in pyrometallurgic separation, release of toxic byproducts in biochemical processes and incapability of uptaking heavy contamination in phytoremediation are few drawbacks of the above-mentioned techniques (Schnoor et al. 1995; Mulligan et al. 2001). Various researchers have pointed out that remediation of pollutants by adsorption on biochar derived from biomasses could be an economical approach towards management of contaminated soils (Beesley et al. 2011; Zhang et al. 2013). Biochar has also proven to play an important role in sequestration of atmospheric carbon dioxide along with rehabilitating degraded land (Barrow 2012). Being highly recalcitrant in soil, the residence time for wood biochar is reported to be 10–1000 times more than the residence times of most soil organic matter (SOM), suggesting that biochar addition could provide a possible sink for carbon (Duku et al. 2011).

Biochar produced from dairy wastes was found to adsorb 100% and 77% of lead (Pb) and atrazine, respectively, from aqueous solutions (Cao et al. 2009). Freely dissolved concentrations of polycyclic aromatic hydrocarbons (PAHs) in sewage sludge reduced up to 57% by addition of different amount of biochar (Oleszczuk et al. 2012). The addition of woodchip biochar also reduced the off-site transport of antibiotics in soils amended by animal wastes (Jeong et al. 2012). Biochar addition has a long history in improving the quality and fertility of soil, but recent studies have supported the use of this material in reducing the bioavailability of organic and inorganic pollutants. Heavy metals were found to get stabilized in soil due to the increase in pH caused due to the addition of biochar (Zhang et al. 2013). Thus with the help of biochar, a sustainable approach for disposal of various organic refuse such as agricultural wastes, manure, industrial wastes, etc. could be attained which will not only lead to a reduction in greenhouse gas production but also will result in reduction of the prevalence of groundwater and surface water contamination (Barrow 2012). The aim of this chapter is to present an overview of (1) types of wastes that may contribute toxicants in open dumpsites particularly in developing nations, (2) effectiveness of biochar as an adsorbent for these toxicants, (3) remediation approaches for contaminated soil using biochar, (4) retention capacity of biochar and (5) future prospects for using biochar in remediation and managing contaminated dumpsite soil in developing countries.

Sources of Organic and Inorganic Wastes in Dumpsite Soil

A cocktail of wastes from multifarious sources end up in the dump yards of the developing nations primarily due to the absence of segregation of waste. In reports by the World Bank, the global waste composition consists of organics (46%), paper (17%), plastic (10%), glass (5%), metals (4%) and others (18%) (Urban Development Series Knowledge; World Bank 2012). Other categories include textile, leather, e-waste, appliances and inert materials. Waste composition can vary considerably depending on the level of economic development, geography, cultural norms and energy sources in each region. Accumulation of these waste results in the release of a wide range of organic and inorganic pollutants due to various activities practised in dumpsites. Contaminated soil in open dumpsites act as a secondary source of persistent organic pollutants (POPs) by re-emission of organic pollutants, like organochlorine pesticides (OCPs) (Chakraborty et al. 2015) or polychlorinated biphenyls (PCBs) (Chakraborty et al. 2013, 2016). The binding capacity of heavy metals and most of the organic pollutants in the soil depends on the pH, total organic carbon (TOC) and quantity of organic matter present in soil (Korthals et al. 1996; Tao et al. 2005; Jiang et al. 2012a). The phenomenon of long-range atmospheric transport (LRAT) of POPs released from a point source results in their atmospheric transportation and re-deposition leading to detection of POPs even in remote arctic areas (Yang et al. 2005).

Sources of Organic Contaminants in Dumpsite Soil

Organic pollutants entering MSW dumpsites can be from industrial, domestic or agricultural sources. Waste from textile industries consists of dye materials and other undesirable chemicals. Major colour effluents come from dyeing and printing process (Tan et al. 2000). Even low concentrations of such dyes in wastewater treatment plant (WWTP) effluents are undesirable due to resistance to degradation and difficulty in decolourization (Willmott et al. 1998; Nigam et al. 2000). Pharmaceutical and personal care products (PPCPs) are a class of emerging pollutants that has recently gained attention due to their ubiquitous presence and biological activities, including antibiotic resistance and effect to the endocrine system. This class of contaminants mainly enters waste streams from biomedical, domestic and industrial rejects from pharmaceutical and cosmetic industry (Jiang et al. 2012b). Bisphenol

A (BPA) and phthalic acid esters (PAEs) are compounds that come under the category of endocrine disruptors (EDCs) and found in variety of general use items like plastic bottles, audio and video technologies, pipe materials, sports equipment, etc. Sewage sludge from sewage treatment plants are also disposed by landfilling or spreading in dumpsites usually in developing countries. Sewage sludge is also a potential source for the release of PPCPs in the dumpsite. A major part of the effluent concentration of most PPCPs in WWTPs is sorbed to sludge and suspended solids. Changes in pH or redox conditions in dumpsites may result in release of contaminants after disposal.

