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Polymer/biomass-derived biochar for use as a sorbent and electron transfer mediator in environmental applications

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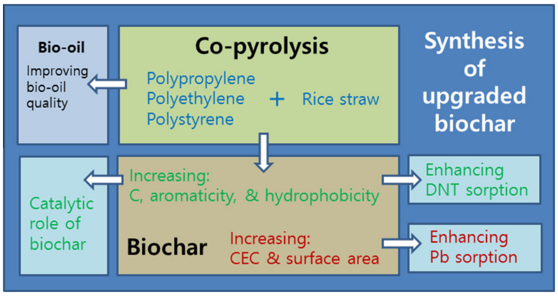
HIGHLIGHTS

- Co-pyrolysis of polymer and rice straw improves the properties of biochar.
- Polymer/rice straw-derived biochar enhances the sorption of DNT and Pb.
- Increasing aromaticity and hydrophobicity account for the sorption of DNT.
- The sorption of Pb is attributed to increasing CEC, pH, and surface area.
- Catalytic role of biochar remains after co-pyrolysis of polymer and rice straw.

GRAPHICAL ABSTRACT



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ABSTRACT

Co-pyrolysis of polymer and biomass wastes was investigated as a novel method for waste treatment and synthesis of enhanced biochar. Co-pyrolysis of rice straw (RS) with polypropylene (PP), polyethylene (PE) or polystyrene (PS) increased the carbon content, cation exchange capacity (CEC), surface area and pH of the biochar. As a result, the sorption of 2,4-dinitrotoluene (DNT) and Pb to polymer/RS-derived biochar was markedly enhanced. The increased aromaticity and hydrophobicity may be responsible for enhancing the DNT sorption to the polymer/RS-derived biochar. In contrast, increasing CEC, higher pH, and the newly developed surface area may account for the enhancement in Pb sorption. The addition of polymer to RS did not significantly change the catalytic role of biochar during the reduction of DNT by dithiothreitol. Our results suggest that co-pyrolysis of RS and polymer can improve the biochar properties to enhance the sorption of DNT and Pb.

1. Introduction

Since plastics (mostly composed of synthetic organic polymers) were introduced in the early 1930s, plastic materials have become integral to human life, and huge amounts of polymers are used in everyday life. The global plastic production in 2010 was 264 million tons (Abnisa et al., 2014). According to the Korean Ministry of Environment, approximately 6000 tons/day of plastic/polymer wastes were generated in South Korea in 2014. Currently, about 60% of plastic wastes are recycled via physical and chemical processes in South Korea. Plastics have a high resistance to biodegradation, which limits the final disposal of plastic wastes to incineration and landfilling. Because polymers have high carbon and hydrogen content, much research in the last few decades has focused on recovering useful energy from thermal decomposition processes, such as pyrolysis (Hovart and Ng, 1999; Murugan et al., 2008). Pyrolysis of plastic wastes produces pyrolysis oil and gas, which can be further treated to produce a product that can be used for practical purposes (Ates et al., 2013; Muhammad et al., 2015).

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Disposal and treatment of agricultural and biomass wastes have also been intensively examined. Unlike plastic wastes, biological treatment (e.g., composting) is a primary option because most biomass wastes are readily biodegradable (United Nation Environment Programme (UNEP), 2009). Recently, pyrolysis of biomass wastes was proposed as an alternative process for developing alternative energy in response to climate change (Lehmann, 2007). The pyrolysis of biomass wastes has also been shown to reduce the release of carbon dioxide by converting the biomass to biochar, a relatively stable form that is resistant to degradation; this is a type of carbon sequestration (Lehmann, 2007; Woolf et al., 2010). Pyrolysis is not only used to treat the biomass waste, it can also be used to produce reusable energy such as heat, bio-oil, and syn-gas (Lehmann, 2007; Sannita et al., 2012). In contrast to pyrolysis oil produced from plastic/polymer wastes, the crude bio-oil produced from biomass is not satisfactory for use in fuels (Czernik and Bridgwater, 2004). Bio-oil is acidic and contains high water and oxygen content (Mohan et al., 2006). Furthermore, the properties of the produced bio-oil varied depending on the composition of the biomass wastes (e.g., lignin, cellulose, hemicellulose, and other compositions) (Czernik and Bridgwater, 2004; Mohan et al., 2006). The quality of bio-oil could be enhanced using several treatment processes (e.g., catalytic hydroprocessing) to produce transportation or engine fuels (Elliott, 2007; Bridgwater, 2012). Though practical usage of bio-oil is possible, the required upgrading treatment processes are costly. Attempts have also been made to improve the quality of crude bio-oil including catalytic fast pyrolysis (Cheng et al., 2012; Liu et al., 2012). However, the improvement in the quality of the crude bio-oil was limited.

