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Characteristics and applications of biochars derived from wastewater solids

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ABSTRACT

Pyrolysis is a thermochemical decomposition process that can be used to generate pyrolysis gas (py-gas), bio-oil, and biochar as well as energy from biomass. Biomass from agricultural waste and other plant-based materials has been the predominant pyrolysis research focus. Water resource recovery facilities also produce biomass, referred to as wastewater solids, that could be a viable pyrolysis feedstock. Water resource recovery facilities are central collection and production sites for wastewater solids. While the utilization of biochar from a variety of biomass types has been extensively studied, the utilization of wastewater biochars has not been reviewed in detail. This review compares the characteristics of wastewater biochars to more conventional biochars and reviews specific applications of wastewater biochar. Wastewater biochar is a potential candidate to sorb nutrients or organic contaminants from contaminated wastewater streams. While biochar has been used as a beneficial soil amendment for agricultural applications, specific research on wastewater biochar is lacking and represents a critical knowledge gap. Based on the studies reviewed, if biochar is applied to land it will contain less organic micropollutant mass than conventional wastewater solids, and polycyclic aromatic hydrocarbons are not likely to be a concern if pyrolysis is conducted above 700 °C. Wastewater biochar is likely to serve as a better catalyst to convert bio-oil to py-gas than other conventional biochars because of the inherently higher metal (e.g., Ca and Fe) content. The use of wastewater biochar alone as a fuel is also discussed. Finally, an integrated wastewater treatment process that produces and uses wastewater biochar for a variety of food, energy, and water (FEW) applications is proposed.

1. Introduction

Typical water resource recovery facilities (WRRFs), formerly referred to as wastewater treatment plants, treat wastewater from homes and industries, producing treated water and residual wastewater solids that are rich in organic content. These facilities are currently energy intensive operations, but a new paradigm has emerged viewing WRRFs as community assets that could recover energy and generate value-added products from wastewater [1,2]. Influent wastewater is rich in carbon, nutrients, and heat, all of which are potentially valuable resources [3]. The nutrients can be recovered as a fertilizer product, e.g. struvite, and used for agricultural purposes [4]. The organics have inherent energy content that can be recovered on-site. The wastewater solids, in particular, represent a potentially valuable energy source.

The United States Environmental Protection Agency (USEPA) estimates that approximately eight million dry tons of wastewater solids are produced each year in the United States alone [5]. Wastewater solids are either land applied as a soil conditioner and nutrient source, landfilled, or incinerated. WRRFs do not capture the inherent energy content from the organic matter of wastewater solids that are used as a soil conditioner or landfilled. Additionally, wastewater solids contain micropollutants, *i.e.,* the organic chemicals derived from consumer products that are released to sewers after use, including antimicrobials, pharmaceuticals, personal care products, hormones, and more [6]. Due to the presence of micropollutants, the long-term environmental and public health impacts of land applying wastewater solids have caused concerns to be raised in recent years [7]. For these reasons, alternative wastewater solids handling methods are being considered to recover energy while generating valuable products [8].

Pyrolysis is the process whereby biomass, such as wastewater solids, is heated between approximately 400 and 900 °C in the absence of oxygen [9,10]. Pyrolysis produces solid, liquid, and gas products. The solid product, biochar, is similar to charcoal. The liquid can consists of multiple phases: including non-aqueous phases often referred to as bio-oil, and an aqueous phase that is sometimes called aqueous pyrolysis liquid. The gas product, referred to as py-gas, consists of H_2, CH_4, CO,

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CO_2 along with lower concentrations of hydrocarbons including C_2H_6, C_2H_4, and C_3H_8 [11,12]. Py-gas is a relatively clean-burning fuel that can be used on-site at WRRFs for energy recovery. The bio-oil also has a high energy content, but contains water, organic acids and oxygenated organics that make it corrosive for combustion; therefore, bio-oil typically requires processing before use. The biochar, as reviewed in this paper, has a wide array of potential applications as a sorbent, soil amendment, energy source, or catalyst [13–16]. It may be most valuable for WRRF operators to optimize pyrolysis parameters to increase py-gas yield and decrease liquid yields because they require further processing. Slow pyrolysis (defined as pyrolysis with a heating rate less than 100 °C/min) yields more biochar and py-gas than fast pyrolysis (defined as pyrolysis with a heating rate greater than 300 °C/min), and fast pyrolysis typically yields more liquid products [17,18]. Therefore, the focus of this review is on biochars derived from slow pyrolysis of wastewater solids.

Wastewater solids are an emerging biomass source of interest for pyrolysis, in part, because they are centrally produced in urban locations. Therefore, one of the most energy intensive components for biochar generation, *i.e.,* biomass collection in a central location, has already been completed. From this logistical standpoint wastewater solids represent a potentially practical and easily accessible biomass stream to produce biochar via pyrolysis. Biochar derived from wastewater solids, referred to hereafter as wastewater biochar, however, has not been studied to the same extent as other biochars, nor has wastewater biochar been comprehensively reviewed. It is important to understand how wastewater biochars differ relative to other commonly studied biochars. The goal of this review is therefore to describe the characteristics of wastewater biochars relative to other biochars, current and future biochar uses, and research needs. The specific objectives of this review paper are to: i) determine how basic properties of wastewater biochar properties differ from other biochars ii) identify the appropriate uses of wastewater biochar for sorption, iii) establish the benefit of wastewater biochar as a soil amendment, iv) determine toxic hazards related to land applying wastewater biochar v) establish the role of wastewater biochar as a catalyst and vi) determine the feasibility of energy recovery from wastewater biochar.