Among developing countries, China is the largest exporter and importer of e-waste and receives about 70% of the total e-waste exported from developed nations. Other countries like India, Pakistan, Vietnam, the Philippines and Malaysia also import a considerable amount of hazardous e-wastes from developed nations (Robinson 2009; Frazzoli et al. 2010). The incomplete combustion of dumpsite waste releases PAHs in soil and air. Open burning of municipal waste has been found to be an important source for dioxin-like compounds in Asian countries (Minh et al. 2003) and PCBs in Indian cities (Chakraborty et al. 2013; Chakraborty et al. 2016). Discarded waste from the informal e-waste recycling workshops, the residues and leftover components are usually dumped in landfills and open dumpsites (Chakraborty et al. 2018). In Bangladesh, for example, around 20–35% of the e-waste were laid in landfills or simply dumped in rivers, open dumps, ponds, drains etc. (Islam et al. 2016).

Sources of Inorganic Contaminants in Dumpsite Soil

Heavy metals from various industries such as plating, plastics, glass, rubber, leather, etc are inorganic waste (Thitame et al. 2010). Environmental problems such as soil pollution, water pollution and groundwater contamination can occur by the release of inorganic pollutants due to inefficient disposal of these inorganic wastes. The methods employed by developing countries such as open burning of electronic equipment are carried out in dumpsites thus making such sites acts as a major source for release of heavy metals to the ambient environment (Olafisoye et al. 2013). Livestock and municipal sludge are also sources of inorganic contaminants. Significant levels of Cd, Cu, Pb, Cr, Ni and Zn are reported in livestock manures such as poultry, pig and cattle slurries (Luo et al. 2009). Buzier et al. (2006) observed that the global yield of WWTPs for metals like Cr, Cd and Pb to be often greater than 75% as sludge is particularly rich in metals. Sludge removed from many of these WWTPs are spread in local dumpsites for final disposal, resulting in the direct release of heavy metals into the environment. Waste from inorganic fertilizers and fungicides are another source of heavy metals that can reach the dumpsites. Except in some of the poorest developing countries of the world where less fertilizers are used, all other countries apply macronutrient fertilizers on agricultural soil. Heavy metals like As, Cd, U, Th, Hg, Ba and Zn are present in phosphatic fertilizers, while nitrogen fertilizers, lime fertilizers and manures are also known to contain metals like Cr, Hg, Co, Cu and As (Kabata-Pendias and Pendias 2001; Eckel et al. 2008). In fields and agroecosystems, various inorganic heavy metals and organometallic compounds are being used as fungicides. Pb and Cu arsenates, Bordeaux mix, Cu oxychloride and phenyl mercuric chloride are some among the fungicides that have been reported from dumpsites. Clearly, soil in dumpsites can be contaminated by heavy metals leaching from a variety of wastes.

Biochar as an Adsorbing Material

What Is Biochar?

Organic material when decomposed thermally in controlled supply of oxygen produces carbon dioxide, some combustible gases (mainly H_2, CO, CH_4) and a solid, black coloured substance, which is rich in carbon referred to as “char”. Being slightly different from char, biochar so far lacks a proper definition in the scientific community. According to the international biochar initiative, biochar can be defined as “a solid material produced from biomass (any substance having good organic content) when heated at pyrolytic temperatures”. Biochar has been available for centuries for use as horticulture and soil amendments but only recently came to light for contaminant remediation. Biochar is composed of three types of carbon (C): recalcitrant C, labile or leachable C and ash. Recalcitrant C is that organic carbon that is tolerant to degradation dominated by charcoal and is unavailable for microbes, whereas labile C are those fractions that are readily leached and mineralizable. Their oxidization drives the flux of CO_2 between soil and atmosphere. The third component, ash, contains macro- and micronutrients for biological uptake. The presence of fused aromatic C structures is the unique natural design that distinguishes biochar from any other organic matter. The occurrence of these structures contributes to the stable nature of biochar (Lehmann et al. 2011). Decarboxylation and demethoxylation along with dehydroxylation are major mechanisms towards the formation of more recalcitrant C fraction during pyrolysis process (Jung et al. 2016).

Different Methods for Production of Biochar

The low oxic or anoxic conditions during pyrolysis result in the thermal decomposition of biomass which eventually lead to the formation of biochar (Kloss et al. 2012). Biochar pyrolysis is a carbon negative activity as more carbon dioxide is sequestered in soil than what is released in the atmosphere (Barrow 2012). There are two types of pyrolysis, namely, conventional/slow pyrolysis and fast pyrolysis. In slow pyrolysis, the biomass is heated slowly to about 500 °C in the absence of air; this would not allow the vapours to escape rapidly. The risk of contamination of the biochar with the production of dioxins and harmful PAHs is reduced to a great extent using slow pyrolysis (Barrow 2012). Fast pyrolysis uses dry feedstock and provides rapid heat transfer which results in rapid escape of vapours. A higher char aromaticity is obtained in biochars prepared by slow pyrolysis (Mohan et al. 2014). There are a wide variety of carbon sources and methods to produce biochar. Some of the methods employed to produce biochar include slow pyrolysis reactors, fluidized bedfast pyrolysis reactors, screw pyrolyzers, hydrothermal carbonization, etc. (Lehmann et al. 2003; Sun et al. 2014). Slow pyrolysis reactors typically produce 15–25% of biochar depending on the feedstock and operating conditions. The biochar produced from fluidized bedfast pyrolysis reactors has distinct properties from those produced using slow pyrolysis due to the relatively high flow rate of gas and low residence time of biochar in the reactor bed, but the process is usually difficult to handle, and there is an interference of sand particles into the biochar during production (Lehmann and Joseph 2015). Screw pyrolyzers are used in biochar production at small scales. The flash carbonizer that uses ignition of a flash fire at elevated pressure in a packed bed of biomass results in significant improvement in yields (Lehmann et al. 2003; Lehmann and Joseph 2015). Biochar produced by the method of hydrothermal carbonization showed relatively high production rate compared to slow pyrolysis inside a furnace in a nitrogen rich environment (Sun et al. 2014).

