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Removal of antibiotics from water using sewage sludge- and waste oil sludge-derived adsorbents

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ABSTRACT

Sewage sludge- and waste oil sludge-derived materials were tested as adsorbents of pharmaceuticals from diluted water solutions. Simultaneous retention of eleven antibiotics plus two anticonvulsants was examined via batch adsorption experiments. Virgin and exhausted adsorbents were examined via thermal and FTIR analyses to elucidate adsorption mechanisms. Maximum adsorption capacities for the 6 materials tested ranged from 80 to 300 mg/g, comparable to the adsorption capacities of antibiotics on various activated carbons (200–400 mg/g) reported in the literature. The performance was linked to surface reactivity, polarity and porosity. A large volume of pores similar in size to the adsorbate molecules with hydrophobic carbon-based origin of pore walls was indicated as an important factor promoting the separation process. Moreover, the polar surface of an inorganic phase in the adsorbents attracted the functional groups of target molecules. The presence of reactive alkali metals promoted reaction with acidic groups, formation of salts and their precipitation in the pore system.

1. Introduction

One of the wastes produced by contemporary society in an abundant quantity is municipal sewage sludge, often referred to as biosolids. Biosolids are a mixture of exhausted biomass generated in the aerobic and anaerobic digestion of the organic constituents of municipal sewage and inorganic materials such as sand and metal oxides. Other sludges include wastes from such industries as shipyards, foundry, electroplating, tobacco, or paper mills. It is estimated that about 10 million dry tons of sewage sludge are produced in the US annually (USEPA, 1999).

Various methods have been used to dispose of or utilize municipal sewage sludge (USEPA, 1999), including incineration, landfilling, road surfacing, conversion to fertilizer, compression into building blocks, and carbonization (Lundin et al., 2004). Since 1976 several patents have been issued on carbonization of sewage sludge and various applications of the final materials (Bandosz and Bagreev, 2005; Lewis, 1977; Nickerson and Messman, 1975). Carbonization of sludge in the

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presence of chemical activating agents such as zinc chloride and sulfuric acid produces new sorbents, with applications in such processes as removal of organics in the final stages of water cleaning, and removal of chlorinated organics. Industrial sludges after dewatering processes/drying are either used in landfills or disposed mainly as hazardous wastes.

Materials resulted from carbonization of sludges have surface areas between 100 and 500 m^2/g. Their performance as adsorbents of hydrogen sulfides (Bagreev et al., 2001), sulfur dioxide (Bashkova et al., 2002), basic or acidic dyes (Seredych and Bandosz, 2007), phenol (Rio et al., 2005), copper (Qian et al., 2009), or mercury (Zhang and Itoh, 2003) has been reported as comparable or better than that on activated carbons. In many processes the excellent sorption ability of these materials is linked to the catalytic action of metals present in various forms in the final products. Their chemical states along with the location on the surface were reported as important factors governing the pollutant removal capacities (Ros et al., 2006).

An estimated 100,000–200,000 tons of antibiotics are produced each year (Wise, 2002) as human and veterinary medicine (Boxall et al., 2003; Sarmah et al., 2006), and as much as 30–90% of administered antibiotics can be excreted without being metabolized (Hirsch et al., 1999). The excreted antibiotics are often discharged into surface waters or leached into soils and groundwater from manure-based fertilizers or sewage sludge (Boxall et al., 2003; Kemper, 2008), and have begun to accumulate in aquatic and terrestrial environments. In aquatic resources, measured antibiotic concentrations are typically μg/L levels in hospital effluent, low μg/L in wastewater, and low to high ng/L in various surface waters (Hirsch et al., 1999; Kemper, 2008; Kümmerer, 2009; Le-Minh et al., 2010). Antibiotics have been shown to affect soil bacterial community structure and respiratory and enzymatic activities (Zielezny et al., 2006). In addition, antibiotics in the environment may lead to the development and spreading of antibiotic resistance, a critical concern as it relates to the effectiveness of antibiotics in the treatment of human disease (Boxall et al., 2003).