One way to improve bio-oil quality is to use plastics/polymer wastes and biomass together in pyrolysis. Co-pyrolysis of polymer and biomass has significantly improved the quality of bio-oil due to the synergistic effect of the high content of carbon and hydrogen in the polymers. The addition of polymers to biomass pyrolysis has resulted in increased yield of bio-oil and higher heating values (Bhattacharya et al., 2009; Paradela et al., 2009; Önal et al., 2014). Co-pyrolysis of polymers with biomass resulted in upgraded bio-oil by reducing the acidity, density, and oxygen content (Bhattacharya et al., 2009; Martínez et al., 2014). Catalytic co-pyrolysis of polymers with biomass also significantly improved the quality of bio-oils (Dorado et al., 2014). Studies on char produced from co-pyrolysis of biomass and polymers were also conducted. Compared to biochar, the yield of char was reduced and the calorific values were improved (Brebu et al., 2010; Sajdak and Muzyka, 2014; Xue et al., 2015). The co-pyrolysis also resulted in aromaticity via the growth of polycyclic aromatic hydrocarbons (PAHs) (Ko et al., 2014; Suriapparao et al., 2014). Bernardo et al. (2012) suggested that the upgraded biochar made from the co-pyrolysis of biomass and polymers can be used as an adsorbent.

Many studies have been conducted on the use of biochar as an alternative sorbent to immobilize toxic metals and organic compounds in environmental applications (Mohan et al., 2014). Various types of biochar have been synthesized based on the pyrolysis conditions, and their sorption characteristics were different. In general, the sorption of contaminants to biochar was less than the sorption on activated carbon. The sorption of contaminants to biochar was enhanced through surface activation with acids and oxidants. However, the sorption capacity was still less than that of activated carbon due to the low carbon content and small surface area. In order to overcome this limitation, we propose a co-pyrolysis of biomass and polymer to upgrade the properties of biochar. Though bio-oil from the co-pyrolysis of polymer and biomass has been well characterized, limited attempts have been made to study biochar produced from co-pyrolysis of polymers and biomass for environmental applications. We hypothesized that polymer/biomass-derived biochar may improve the properties of biochar for sorbents and catalysts due to residues from the polymers. The objectives of this study were to characterize biochar that was co-pyrolyzed with polymer and biomass and to evaluate the polymer/biomass-derived biochar as a sorbent and an electron transfer mediator. 2,4-Dinitrotoluene (DNT) and Pb were selected as model contaminants because their sorption to biochar was previously investigated in detail (Oh and Seo, 2014). Using rice straw and three different types of polymers (polypropylene, polyethylene, and polystyrene), polymer/biomass-derived biochars were synthesized and characterized. The sorption of DNT and Pb were determined in batch experiments. The role of the electron transfer mediator was examined during the reductive transformation of DNT using a model reductant, dithiothreitol ($Eh^0 = -0.33$ V at pH 7).

2. Materials and methods

2.1. Chemicals

Polypropylene (PP, amorphous, average molecular weight ~ 14,000), polyethylene (PE, low density, melt index 25 g/10 min), polystyrene (PS, average molecular weight ~ 19,200), 2,4-dinitrotoluene (DNT, 97%), 2-amino-4-nitrotoluene (2A4NT, 99%), 4-amino-2-nitrotoluene (4A2NT, 97%), 2,4-diaminotoluene (DAT, 98%), and $PbCl_2$ (98%) were purchased from Aldrich (Milwaukee, WI, USA). HEPES (N-[2-hydroxyethyl]piperazine-N′-[ethanesulfonic acid]) was obtained from Sigma (St. Louis, MO, USA). All chemicals were used as received without further purification.

2.2. Synthesis of polymer/rice straw-derived biochar

Rice straw (RS) collected from rice farms in the city of Ulsan, Korea was used as a biomass to synthesize polymer/biomass-derived biochar. The sampled RS was dried in an oven at 105 ± 5 °C for at least 2 h. After storing in a desiccator overnight, the dried RS was pulverized to smaller sizes (less than 5 mm) using an electric mixer. Then, one of the purchased polymers was mixed with the RS at volumetric ratios of 40:60, 20:80, and 5:95. The completely mixed polymer/RS mixtures were co-pyrolyzed at 550 °C for 4 h using a tube-type electrical furnace under N_2 at 1000 cc/min. To prevent producing ash from biomass during pyrolysis, the relatively high nitrogen flow rate was applied. After cooling down to room temperature, the co-pyrolyzed polymer/RS-derived biochar was put in a desiccator for additional drying. In order to determine the effect of pyrolysis temperature, the temperature was changed to 700 and 900 °C. Properties of the synthesized polymer/RS-derived biochar were characterized including pH, Brunauer-Emmett-Teller (BET) surface area, cation exchange capacity (CEC), pH at zero point charge (pH_{zpc}), and elemental compositions (Table 1). Fourier transform infrared spectroscopy (FT-IR, Nicolet iS5 ThermoFisher Sci., Waltham, MA, USA) spectra and scanning electron microscopy (SEM, JSM 600F, JEOL, Japan) images were also obtained to identify the surface functional groups and investigate the surface morphology. Thermogravimetric analysis (TGA) was conducted to determine the mass change as a function of the pyrolysis temperature under anaerobic conditions using a TGA system (STA409C/3/F, Netzsch, Germany).

2.3. Batch sorption experiments

DNT and Pb stock solutions were prepared using a magnetic stirrer and an Erlenmeyer flask (1 L) to concentrations of 200 mg/L and 1000 mg/L, respectively. To prevent precipitation of Pb in the stock solution, a couple of drops of 1 N HCl were added. Batch