Properties of feedstock and the pyrolysis conditions have high influence on the physical and chemical properties of biochar (Downie et al. 2009). Feedstocks differ from each other in their elemental compositions, which is attributed to the presence of soil and dust particles, lignin, cellulose and hemicellulose and moisture content. This elemental composition eventually determines the properties of biochar formed (Ubbelohde and Lewis 1960; Boehm 1994; Yip et al. 2007; Alexis et al. 2007). Pyrolysis causes volatilization which results in mass loss, volume reduction and shrinking of the biomass without altering its original structure. Also, pyrolysis alters the C/N, O/C and H/C ratios, porosity, surface area, cation exchange capacity, crystallinity and functional groups in the biomass (Kloss et al. 2012). Increasing the pyrolytic temperature is linked with the increase in specific surface area which in turn leads to an increase in adsorption (Zhang et al. 2013). Also the biochars produced at higher temperatures contain mainly micropores, while the biochars produced at lower temperature are not microporous which indicates that adsorption capacity could be more for biochars prepared at higher temperatures (Zhang et al. 2013). Table 1.1 gives the specific surface area attained by biochar produced from different feedstock at different temperatures. It has been observed that generally, as the pyrolytic temperature increases, the specific area of biochar increases for the same biochar feedstock considered. Thus, as the pyrolytic temperature increases, the specific surface area of biochar increases and ultimately increases the adsorption capacity of biochar. Novak et al. (2009) worked on biochar produced from peanut hulls, pecan shells, poultry litter and switch grass at different pyrolytic temperatures and observed that the biochar produced at higher temperatures attained higher specific surface areas. Chen et al. (2008) studied the characteristics of pine needle biochar by increasing the temperatures from 100 °C to 700 °C and found that the surface area increased from 0.65 m^2/g to 490.8 m^2/g. Thus, it can be concluded that the temperature range of 500–700 °C can increase the adsorption capacity of biochar due to increase in pore volume attained (Table 1.1). According to the data provided in Table 1.2, Ma et al. (2007) observed that application of bamboo-derived biochar on soil helped in the removal of extractable Cd by 79.6% within 12 days of application, while hardwood-derived biochar produced at 450 °C reduced Pb in soil pore water by tenfolds and Zn concentrations by 300 fold in column leaching tests (Beesley et al. 2011). Beesley et al. (2011) reported that hardwood biochar enhances the soil mobility of As and Cu, while wood biochar reduced the Zn and Cd leaching loss by greater than 90%. Cotton stalk- and hardwood-derived biochars reduced the bioavailability of Cd and As, respectively (Zhou et al. 2008; Hartley et al. 2009). Similarly, biochar derived from eucalyptus, orchard prune residue, chicken manure, green waste, rice straw, quail litter, oakwood, etc. reduced the bioavailability of various metals like Cd, Cu, Pb and Cr (Table 1.2). Among these source materials, hardwood biochar was more commonly used and has been found to be more effective especially at higher pyrolytic temperatures (500–700 °C) due to increased surface area for adsorption. Biochar produced at these temperatures also showed maximum cation exchange capacity (Jung et al. 2016). Yu et al. (2009) and Spokas and Reicosky (2009) concluded that high pyrolytic temperature and higher application rates of biochar increases the sorption of organic compounds like carbofurans, acetochlor, diuron, chlorpyrifos and atrazine. Dairy manure, pinewood, green waste, pine needle, eucalyptus, wheat straw and swine manure were used in treating compounds like atrazine, terbuthylazine, phenanthrene, and carbaryl. Also, the bioavailability of organic compounds like pentachlorophenol, PAHs, chlorobenzene, chlorpyrifos, fipronil and diuron were reduced by applying biochar derived from eucalyptus, hardwood, cotton straw, wheat straw and bamboo produced at high temperatures. It can be concluded that biochar produced at 600 °C can be efficiently used in remediating many organic pollutants and this can be attributed to the high surface area attained during its production (Table 1.2).