Advanced treatment processes including ozonation, chlorination, ultraviolet (UV) irradiation, nanofiltration (NF) and reverse osmosis (RO), and activated carbon adsorption have been applied to remove antibiotics from secondary effluent (Le-Minh et al., 2010). Ozonation is effective in removal of antibiotics from water and wastewater effluent but the potential transformation of antibiotics to products that are biologically active and resistant to further ozonation is a concern (Radjenovic et al., 2009). Likewise, a major concern for treating pharmaceuticals by chlorination is the formation of chlorinated byproducts that may be more toxic than the parent compounds (von Gunten et al., 2006). High UV radiation doses (20–100 times the typical disinfection dose) are often required to effectively degrade antibiotics in wastewater effluent due to the presence of dissolved organic carbon (Adams et al., 2002; Kim et al., 2009). In NF/RO filtration, fouling by the buildup of precipitated chemicals or microbial biomass and membrane degradation due to exposure to residual chlorine can impact rejection of some antibiotics (Simon et al., 2009). Adsorption capacity of 1–2 mmoL/g of nitroimidazoles on activated carbon was reported (Rivera-Utrilla et al., 2009). In general, non-polar antibiotics can be effectively removed with activated carbon by hydrophobic interactions but the adsorption of more polar and charged compounds on these materials is much more difficult to predict (Le-Minh et al., 2010). Other methods of antibiotic removal reported in the literature include photodegradation with UV/catalysts or Fenton's reagent (Elmolla and Chaudhuri, 2010; Gonzalez et al., 2007), adsorption by carbon nanotubes (Wang et al., 2010) or clays (Avisar et al., 2010), and ion exchange (Bajpai and Bhowmik, 2011), and each has its limitations.

Since adsorption is one of the most promising methods for separation of various water pollutants, the objective of this paper was to evaluate sewage and waster oil sludge-derived materials as antibiotic removal media. Two anticonvulsants (carbamazepine and primidone) that are barely removed during wastewater treatment were also included here, as adsorption might be an effective method of their separation. The sludge-derived materials were shown previously as excellent adsorbents of dyes (Seredych and Bandosz, 2007). Taking into account the similarity in the sizes and chemistries of dyes and antibiotics, we hypothesized that the surface of sludge-derived carbonaceous adsorbents would also be active to retain antibiotics. We measured the adsorption capacities and linked them to the specific surface features of adsorbents and to the properties of adsorbates. Finding applications of the sludge-derived materials as adsorbents is an important issue from the point of view of environmental remediation. The process applied has the potential of turning hazardous wastes to adsorbents that could be used in wastewater and drinking water treatment.

2. Materials and methods

2.1. Adsorbents

The materials used in this study were described previously (Seredych and Bandosz, 2006, 2007). They were obtained by pyrolysis of industrial waste oil sludge (WO) from Newport News Shipyard, dewatered sewage sludge from Wards Island Water Pollution Control Plant (SS), or their mixtures (SSWO, 50:50 ratio based on the wet mass), at 950 °C or 650 °C in a nitrogen atmosphere in a fixed bed (horizontal furnace). The materials are referred to as SS, WO and SSWO based on their composition, followed by 950 or 650 reflecting the pyrolysis temperature.

2.2. Characterization of adsorbents

Textural characterization was carried out using nitrogen adsorption–desorption isotherms (ASAP 2010, Micromeritics) at −196 °C. The isotherms were used to calculate the specific surface areas, micropore volumes, mesopore volumes, total pore volumes, and pore size distributions. The latter was determined using the BJH method.

Potentiometric titration measurements were performed with a DMS Titrino 716 automatic titrator. The instrument was set in the equilibrium mode when the pH was collected. Each sample was titrated with 0.1 M HCl. Experiments were carried