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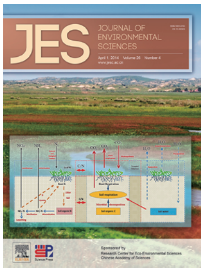

Removal of polycyclic aromatic hydrocarbons from aqueous solution by raw and modified plant residue materials as biosorbents

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ABSTRACT

Removal of polycyclic aromatic hydrocarbons (PAHs), e.g., naphthalene, acenaphthene, phenanthrene and pyrene, from aqueous solution by raw and modified plant residues was investigated to develop low cost biosorbents for organic pollutant abatement. Bamboo wood, pine wood, pine needles and pine bark were selected as plant residues, and acid hydrolysis was used as an easily modification method. The raw and modified biosorbents were characterized by elemental analysis, Fourier transform infrared spectroscopy and scanning electron microscopy. The sorption isotherms of PAHs to raw biosorbents were apparently linear, and were dominated by a partitioning process. In comparison, the isotherms of the hydrolyzed biosorbents displayed nonlinearity, which was controlled by partitioning and the specific interaction mechanism. The sorption kinetic curves of PAHs to the raw and modified plant residues fit well with the pseudo second-order kinetics model. The sorption rates were faster for the raw biosorbents than the corresponding hydrolyzed biosorbents, which was attributed to the latter having more condensed domains (i.e., exposed aromatic core). By the consumption of the amorphous cellulose component under acid hydrolysis, the sorption capability of the hydrolyzed biosorbents was notably enhanced, i.e., 6–18 fold for phenanthrene, 6–8 fold for naphthalene and pyrene and 5–8 fold for acenaphthene. The sorption coefficients (K_d) were negatively correlated with the polarity index [(O+N)/C], and positively correlated with the aromaticity of the biosorbents. For a given biosorbent, a positive linear correlation between $\log K_{oc}$ and $\log K_{ow}$ for different PAHs was observed. Interestingly, the linear plots of $\log K_{oc}$–$\log K_{ow}$ were parallel for different biosorbents. These observations suggest that the raw and modified plant residues have great potential as biosorbents to remove PAHs from wastewater.

Introduction

Polycyclic aromatic hydrocarbons (PAHs), predominantly originating from the combustion of fossil fuels and biomass, have been widely detected in numerous surface water and groundwater (Boving and Zhang, 2004; Chen et al., 2004). PAHs are of significant environmental concern due to their high bioaccumulation and potential mutagenic and carcinogenic properties (Nizzetto et al., 2008; Chen et al., 2010; Pan et al., 2011). Due to their low solubility and resistance to mineralization, some typical treatment methods, including chlorination, oxidation and ultrasonic irradiation, are not effective in removing PAHs from aqueous solution (Changchaivong and Khaodhiar, 2009).

Sorption is one of the most effective methods to remove organic pollutants at low concentration, and conventional sorbents such as activated carbon and resin have been widely used and displayed good performance in PAHs removal (Zimmerman et al., 2004). However, their comparably high cost limits the treatment of large amounts of wastewater and storm water. Biosorption is considered a

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cost-effective method to remove pollutants from wastewater. For example, the biosorption of heavy metal, dyes and pesticides by biomaterials such as fungi, bacteria, algae, peat and wood fiber have been extensively investigated (Ho et al., 2005; Montazer-Rahmati et al., 2011; Aksu, 2005; Boucher et al., 2007; Calderóna et al., 2008; Eberhardt et al., 2006). However, the use of biosorbents for removing PAHs in the environment has received considerably less attention (Chung et al., 2007). So far, studies on the biosorption of PAHs have mainly concentrated on microorganism and algae biomass, and the roles of raw and modified plant residues on the removal of PAHs need more study (Aksu, 2005; Huang et al., 2006; Chen et al., 2010, 2011; Li et al., 2010).