Developing nations are facing a serious problem with the huge amount of waste generated and improper disposal techniques. Biochar has proven to have equivalent or even greater sorption efficiency for both organic and inorganic pollutants from waste resources as shown in Table 1.2. In developing nations, biomass resources are available, such as forestry residues, wood waste, MSW, industrial wastewater and manure which contribute to country's primary energy supply. Biomass waste generally has an elemental composition of $CH_{1.4}O_{0.6}$ and mainly composed of cellulose, hemicelluloses, lignin and small amount of extractives (Duku et al. 2011). Biochar production from MSW is a safe and beneficial disposal option than the conventional methods such as incineration, landfilling, aerobic/anaerobic digestion, open air burning and composting (Serio et al. 2000). Open burning that is widely practised in developing nations lead to the emission of dangerous contaminants such as POPs, thereby degrading the environment. Biochar typically has more hydrogen and oxygen in its structure making it less carbonized than activated carbon. Biochar could potentially replace coal, coconut shell and wood-based activated carbons as a low-cost sorbent for contaminants and pathogens (Mohan et al. 2014). Theoretically

Table 1.1 Influence of pyrolytic temperature on the specific surface area of biochar produced from different feedstock material

Biochar Feedstock	Temperature (°C)	Surface Area (m^2/g)	References
Cow manure	500	21.9	Zhao et al. (2013)
Shrimp hull	500	13.3	
Bone dregs	500	113	
Wastewater sludge	500	71.6	
Waste paper	500	133	
Saw dust	500	203	
Grass	500	3.33	
Peanut shell	500	43.5	
Chlorella	500	2.78	
Water weeds	500	3.78	
Pig manure	200	3.59	
	350	4.26	
	500	47.4	
	650	42.4	
Wheat straw	200	2.53	
	350	3.48	
	500	33.2	
	650	182	
Pine needle	100	0.65	Chen et al. (2008)
	200	6.22	
	250	9.52	
	300	19.92	
	400	112.4	
	500	236.4	
	600	206.7	
	700	490.8	
Peanut hull	400	0.52	Novak et al. (2009a)
	500	1.33	
Pean shell	350	1.01	
	700	222	
Poultry litter	350	1.1	
	700	9	
Switchgrass	250	0.4	
	500	62.2	
Soya bean stover	300	5.61	Ahmad et al. (2012)
	700	420.3	
Peanut shell	300	3.14	
	700	448.2	

(continued)

Table 1.1 (continued)

Biochar Feedstock	Temperature (°C)	Surface Area (m^2/g)	References
Cotton seed hulls	350	4.7 ± 8	Tang et al. (2013)
	500	0	
	650	34 ± 3	
	800	322 ± 1	
Oak wood	350	450	
	600	642	
Corn Stover	350	293	
	600	527	
Broiler litter manure	350	59.5 ± 19.7	
	700	94.2 ± 5.1	
Soya bean stalk	300	144.14	
	400	138.76	
	500	152.98	
	600	179.03	
	700	250.23	
Broiler litter	350	60	Uchimiya et al. (2010)
	700	94	
Feed lot	350	1.3	Cantrell et al. (2012)
	700	145.2	
Fescue straw	100	1.8	
	200	3.3	
	300	4.5	
	400	8.7	
	500	50	
	600	75	
	700	139	
Oak bark	450	1.9	Mohan et al. (2011)
Oakwood	400–450	2.7	
Orange peel	150	22.8	Chen and Chen (2009)
	200	7.8	
	250	33.3	
	300	32.3	
	350	51	
	400	34	
	500	42.4	
	600	7.8	
	700	201	

the primary cost for biochar production is the cost incurred in feedstock collection, processing and pyrolysis operations in which the cost for transportation of the feedstock and the produced biochar is negligible in the total cost (Inyang and Dickenson 2015).The estimated break-even price for biochar is US $246/t, which is approximately one sixth of commercially available activated carbon (US $1500/t) (McCarl

Table 1.2 Effect of biochar on organic and inorganic pollutants in soil

Feedstock	Production temperature	Contaminant	Effect	References
Effect of biochar application on the mobility of heavy metals in soils				
Bamboo	Not available	Cd	Combined effect of electrokinetics, removal of extractable Cd by 79.6% within 12 days	Ma et al. (2007)
Hardwood	450 °C	As, Cd, Cu, Zn	Reduction in Cd in soil pore water by tenfold; Zn concentrations reduced 300- and 45-fold, respectively, in column leaching tests	Beesley and Dickinson (2011) and Beesley and Marmiroli (2011)
Hardwood	450 °C	As, Cd, Cu, Pb, Zn	Biochar surface mulching enhanced As and Cu mobility in the soil profile; little effect on Cd and Pb	Beesley and Dickinson (2011)
Wood	200 °C and 400 °C	Cd, Zn	Reduction in Zn and Cd leaching loss by >90%	Debela et al. (2012)
Effect of biochar application on the bioavailability of heavy metals in soils				
Cotton stalks	450 °C	Cd	Reduction of the bioavailability of Cd in soil by adsorption or co-precipitation	Zhou et al. (2008)
Hardwood-derived biochar	400 °C	As	Significant reduction of As in the foliage of *Miscanthus*	Hartley et al. (2009)
Eucalyptus	550 °C	As, Cd, Cu, Pb, Zn	Decrease in As, Cd, Cu and Pb in maize shoots	Namgay et al. (2010)
Orchard prune residue	500 °C	Cd, Cr, Cu, Ni, Pb, Zn	Significant reduction of the bioavailable Cd, Pb and Zn, with Cd showing the greatest reduction; an increase in the pH, CEC and water-holding capacity	Fellet et al. (2011)
Chicken manure and green waste	550 °C	Cd, Cu, Pb	Significant reduction of Cd, Cu and Pb accumulation by Indian mustard	Park et al. (2011)
Chicken manure	550 °C	Cr	Enhanced soil Cr(VI) reduction to Cr(III)	Choppala et al. (2012)
Sewage sludge	500 °C	Cu, Ni, Zn, Cd, Pb	Significant reduction in plant availability of the metals studied	Méndez et al. (2012)

