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Research paper

Adsorption of bisphenol A and ciprofloxacin by palygorskite-montmorillonite: Effect of granule size, solution chemistry and temperature

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ABSTRACT

Adsorption and desorption studies of the endocrine-disrupting compound, bisphenol A (BPA), and the antibiotic ciprofloxacin (CIP) with palygorskite-montmorillonite (Pal-Mt) granules (0.3–0.6 mm, 1.7–2.0 mm and ≈2.8 mm), were done as a function of solution chemistry, temperature, and particle size. The data best fit the Langmuir adsorption model with the smallest and the largest granule sizes, respectively, exhibiting the highest (in mg kg^{-1}, $q_m = 77.3$ for BPA; $q_m = 107{,}000$ for CIP) and the lowest ($q_m = 41.0$ for BPA; $q_m = 81{,}000$ for CIP) adsorption capacities. CIP adsorption was strongly pH dependent, while BPA adsorption was slightly pH and ionic strength dependent. Thermodynamic parameters indicated BPA and CIP adsorption were spontaneous. Net-adsorption-desorption hysteresis were indicative of irreversible adsorption. FTIR and thermogravimetric analysis (TGA) data corroborate the mechanisms and the level of adsorption for CIP but not for BPA. The smallest and the medium granule sizes, respectively, are appropriate for potential BPA and CIP removal.

Capsule abstract: BPA and CIP adsorption-desorption data was granule size, experimental pH, ionic strength, and temperature dependent. Adsorption-desorption hysteresis indicated irreversible adsorption.

1. Introduction

Contamination of water resources by pharmaceuticals and endocrine disrupting compounds (EDC) is widespread (Kolpin et al., 2002; Lapworth et al., 2012). Multiple sources of these compounds are known with sewage treatment plants (STP) representing the main gateway to the natural environment (Lapworth et al., 2012). Treatment technologies are inefficient and consequently STP often fail to remove most of these compounds (Kolpin et al., 2002; Zhang et al., 2008; Lapworth et al., 2012). Once discharged from a STP, contamination of surface water by these compounds poses acute and chronic health risks to aquatic organisms and a potential human health concern through induced infiltration of surface water to municipal groundwater supplies (Lapworth et al., 2012).

Bisphenol A (BPA), a petrochemical product and a basic monomer used for synthesis of epoxy and polycarbonates, is one of the four most frequently detected EDC in the environment (Seyhi et al., 2011; Lapworth et al., 2012; Liao et al., 2012). Due to the ineffectiveness of various sewage treatment procedures and a longer half-life than other natural estrogens, the rate of BPA addition to the natural environment far exceeds its degradation rate (Flint et al., 2012; Li et al., 2013). The reported concentrations detected in the environment could potentially interfere with the endocrine systems of organisms (Mohapatra et al., 2010; Seyhi et al., 2011).

Ciprofloxacin (CIP), a fluoroquinolone antibiotic and a metabolite of enrofloxacin used to treat bacterial infection, is another organic compound that has been extensively used and widely detected in the environment (Kolpin et al., 2002; Chen et al., 2013). CIP could have an imminent and a pronounced environmental impact due to its effectiveness in suppressing microbial activities, thereby potentially hindering vital microbial ecosystem functions such as nutrient cycling and contaminant degradation (Kuemmerer, 2009). Moreover, CIP in the environment could increase the antibiotic resistance of pathogenic organisms (Kuemmerer, 2009; Wu et al., 2010; Peng et al., 2014).

