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Anaerobic digestibility of estrogens in wastewater sludge: Effect of ultrasonic pretreatment

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ABSTRACT

Background: Estrogenic compounds have been detected in the secondary effluents and in the biosolids from conventional wastewater treatment plants, which are not designed for their removal. Furthermore, existing limited studies on anaerobic digestibility of estrogens report conflicting results. The objective of the present work was to determine the fate and anaerobic digestibility of estrogenic compounds in various types of sludge including primary sludge (PS), waste activated sludge (WAS), and anaerobically digested sludge (seed).

Methods: Estrone (E1) and 17-β estradiol (E2) were chosen as the model estrogenic compounds. Initially batch adsorption was conducted to determine the extent of adsorption and isotherm of E1 on various sludge. Thereafter, batch anaerobic digestion of E1 and E2 was conducted in various sludge using So/X ratio of 4 gCOD/gVSS in 250 ml bottles. The effect of earlier optimized ultrasonication dosage on the anaerobic digestion of E1 and E2 was also characterized. Estrogenicity of the digested samples was determined by the YES assay.

Results: Most of E1 and E2 was adsorbed on the biosolids and the Freundlich isotherm fitted the experimental data well. No anaerobic digestion of E1 and E2 was found in any of the sludge tested, and the estrogenicity of the sludge measured by YES assay increased during digestion due to the formation of E2 from E1 in a reduced environment. Ultrasonication decreased the initial mass of E1 and E2 by 20% in the sonicated digester as compared to control digester, however, there was no further decrease in E1 and E2 during digestion.

Conclusions: Most of the estrogenic compounds partitioned onto the solids and remained there during digestion. Ultrasonication pretreatment reduced the estrogen burden for the digester due to advance oxidation, but no further removal of the estrogens occurred in the digester.

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1. Introduction

Natural estrogens such as estrone (E1), 17-α, β estradiol (E2) and estriol (E3) and synthetic estrogen17-α-ethinylestradiol (EE2) are "emerging contaminants" and endocrine disrupting chemicals (EDCs). They have been detected in trace concentrations in surface waters mostly due to the effluents from conventional wastewater treatment plants, which are not designed for their removal)(Andersen et al., 2003). Ternes et al. (1999) reported 0.015 μg/L and 0.027 μg/L of 17β-estradiol and estrone, respectively in the effluents of wastewater treatment plant (WWTPs), whereas, estrogen content in primary sludge and waste activated sludge has been reported to be around 83 ng/l (Andersen et al., 2003) and 1–70 ng/l (Desbrow et al., 1998), respectively. Estrogens were found to affect the regional fauna and induce hormonal changes in aquatic organisms such as male rainbow trout (Desbrow et al., 1998). Besides wastewater effluents, natural estrogens had been detected in considerable amounts in anaerobically digested biosolids generated from WWTP (Citulski and Farahbakhsh, 2010). With low Henry's constants (e.g., 3.8×10^{-10} atm m^3/mol for E1) and high log K_{ow} values (3.13 for E1, 4.01 for E2, and 2.45 for E3 (Lai et al., 2000; Hansch et al., 1995)) estrogenic compounds sorb on the solid fractions of wastewater and accumulate on primary sludge (PS) and waste activated sludge (WAS).

Anaerobic digestion is one of the most economically viable stabilization processes to treat PS and WAS prior to their disposal or further use. With significant amount of nutrients present, land application of digested sludge (biosolids) has become more

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common in many countries around the world (Apedaile, 2001). However, the presence of recalcitrant compounds such as natural and synthetic estrogens in biosolids may restrict their land application. Studies conducted on the anaerobic digestibility of estrogens so far have produced contradictory results. For example, Carballa et al. (2006) reported 85 ± 10% removal of estrone+17-β estradiol, and ethinylestradiol at influent concentrations ranging from 4 to 400 μg/L, in a pilot scale anaerobic digester operated at sludge retention times of 20 and 10 days at mesophilic and thermophilic conditions, respectively. Contrary to the above, Czajka and Londry (2006) observed no anaerobic degradation of 5 mg/L of EE2 for an incubation period of 3 years in a lab scale study. These authors also observed reversible inter-conversion between E1 and E2 and racemization of E1 into 17α estradiol, a stereo-isomer of 17β estradiol with 30 times less estrogenic activity (Huang et al., 2010). It was also reported that estrogens have the potential to be recalcitrant in anoxic sediments (Czajka and Londry, 2006). de Mes et al. (2008) did not observe any decline in E1, E2 (spiked initial concentration of 5 mg/L) in an upflow anaerobic sludge blanket (UASB) system, digesting pig manure, and activated sludge after 45–205 days of incubation. The contradictory findings in literature indicate that the anaerobic digestibility of estrogens under controlled conditions instead of pilot scale, merits further investigation.