(continued)

Table 1.2 (continued)

Feedstock	Production temperature	Contaminant	Effect	References
Rice straw	Not clear	Cu, Pb, Cd	Significant reduction in concentrations of free Cu, Pb and Cd in contaminated soils; identification of functional groups on biochar with high adsorption affinity to Cu	Jiang et al. (2012a)
Quail litter	500 °C	Cd	Reduction of the concentration of Cd in physic nut; greater reduction with the higher application rates	Suppadit et al. (2012)
Oakwood	400 °C	Pb	Bioavailability reduction by 75.8%; bioaccessibility reduction by 12.5%	Ahmad et al. (2012)
Effect of biochar application on sorption of organic pollutants in soils				
Eucalyptus wood	450 °C and 850 °C	Diuron, chlorpyrifos and carbofuran	Higher pyrolysis temperature and higher rates of biochar applied to soils result in stronger adsorption and weaker desorption of pesticides	Yu et al. (2006)
Woodchip	500 °C	Atrazine and acetochlor	Acetochlor adsorption increased 1.5 times; atrazine adsorption also increased	Spokas and Reicosky (2009)
Dairy manure	200 °C and 350 °C	Atrazine	At 200 °C, partitioning of atrazine is positively related to biochar carbon content	Cao et al. (2009)
Pinewood	350 °C and 700 °C	Terbuthylazine	Soil sorption increased 2.7- and 63-folds in the BC350 and BC700 treatments, respectively	Wang et al. (2010)
Green wastes	450 °C	Atrazine	Biochar-enhanced adsorption of pesticide	Zheng et al. (2010)
Pinewood	350 °C and 700 °C	Phenanthrene	Biochar produced at 700 °C showed a greater ability at enhancing a soil's sorption ability than that prepared at 350 °C	Zhang et al. (2010)

(continued)

Table 1.2 (continued)

Feedstock	Production temperature	Contaminant	Effect	References
Pine needles	100 °C, 300 °C, 400 °C, and 700 °C	PAHs	Sorption capacity increased with pyrolysis temperature	Chen and Yuan (2011)
Eucalyptus woodchips	850 °C	Diuron	Pesticide absorption increases with the biochar contact time with soil and application rate	Yu et al. (2011)
Poultry litter, wheat straw and swine manure	250 °C and 400 °C	Herbicides	Biochars showed high sorption ability for two herbicides, fluridone and norflurazon	Sun et al. (2012)
Swine manure	350 °C and 700 °C	Carbaryl	At low carbaryl concentrations, the sorption capacity BC700 > BC350; similar sorption capacity at high carbaryl concentrations	Zhang et al. (2013)
MgO-impregnated magnetic biochar, sugarcane harvest residue biochar, magnetic biochar	550 ° C	Phosphate	Adsorption was higher in MgO-impregnated magnetic biochar	Li et al. (2016)
Effect of biochar application on bioavailability of organic pollutants in soils				
Eucalyptus	450 °C and 850 °C	Diuron, chlorpyrifos and carbofuran	Reductions of chlorpyrifos and carbofuran in total plant residues, respectively	Yu et al. (2009)
Hardwood	450 °C	PAHs	Pore water concentrations of PAHs were reduced by biochar, with greater than 50% decrease of the heavier, more toxicologically relevant PAHs	Beesley et al. (2010)
Cotton straw	450 °C and 850 °C	Chlorpyrifos and fipronil	Chinese chive uptake of fipronil and chlorpyrifos reduced by 52% and 81%, respectively, with 1% of 850 °C biochar addition	Yang et al. (2010)
Bamboo	600 °C	Pentachlorophenol	Biochar reduced PCP bioavailability in soil	Xu et al. (2012)

(continued)

Table 1.2 (continued)

Feedstock	Production temperature	Contaminant	Effect	References
Hardwood	600 °C	PAHs	Biochar application reduced concentration and biological activity of PAHs in soil	Gomez-Eyles et al. (2011)
Wheat straw	500 °C	Chlorobenzenes (CBs)	Biochar amendment significantly reduced the bioavailability of CBs	Song et al. (2012b)
Wheat straw	250 °C, 300 °C, and 500 °C	Hexachlorobenzene (HCB)	Biochar amendment of soil resulted in a rapid reduction in the bioavailability of HCB, even at 0.1% biochar application rate	Song et al. (2012a)

et al. 2009; Ahmad et al. 2012, 2014). Furthermore due to the ubiquity and cost-effectiveness of fresh biochar, exhausted biochar can be replaced easily and can be recycled by burning it to produce ash for use as liming agent in acidic soil (Feng et al. 2013).

Why Biochar Acts as a Potential Adsorbent?