Adsorption is one of the main treatment mechanisms employed in sewage- and drinking-water-treatment plants due to its low cost, simplicity and effectiveness (Pan et al., 2008; Zhou et al., 2012). Previous studies have investigated various potential alternatives to achieve higher removal rates at STP (Xu et al., 2012; Li et al., 2014). This includes but not limited to the use of carbon nanomaterials for BPA and estradiol removal where adsorption was significantly specific surface area-dependent with higher adsorption capacity for BPA than for estradiol (Pan et al., 2008). Graphene was found to be the most promising

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adsorbent for BPA among other carbonaceous materials (Xu et al., 2012). Moreover, the highest adsorption capacity for CIP was by single wall carbon nanotubes as compared to other functionalized carbon nanotubes (Li et al., 2014). However, most of these and other sewage treatment materials studied, however, are either expensive or require a long and costly pre-processing procedures and/or the need to synthesis artificial materials under complicated and often expensive laboratory settings (Pan et al., 2008; Xu et al., 2012; Li et al., 2014). Consequently, studies using readily available materials are needed to develop ways of removing compounds by a STP. One natural adsorbent with a documented record of applicability as an excellent adsorbent for various organic compounds including tetracycline (Chang et al., 2009a) and p-nitrophenol (Chang et al., 2009b) is palygorskite (Pal). Montmorillonite (Mt) with expandable layer structure containing variable amount of exchangeable cations and water molecules that imparts a high adsorption capacity for different ions, inorganic and organic molecules (Zhang et al., 2010) is another clay mineral that has been used for removing various emergent contaminants of concern including carbamazepine (Zhang et al., 2010) and tetracycline (Wu et al., 2016). The advantage of using the Pal-Mt mix is that it can be granulated into various size fractions to optimize effluent flow while maximizing contaminant removal (Nasedkin et al., 2009; Berhane et al., 2015). In addition, Pal compared to other clay minerals has a high mechanical strength and has the unique property in that upon heating above 300 °C, the modular structure of the particles folds, collapsing the zeolite-like tunnels; then the structure can go back to its original form when it is allowed to cool down (Haden and Schwint, 1967). This process maintains its crystalline structure before and after the adsorbed organic contaminant is oxidized through heating. Hence, a natural Pal-Mt mixture represents an inexpensive and potentially recyclable sewage effluent treatment material.

The adsorption of carbamezapine, structurally a substituted urea compound neutral in charge at pH 7, by Pal-Mt was previously found to be significant (Berhane et al., 2015). However, the adsorption of other organic compound structure types by Pal-Mt have not been studied. BPA is a neutral aromatic hydrocarbon with no nitrogen atoms and also neutral in charge at pH 7. CIP is an aromatic amine which is a monocation at pH 7. The objectives of this study, therefore, are to investigate the efficacy of a Pal-Mt clay mix as STP filter material for BPA and CIP, two compounds that have basic structural features common to many pollutants, particularly pharmaceuticals. Adsorption/desorption experiments under a variety of STP conditions (varying temperature, pH and ionic strength) are described to ascertain the feasibility of three different Pal-Mt granule sizes for potential use as alternative (Supplementary) STP treatment technology.

2. Materials and methods

2.1. Material characterization

A bulk sample of mixed granule sizes of natural Pal-Mt was obtained from Oil-Dri Corporation of America®. The material was sieved to separate the sample into Pal-Mt granules of three different sizes: 0.6 mm, 1.7–2.0 mm and ≈2.8 mm. Previously an extensive qualitative and quantitative characterization of the physicochemical properties, the mineralogy and the particle morphology of the three Pal-Mt granule sizes used in this study has been published (Berhane et al., 2015). Accordingly, the surface area of the three granules determined by BET N_2-adsorption-desorption experiments at 77 °K using an Accelerated Surface Area and Porosimetry (ASAP) System® were 104.4 $m^2\ g^{-1}$, 130.3 $m^2\ g^{-1}$, and 127.7 $m^2\ g^{-1}$, for the smallest, medium and largest granule sizes, respectively.

Smear mount and powder X-ray diffraction (XRD) patterns of unmodified Pal—Mt and, Pal-Mt samples with adsorbed BPA and CIP at different concentrations were collected on Scintag × 1 X-ray powder diffractometer with Cu Kα radiation (lambda, $\lambda = 1.54$ Å), a fixed slit scintillation detector, and a power of 1400 W (40 kV, 35 mA). Samples were scanned from 2 to 40° 2θ. Minerals present in the samples were identified using the Jade 7 program® by comparing XRD patterns of commonly found minerals with the International Center for Diffraction Data (ICDD) Powder Diffraction File database (ICDD PDF-2, Sets 1–46, 1996).