Many pretreatment methods such as chemical addition (alkaline and acidic), thermal, mechanical, ultrasonic, or the combination of different pre-treatment methods were studied to improve anaerobic digestion by enhancing chemical oxygen demand (COD) solubilization, solids destruction, and biogas production (Aldin et al., 2010). Ultrasonication was demonstrated to improve VS reduction (38%–50%), gas production, and dewaterability of anaerobic sludges in full scale studies (Hogan et al., 2004). Improvement in the anaerobic digestibility using ultrasonication was attributed to particle disintegration and solubilization of complex organic matter (Tiehm, 1999). The effects of ultrasonication on environmental pollutants such as chlorobenzene, 4-chlorophenol, benzene, ethylbenzene and styrene (Petrier et al., 1998; Ragaini et al., 2001; Goel et al., 2004), 2 chlorophenol and tri-halomethanes (Shemer and Narkis, 2005) were studied earlier. Tiehm (1999) reported an enhancement in biodegradation of sonochemical products of phenanthrene and naphthalene via their transfer to the aqueous phase. Sonication produces extreme chemical and physical environment by implosion of cavitation micro-bubbles, which degrade complex molecules either by thermal disintegration, or by reaction with hydroxyl radicals, or by the combination of both. Our previous research had shown the beneficial effects of ultrasonic pretreatment on anaerobic digestion of primary and waste activated sludge and hog manure (Aldin et al., 2010; Elbeshbishy et al., 2011). Based on total suspended solids concentration of the sludge, there was an optimum ultrasonication energy, beyond which the beneficial effect of ultrasonication was not economically viable. Although, ultrasonic and advanced oxidative degradation of E1 in pure water was earlier reported by Cui et al., (2010) and Suri et al. (2007), an extensive literature search indicated that no studies were conducted on the effect of ultrasonic pretreatment on anaerobic digestibility of estrogenic compounds.

Therefore, the objective of the present work was to determine the fate and anaerobic digestibility of estrogenic compounds in various types of sludge including primary sludge (PS), waste activated sludge (WAS), and anaerobically digested sludge (seed). Estrone (E1) and 17-β estradiol (E2) were chosen as the model estrogenic compounds. E1 is a secondary metabolite of E2 and E2 has the highest estrogenic potential amongst the natural estrogens. Both are poorly removed in conventional wastewater treatment plant (Khanal et al., 2006). Anaerobic digestion of E1 and E2 was conducted using PS, WAS and anaerobic digester sludge, and the concentrations of E1, E2, and estriol (E3) were monitored during digestion. The effect of earlier optimized ultrasonication dosage (Aldin et al., 2010; Elbeshbishy et al., 2011) on the anaerobic digestion of E1 and E2 was characterized. Furthermore, estrogenicity of the digested samples was determined by YES assay as described by Routledge and Sumpter (1996).

2. Materials and methods

E1, E2, and E3 were obtained from Sigma Aldrich (Oakville, ON, Canada) with 98% purity. All organic solvents such as acetone (distilled-in-glass grade), methanol (distilled-in-glass grade), ethyl acetate (HPLC grade), dichloromethane (HPLC grade), mirex (internal standard) were obtained from Caledon Laboratories (Georgetown, ON, Canada). Derivatization agents N, O-Bis (Trimethylsilyl) trifluoroacetamide (BSTFA) and pyridine were obtained from Supelco (Oakville, ON, Canada) and Caledon Laboratories (Georgetown, ON, Canada), respectively. Ultrapure water (conductivity of 18Ω) was obtained from Millipore water systems (Billerica, MA). Supelclean™ ENVI-18 SPE cartridge (from Sigma Aldrich, ON, Canada) tube with bed wt of 500 mg and a volume of 3 ml was used for extraction of estrogen.

PS and WAS were collected from the Adelaide Pollution Control plant located in London (ON, Canada) and stored at a temperature of 4 °C prior to use. Anaerobic inocula (digester sludge) were collected from the primary anaerobic digester at the St Mary's (Ontario, CA) wastewater treatment plant.

3. Analytical methods

All water quality parameters were analyzed according to the standard APHA methods (APHA, 1998). Soluble parameters were analyzed after filtering the samples through 0.45 μm membrane filters. HACH vials were used to measure the total and the soluble chemical oxygen demand (TCOD and SCOD) in a HACH reactor, while pH and ORP were measured using Oakton pH meter and ORP meter (Eutech instruments, IL, USA), respectively. Biogas production was measured by releasing gas pressure in the vials using glass syringes (Perfektum; Popper and Sons Inc. NY, USA) to equilibrate with the ambient pressure (Owen et al., 1979). Biogas composition was determined by a gas chromatograph (Model 310, SRI Instruments, Torrance, CA) equipped with a thermal conductivity detector (TCD) and a molecular sieve column (Molesieve 5A, mesh 80/100, 182.88 × 0.3175 cm).

Solid phase extraction (SPE) was used to extract E1 and E2 for analysis in water. The digested sludge samples were centrifuged at 4000 *g* for 10 min (Sorvall RC 5B Superseed Centrifuge, DU Pont Instruments, and USA). The samples were then filtered through 0.45 μm glass microfiber binder free filter papers (Whatman, GE Health care, USA), subsequently the filtrate was passed through Envi18 SPE cartridges at an optimized flow rate of about 1 ml/min. The SPE extract was concentrated (Turbo Vap II, Caliper Life Sciences, MA, and USA) under a gentle stream of nitrogen at 45 °C and 11–12 psi. The extracted sample was subjected to solvent exchange with dichloromethane (DCM) and concentrated further to 0.5 ml, which was reconstituted to 1 ml using DCM, and used for derivatization prior to injection in the GC–MS. The recovery from the SPE cartridges was determined by direct injection of the known mass of estrogenic compounds in stock solution after solvent extraction and derivatization. The recovery varied from 67% to 80% depending on the sample flow rate of 1–4 ml/min, with the highest recovery occurring at 1 ml/min.

The solids of the sludge samples were extracted using Soxhlet extractor. The solid phase was frozen (−20 °C) for 1 day, and then it was lyophilized for 48 h to remove moisture in the solids. About

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