Biochars, generally used for soil conditioning and carbon sequestration, are now finding use in contaminant remediation (Mohan et al. 2014). Biochar can be considered as a sustainable material as it requires less investment and, unlike activated carbon, the hydrogen and carbon remain in its structure along with the ash that originates from its biomass. One of the most important properties of biochar is its adsorption capacity. Biochars with high specific area are usually used as sorbents (Zhao et al. 2013). Several studies have demonstrated the effectivity of biochar in stabilizing some inorganic pollutants like heavy metals. They can stabilize the heavy metals in polluted soils, thus improving the soil quality and reducing heavy metals uptake by crops. Also, studies have demonstrated that the high surface area, high aromatic nature, micropore volume and abundance of polar functional groups present in biochar have aided in effective sorption of organic contaminants like POPs viz., PCBs, PAHs and emerging pollutants such as steroid hormones and pharmaceuticals (Zhang et al. 2013; Zhao et al. 2013; Arun et al. 2017). Sludge-derived biochar was found to be an excellent adsorbent for amoxicillin in wastewater mainly due to large Brunauer–Emmett–Teller (BET) specific surface area (Arun et al. 2017). As shown in Fig. 1.2, scanning electronic microscope (SEM) images showed the distinct pattern and pores available before exposure of the biochar to water containing amoxicillin. Reduction of the particle size indicates the adsorption of amoxicillin to the pores of the biochar, and this property may be important for

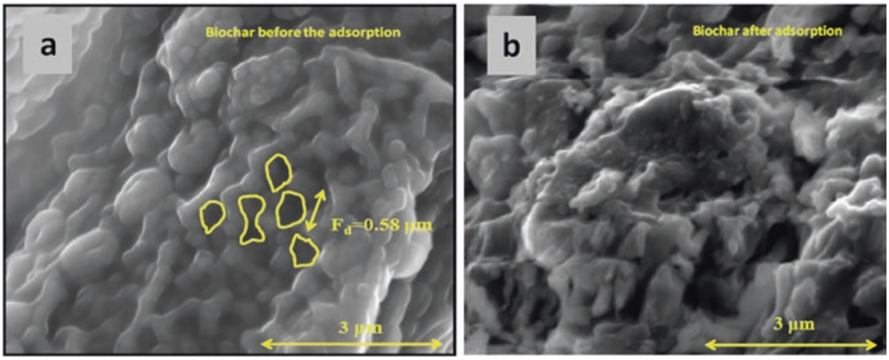

Fig. 1.2 SEM images given by Arun et al. 2017, for sludge-derived biochar (**a**) before amoxicillin exposure and (**b**) after amoxicillin exposure

sequestration of a variety of contaminants. Li et al. (2016) reported that increasing the Mg content in MgO-impregnated magnetic biochar (MMSB) increased the adsorption of phosphate compared to sugarcane harvest residue biochar and magnetic biochar without Mg. Also studies on Mg/Al-layered double hydroxide-modified biochar showed that the Mg/Al ratio and pH of solution affected the adsorption of phosphates from aqueous solution (Li et al. 2016). One of the main aspects to be considered is the effect of biochar properties on the bioavailability of these contaminants. The risk of these organic and inorganic pollutants from entering the food chain, surface runoff, and leaching to groundwater is highly reduced due to adsorption. The effect of biochar on the bioavailability of metals depends on the feedstock materials used for preparing biochar and the type of heavy metal considered (Zhang et al. 2013). The amendment of soil contaminated by Cd and Zn using hardwood-derived biochar reduced the concentration of both the metals in pore water (Beesley et al. 2010; Karami et al. 2011).

Soil Treatment Using Biochar

Remediation of Organic Pollutants

POPs are those categories of pollutants that resist photolytic, biological or chemical degradation to a varying degree. Characterized by low water solubility and high lipid solubility, many are found to deposit in fatty tissues of organisms leading to their bioaccumulation in the environment due to their persistent nature. Some classes of organic pollutants well known for their persistence and toxicity are PCBs, OCPs and PAHs. Due to their everlasting effects on human health and environment, the need for cost-effective sustainable methods to remediate soils, especially dumpsite soils where they are detected frequently, is a necessity. Several studies

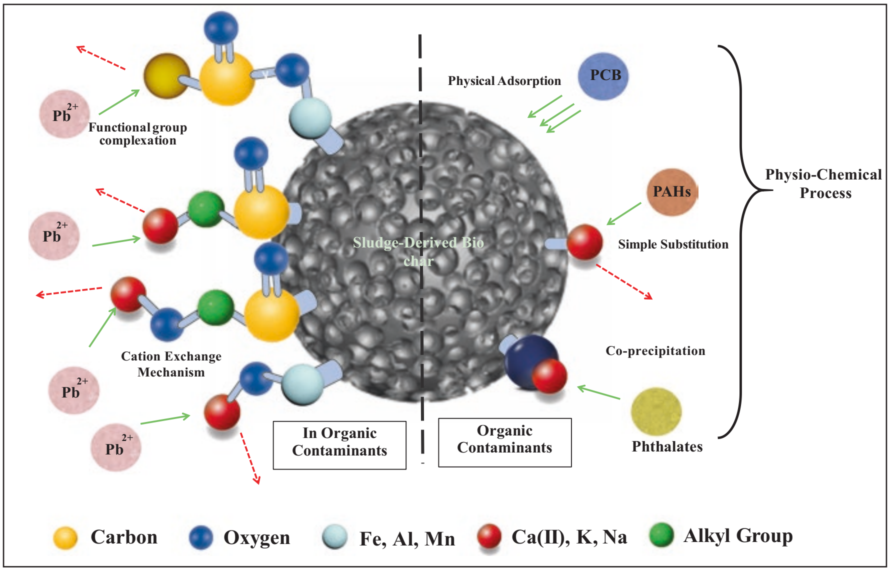

Fig. 1.3 Mechanism on the use of biochar for the removal of inorganic and organic pollutants as given by Zhang et al. 2013