2. Basic properties of wastewater biochars compared to other biochars

Wastewater biochars have a lower concentration of carbon (C) than other biomass-derived biochars (Table 1). This is not surprising considering that wastewater solids are comprised of organic and inorganic solids whereas biochars derived from other biomass streams such as switchgrass are composed primarily of organic matter. Wastewater biochars, on the other hand, typically have higher concentrations of nitrogen (N), phosphorus (P), and potassium (K), i.e., essential nutrients for plant growth. The relatively high abundance of N, P, and K in wastewater biochars indicate that a beneficial use would be as a soil amendment for agriculture (discussed in Section 4), whereas other biochars that have higher carbon contents might be more appropriately used as an adsorbent (discussed in Section 3). Wastewater biochars also have a higher abundance of micronutrients as well as potential toxicants, including metals (Table 1), so it is important to investigate if these metals are a leaching concern when applied to soils (discussed in Section 5.1) or potentially beneficial for using biochar as a catalyst to convert bio-oil to py-gas (discussed in Section 6).

Wastewater biochars typically have higher H to C ratios than other biochars, concomitant with their lower C content (Table 2). For energy purposes, a higher H/C ratio is preferred compared to a higher O to C ratio because a higher H/C ratio results in a fuel that is more reduced and releases more heat energy per unit mass. However, the total C content also affects the energy content and wastewater biochars typically have lower volatile and fixed C content (Table 2). The prospect~~ive~~ of using wastewater biochar as a fuel is discussed in Section 7. Both surface area and pore volume ranges for wastewater biochars are within ranges similar to those of other biochars; these parameters are important when considering the use of biochar as an adsorbent (discussed in Section 3).

3. Wastewater biochar as an adsorbent for pollutant removal from wastewater

3.1. Nutrients removal

Biochar derived from a wide range of feedstocks, including wastewater solids, can adsorb nutrients in the form of ammonium and phosphate. Table 3 summarizes research regarding biochars produced from different feedstocks and at different temperatures and washing/preconditioning protocols to adsorb ammonium or phosphate. Among the biochars reviewed, wastewater biochar had intermediate to high ammonium adsorption capacity and high phosphate adsorption capacity.

Surface area, surface chemistry, and functional groups are factors that affect interactions between adsorbents and adsorbates. As pyrolysis temperature increases, in general, the biochar surface area increases [47,49], but the surface area increase does not necessarily confer higher ammonium or phosphate adsorption capacities [49,51]. Cation exchange capacity, which results from the negatively charged biochar surface, is correlated with ammonium ion adsorption because ammonium is a cation [50–53]. In general, the phosphate adsorption capacities are not as high as ammonium adsorption capacities on biochar because biochar surfaces are negatively charged, and phosphate ions are likely repulsed. In some cases, phosphorus was even released from biochar upon addition to water [50,51,53]. The binding of phosphate to biochar surfaces can depend on formation of ligand bonds or precipitates onto biochar with biochar surface functional groups, *e.g.,* cations such as Ca, Mg, Al and Fe [47,54]. Indeed, when corn cob was modified with the addition of $MgCl_2$, the derived biochar had higher phosphate adsorption capacity than other types of biochar (Table 3) [47]. Normally, wastewater solids contain~~s~~ high metal contents (e.g., Ca, Mg, Fe, etc.) relative to other carbon feedstocks ([20]; Table 1) that can provide binding sites for negatively charged phosphate ions.

Nutrient adsorption capacities can vary by orders of magnitude, not only between different types of feedstocks, but also among biochars derived from the same type of biomass under different conditions (Table 3). Also noteworthy is that washing biochars with de-ionized water, acid or base did not necessarily increase nutrient adsorption [46,51]. Therefore, the intrinsic properties of a feedstock and the nature of the pyrolysis system might play more essential roles in facilitating ionic bonds between biochar and nutrient ions than washing steps.

In addition to wastewater biochar sorbing nutrients, wastewater biochars are also nutrient-rich and could be good agricultural soil conditioners (discussed in Section 4). After pyrolysis of wastewater solids, N content in biochar was between 1.5% and 3.5% and P content was between 2% and 12.8% by weight [20,55]. Absorbing external ammonium and phosphate could augment the nutrient content of wastewater biochar to use as a fertilizer. Pyrolysis may be promising for WRRFs that must capture N and P from the effluent while recovering energy. However, the unstable and non-homogeneous properties of wastewater solids and heavy metals such as Zn, Cu, Ni, Cr, and Hg [56] could be obstacles for applying nutrient-enhanced wastewater biochar on lands [57]. The risks of heavy metals in wastewater biochars are evaluated in Section 5.1.

3.2. Heavy metals removal

Various types of biochars can sorb heavy metals from water streams, including Pb, Cu, Cr, Cd, and Zn [58–60]. While many of the previous studies have focused on wood-derived biochars, wastewater biochar has