2.2. Chemicals

BPA and CIP have different adsorption properties based on their physicochemical characteristics which, in turn, affect their fate in a STP and in the natural ecosystem (Table 1).

Bisphenol A (4,4′-(propane-2,2-diyl)diphenol, $C_{15}H_{16}O_2$, CAS # 80057) and ciprofloxacin hydrochloride ($C_{17}H_{18}FN_3O_3HCl{\cdot}H_2O$, CAS # 86393-32-0) with purity >98% and >99.5%, respectively, were purchased from Sigma-Aldrich® (Milwaukee, WI). Calcium chloride dihydrate ($CaCl_2 2H_2O$, CAS # 10,035–04-8) with purity >99%, sodium azide (NaN_3, CAS # 26628-22-8) with purity >99%, methyl alcohol (CH_4O, CAS # 67-56-1) with purity >99.9%, and HPLC-grade acetonitrile (C_2H_3N, CAS # 75-05-8) and water (CAS # 7732-18-5) were purchased from Fisher Scientific® (Hanover Park, IL). All other reagents and chemicals used were analytical grade.

2.3. Batch adsorption and desorption hysteresis experiments

Three Pal-Mt granule sizes were used for batch equilibrium adsorption experiments. Standard working and control solutions were prepared from 0.01 to 10 mg L^{-1} for BPA and from 100 to 1500 mg L^{-1} for CIP; these correspond to the initial aqueous concentrations, C_0. The background solution contained 10 mM $CaCl_2$ to maintain a constant ionic strength (IS) and 1.5 mM NaN_3 to suppress any microbial activity. The experiments were conducted in 50 mL Oak Ridge Teflon® centrifuge tubes where 25 mL of working solution were used with 3.0 g for BPA and 0.2 g for CIP. Following Organization for Economic Cooperation and Development guidelines (OECD, 2000), each concentration was run in duplicate including blank and control samples. The samples were centrifuged at 5000 rpm for 10 min and 1 mL of the supernatant was taken for determination of aqueous BPA or CIP analyte concentrations following >48 h of equilibration with the use of a mechanical shaker at 150 rpm. Half of the volume of the original supernatant was then replaced with the analyte-free background solution. Mass balance was used to compute the amount of adsorbed/desorbed analyte concentrations. For the pH-effect adsorption experiments, 3.0 g and 0.1 g quantities of Pal-Mt were mixed with 10 mg L^{-1} and 500 mg L^{-1} solutions of BPA and CIP, respectively. The pH was adjusted between 1.5 and 11.5 at 1-pH-unit increments using 100 mM NaOH and H_2SO_4. Similarly, the adsorption isotherm behavior at different ionic strengths using 0, 10 and 100 mM $CaCl_2$ solutions was studied for BPA. No such experiments were conducted for CIP due to possible precipitation by the high CIP concentrations in the working solutions. Adsorption isotherms were also developed at 25, 60 and 75 °C for BPA and at 25, 40 and 65 °C for CIP. Except for the temperature-effect experiments, all experiments were conducted at room temperature with working solutions and reaction tubes covered with aluminum foil to avoid photo-degradation of the compounds.

2.4. Analytical methods

The equilibrium aqueous concentration of BPA was analyzed using high-performance liquid chromatography (HPLC) with UV detection. Details of the instrument setup are explained in the paper by Berhane et al. (2015). In brief, a LiChrospher® HPLC column RP-18, 5 μm particle size, 25 cm × 3.2 mm ID (Sigma Aldrich®, Milwaukee, WI) was used for all separations. Respectively, the mobile phase, eluent flow rate, injection volume and detection wavelength were 60:40 (acetonitrile: water), 1.0 mL min^{-1}, 50 μL and 280 nm (Figs. S1 & S2). CIP was

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