have proved the effectivity of biochar in uptake of such POPs (Tong et al. 2011; Ahmad et al. 2014). The high aromaticity, high surface area, micropore volume and abundance of polar functional groups in biochar are the major factors that suffice the adsorption of organic pollutants by biochar. As shown in Fig. 1.3, the main phenomena governing are physical adsorption, co-precipitation and simple substitution. Arun et al. (2017) reported sludge-derived biochar produced at pyrolytic temperature of 300 °C to be effective in removal of amoxicillin by adsorption from wastewater, which was evident from the distinct pattern observed before and after adsorption in UV spectroscopy. Beesley et al. (2011) have observed that the PAH concentration in soil pore water reduced to 50% after treating with biochar. The reduction in bioavailability of various organic pollutants due to adsorption in biochar derived from different sources have been given in Table 1.2. When soil polluted with chlorpyrifos and fipronil was treated with biochar produced from corn straw, it was observed that uptake rate of chlorpyrifos and fipronil by plant reduced to 52% and 81%, respectively (Yang et al. 2010). A 95% removal of malachite green (MG) was attained within 40 min by adsorption into rice straw biochar applied on 25 mg/L of MG solution (Hameed and El-Khaiary 2008). Acid-treated straw biochar used to remove reactive brilliant blue and rhodamine B resulted in high adsorption by biochar than the activated charcoal (AC) accounting to the high surface area and less carbonization of AC compared to charcoal. Studies across a variety of locations globally suggest that biochar can be a better option in amending soil polluted with organic pollutants (Chun et al. 2004; Qiu et al. 2009).

Remediation of Toxic Metals

The indiscriminate use and occurrence of heavy metals in the industrial, medical and technological sector has resulted in its widespread distribution in the environment, raising concerns over their possible effects on the environment and human health. Some of the sources of heavy metals release into the environment include geogenic, industrial, pharmaceutical, agricultural, domestic effluent and atmospheric sources (He et al. 2005). Among heavy metals arsenic, cadmium, mercury, lead and chromium are the top priority as they have been identified as possible human carcinogens by the United States Environmental Protection Agency (USEPA) and International Agency for Research on Cancer. Thus, there is a necessity to develop eco-friendly and cost-effective methods to deal with these pollutants that ultimately reach the dumpsites.

As stated by Zhang et al. 2013, the various mechanisms involved in stabilization of heavy metals using biochar are (a) ion exchange between the cations associated with biochar and concerned heavy metals along with co-precipitation and inner sphere complexation with humic matter and mineral oxides of biochar and (b) surface complexation – metals undergo surface complexation with several functional groups and inner sphere complexation with free hydroxyl present in the mineral oxides (Fig. 1.3). Physical adsorption is a process involving simple adsorption and surface precipitation that lead to the stabilization of the heavy metal content (Lu et al. 2012). Heavy metal stabilization can further depend on the type of soil considered and the cations present in both biochar and soil (Zhang et al. 2013). Ahmad et al. (2014) observed that the bioavailability of Pb in military shooting range soil reduced to 75.8% after the treatment. Chen et al. (2016) found that biochar prepared from corn straw could remove around 95% of Cu and 90% of Zn. On the other hand, pinewood biochar showed adsorption capacities of 4.13 mg/g, 1.2 mg/g and 2.62 mg/g, while oakwood char showed 0.37 mg/g, 5.85 mg/g and 3 mg/g for Pb, Cd and As, respectively (Mohan et al. 2014). The adsorption capacity of Cu by biochar prepared from peanut straw, soybean straw and canola straw was 0.09 mg/g, 0.05 mg/g and 0.04 mg/g, respectively (Tong et al. 2011). Recently, research has focused on enhancing biochar's affinity for contaminant oxyanions such as AsO_4^{3-}, AsO_3^{3-} and CrO_4^{2-} due to generally negative charge of pristine biochar. Development of metal oxide-impregnated biochar composite has shown promising adsorption of these metals present as oxyanions (Agrafioti et al. 2014; Li et al. 2016; Wang et al. 2016).

Retention Capacity of Biochar

The retention capacity of biochar depends on the pyrolytic temperature, specific surface area, total pore volume, mechanism employed in adsorption, etc. Wood-derived activated charcoal and dairy manure biochar showed that despite having lower surface area than activated charcoal, biochar could retain Pb six times more than activated carbon (Cao et al. 2009). The charge and surface area properties are the factors that usually help in reducing nutrient losses from biochar when it is used in soil (Glaser et al. 2002; Lehmann et al. 2003). The presence of functional groups in biochar affects the sorption capacity depending on the surface charge on it, thus helping in the adsorption and retention of both transitional and nontransitional metals on the biochar particles (Amonette and Joseph 2009). Interaction of biochar with natural organic molecules and clay minerals present in soil can suppress the sorption of the organic pollutants from soil (Pignatello et al. 2006). Wang et al. (2010) observed that the retention capacity of herbicide terbuthylazine decreased due to high organic content in the soil because dissolved organic carbon competed for sorption sites thereby reducing the retention capacity.