Plant residues, mainly generated from the agricultural industry, are significant components of bio-solid waste, and are considered one of the most abundant, cheap and renewable resources (Santana-Méridas et al., 2012). Developing plant residues as biosorbents for wastewater treatment is of increasing concern due to their relative high sorption capacities for persistent organic pollutants and ease of modification to higher sorption capacity materials (Ho et al., 2005; Huang et al., 2006; Li et al., 2010). Boving and Zhang (2004) found that aspen wood was an effective sorbent for PAH removal. High sorption affinity with phenanthrene by raw and brewed tea leaves was also reported (Lin et al., 2007). However, the sorption of PAHs by modified plant residues has drawn less attention.

The sorption properties of biosorbents are significantly influenced by their structural characteristics, such as polarity and aromaticity. Li et al. (2010) reported that lignin was the main aromatic component of natural plant residues, and the powerful sorption potential of lignin was seriously restricted by the coexisting polysaccharide (polar component). By removing the sugar component with acid hydrolysis, the sorption capacity of modified plant residues could be notably enhanced. However, more studies on raw and modified biosorbents are needed to further elucidate the relationship between sorption properties and kinetics of biosorbents with their structural characteristics, providing an engineering basis for the application of modified plant residues in persistent organic pollutants removal.

The main objective of this study was to elucidate the relationship between PAH sorption with the structural characteristics of biosorbents. To this end, four plant residues including bamboo wood (BW), pine wood (PW), pine needles (PN) and pine bark (PB) were selected and modified via acid hydrolysis to obtain different biosorbents. All samples were characterized by elemental analysis, Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). Naphthalene, acenaphthene, phenanthrene and pyrene were chosen as the model PAHs because they are widespread in wastewater and surface water.

1 Materials and methods

1.1 Preparation of plant samples

Four plant residues samples, i.e., BW, PW, PN and PB, were collected from Zhejiang Province, China on October 2012. These plant samples were washed with deionized distilled water to remove dust and were then oven-dried for 12 hr at 70°C, ground with a pulverizer, and sieved to less than 0.154 mm, yielding raw biosorbent samples. The raw plant samples were modified by acid hydrolysis, using a reported method (Chen et al., 2008). Acid hydrolysis, conducted in 6 mol/L HCl solution with refluxing for 6 hr at 100°C, was used to eliminate the polysaccharide component from BW, PW, PN and PB, and produced de-sugared bamboo wood (BW-DS), de-sugared pine wood (PW-DS), de-sugared pine needles (PN-DS) and de-sugared pine bark (PB-DS), respectively. All de-sugared residues were separated from the acidic solution by filtration and then were washed with deionized distilled water to adjust these residues to neutral conditions and to remove dissolved organic matter sorbed by the residues. All raw and modified plant samples were oven-dried at 60°C, ground, and sieved to less than 0.154 mm before analysis and sorption experiments. The sugar contents of the four raw plant samples were calculated from the yields of the modified fractions.

1.2 Characterization of plant samples

The contents of C, H and N in the raw and modified biosorbents were determined via a Flash EA 1112 CHN elemental analyzer (ThermoFinnigan), while the oxygen content was calculated by the mass difference. The atomic ratios of H/C and (O+N)/C were calculated to measure the aromaticity and polarity of samples, respectively. FT-IR spectra of plant samples were obtained over a wave number range of 4000 to 400 cm^{-1} on a Nicolet 6700 FT-IR with a resolution of 4.0 cm^{-1}. Plant samples (1.5 mg) were mixed with 100 mg KBr (to ensure 20%–80% transmittance rate) and compressed into pellets, then subjected to FT-IR analysis. The raw and modified plant samples were examined with a Hitachi S4800 scanning electron microscope (Japan) under high vacuum conditions and at an accelerating voltage of 3.0 kV in order to observe the surface morphology of the samples. For SEM, all samples were coated with gold in a sputter coater before being examined.

1.3 Kinetic sorption experiments

Phenanthrene, naphthalene, acenaphthene and pyrene were chosen as representative PAHs due to their different molecular properties and ubiquity in the environment. Their respective physicochemical properties are listed in **Table 1**. All chemicals were of analytical grade, and used without