Future Prospect for Remediation of Dumpsite Soils

Municipal waste is a growing health and ecological problem particularly in the developing countries because of the toxic contaminants that enter poorly maintained dumpsites. Several developing nations have used biochar to decontaminate the surface soil. Dumpsite soil quality can be easily improved through the targeted use of low-cost biochar soil amendments that sequester and treat these contaminants. Ageing is a phenomenon where the presence of natural organic matter and clay minerals in the soil clogs the micropores of biochar and decreases the sorption of organic pollutants by biochar. Such high concentrations of organic matter in soil compete with the organic pollutants for sorption sites eventually decreasing the adsorption efficiency of biochar (Zhang et al. 2013). One important aspect yet to be investigated is the impact of biochar on the soil fauna as there are reports showing adverse effect of biochar on earthworms and soil microbes (Beesley et al. 2011). A high rate of biochar application can decrease the soil fertility by adsorbing the required soil nutrients (Frazzoli et al. 2010). Furthermore there are evidences for release of toxic pollutants like PAHs from the biochar itself due to high rate of application on soil (Thies and Rillig 2009). Based on literature, it seems that biochar can be more widely used in remediation of the organic and inorganic pollutants from soil by addition in layers on the polluted dumpsite soil. Incorporated biochar would act as an adsorptive medium for sequestering pollutants. Thus, biochar can be produced at high pyrolytic temperatures which would improve its adsorption characteristics by increasing the specific surface area and total pore volume available for adsorption of pollutants. Biochar has to be incorporated and maintained in the soil for the optimum time period. Bioaugmentation can be used for bioremediation of the biochar which has adsorbed different types of pollutants from the dumpsite soil. Bioaugmentation employs soil microorganisms that would pre-concentrate the contaminants on the biochar. Later on the immobilized microbial organisms would degrade the pollutants (Zhao et al. 2013).

Biochar amendments prepared using wooden pellets for amending landfill soil covers facilitated the growth of methanotrophic bacteria that are effective in reducing methane emissions. The highest oxidation rates were observed in the upper layers of amended soil (up to 30 cm depth) with more oxygen availability (Reddy et al. 2014). Sea mango-based biochar utilized for removal of organic and inorganic pollutants from landfill leachates gave the highest adsorptive removal for colour (95.1%), chemical oxygen demand (COD) (84.94%) and NH_3-N (95.77%) (Shehzad et al. 2016). Asia alone generates 4.4 billion tones and 790 MT of solid waste and MSW, respectively, per year, of which 6% is attributed to the Indian subcontinent. The land allotment for 48MT of waste from India is only 20.2 km^2 which should be increased to 169.6 km^2 by the end of 2047 with a projected amount of 300 MT of waste generated. Urban waste is predominantly rich in organic matter (46%) followed by paper (6%), glass (0.7%), rags (3.2%) and plastic (1%) and the rest is moisture. About 600 MT of waste is generated in India alone from agricultural waste of which sugar industries contribute 90 MT. With such rich amount of organic waste composition in the MSW, it can very obviously be used for the production of high-quality biochar for the removal of organic and inorganic contaminants as discussed in the previous sections. Furthermore, 730 Tg of biomass are burnt in Asia of which 250 Tg come from agricultural burning that leads to the emission of SOx, NOx, CO, CO_2, PAHs and PCDD/Fs (Gadde et al. 2009). Biochar production can thereby reduce the load of open burning of crop residues and therefore, significantly contribute in arresting air pollution and concurrently help in conserving carbon. The versatility of biochar technologies also offers the potential for equitable technology transfer and use in developing countries (Pratt and Moran 2010). Cost-effectiveness in developed and developing nations using marginal abatement cost curve (MACC) was done by Pratt and Moran (2010). Several considerations were taken in to account, including price of electricity, carbon, biochar application rates and potential yield gain. Electricity generated from the biochar plants as byproduct such as syngas and bio-oil were used to operate the plants in developed nations. On the other hand, taking into consideration the developing nations where biochar kiln and stoves are employed, there was far better abatement of carbon emissions in comparison to fossil fuels. In developed nations with the advantage of adequate infrastructure and abundance of biomass for feedstock, it may appear that due to the high carbon market prices, biochar-producing plants will be highly cost-effective. However, MACC output clearly suggests otherwise and even without substantial infrastructure, waste management in developing nations was found to be more profitable by offering more abatement potential at lower costs than carbon capture and storage (CCS) (Pratt and Moran 2010).

Conclusion

With consideration of relatively simple low-cost methods for producing biochar and its remarkable adsorption capacity, it seems likely that biochar would provide a cost-effective solution for cleaning and managing contaminated soil in addition to its soil amendment benefits for dumpsite soils in developing and underdeveloped countries. The major influential factors governing the characteristics of biochar produced are the pyrolytic temperature employed and the feedstock utilized for its preparation. More in-depth research is needed to help facilitate production of biochar in these countries to increase the retention capacity of the pollutants. Furthermore, local municipalities would be expected to create a demand for improved biochar as an effective remediation technique and dumpsite management alternative. To meet the increasing demand, there can be a new market venture for such inexpensive remediation technique in the developing world.

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