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PAH removal from spiked municipal wastewater sewage sludge using biological, chemical and electrochemical treatments

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) have been widely studied due to their presence in all the environmental media and toxicity to life. These molecules are strongly adsorbed on the particulate matters of soils, sludges or sediments because of their strong hydrophobicity which makes them less bioavailability, thus limiting their bioremediation. Different sludge treatment processes were tested to evaluate their performances for PAH removal from sludge prealably doped with 11 PAHs (5.5 mg each PAH kg^{-1} of dry matter (DM)): two biological processes (mesophilic aerobic digestion (MAD) and simultaneous sewage sludge digestion and metal leaching (METIX-BS)) were tested to evaluate PAH biodegradation in sewage sludge. In parallel, two chemical processes (quite similar Fenton processes: chemical metal leaching (METIX-AC) and chemical stabilization (STABIOX)) and one electrochemical process (electrochemical stabilization (ELECSTAB)) were tested to measure PAH removal by these oxidative processes. Moreover, PAH solubilisation from sludge by addition of a nonionic surfactant Tween 80 (Tw80) was also tested. The best yields of PAH removal were obtained by MAD and METIX-BS with more than 95% 3-ring PAH removal after a 21-day treatment period. Tw80 addition during MAD treatment increased 4-ring PAHs removal rate. In addition, more than 45% of 3-ring PAHs were removed from sludge by METIX-AC and during ELECSTAB process were quiet good with approximately 62% of 3-ring PAHs removal. However, little weaker removal of 3-ring PAHs (<35%) by STABIOX. None of the tested processes were efficient for the elimination of high molecular weight ($\geqslant$5-ring) PAHs from sludge.

Keywords: Sewage sludge; PAH; Leaching; Surfactant; Chemical oxidation; Biodegradation

1. Introduction

Sewage sludge is an end product of wastewater treatment process. For instance, using the stabilized sludge as a fertilizer can benefit the environment with turning the wastes into valuable resources (Duvaud et al., 1999; USEPA, 1999). However, certain pathogens, inorganic and organic toxics present in the sewage sludge may threaten crop yields, long term soil quality, cattle and wildlife health, and eventually human health (Gardiner et al., 1995; Lee et al., 1996).

Risks associated to pathogens in sewage sludge, such as bacteria, viruses, parasites, can be reduced, for example, by biological or chemical stabilization techniques (USEPA, 1999; Spinosa and Vesilind, 2001). Moreover, many remediation methods for heavy metals removal from sludge have been proposed in the last 15 yr (Mercier et al., 2002; Chan et al., 2003). However, the removal of persistant organic pollutants (POP) is much more difficult because of their stable physical and chemical properties.

PAHs are an important class of the POP in causing environmental problems due to their high potential of toxicity, mutagenicity, and carcinogenicity to mammals and aquatic organisms (Wilson and Jones, 1993; Mangas et al., 1998). The United States Environmental Protection Agency (USEPA) has specified 16 main PAHs as priority pollutants because of their known toxicity to mammals and

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aquatic organisms (USEPA, 1987). Currently, the PAH concentration limitations in sewage sludge were not released and enforced in North America but only they are in a few European countries. In 2000, a release of the draft by the European Union (EU) imposed the maximum concentration of 11 main PAH [1] compounds in sewage sludge could not exceed 6 mg kg^{-1} of dry matter (DM) if the sludge is designated to be applied on agricultural land (EU, 2000). Therefore, the accurate determination of PAH concentrations in sewage sludge has become a closely relevant topic.

Even though PAHs are considered among the most difficult POP to be treated because of their highly stable physical–chemical characteristics and frequent occurrences (Volkering and Breure, 2003), different approaches have been studied for the removal of PAHs from contaminated soils or solid wastes in the past few years: biodegradation (Cerniglia, 1993; Chang et al., 2002), chemical oxidation (Flotron et al., 2003; N'Guessan et al., 2004) and photodegradation (Miller and Olejnik, 2001); moreover, some extraction methods using surfactants have been successfully applied for remediation of PAH-contaminated soils or sediments (Li and Chen, 2002; Zhou and Zhu, 2005). There are also a few studies for PAH removal form sludge: anaerobic PAH degradation in sludge (Christensen et al., 2004), biodegradation in aerobic processes treating urban sludge (Trably and Patureau, 2006). In addition, the influence of process parameters such as pH, ionic strength, organic matter content and temperature have been investigated: Schlautman and Morgan (1993) reported a decrease in the binding of PAHs with particular humic material (well-characterized) when the pH was increased in NaCl solutions and also general decrease with increasing ionic strength when the pH was fixed (Schlautman and Morgan, 1993); PAH binding to dissolved organic matter from different soils has been studied in detail by Raber and his co-workers (Raber et al., 1998) and PAH adsorption in soil was higher in lower pH and /or lower temperature concondition was also discussed (Ping et al., 2006).

The aim of this study is to evaluate the potential of different sludge treatment processes for the removal of PAHs from municipal sewage sludge. This notably includes two biological methods (mesophilic aerobic digestion (MAD) and METIX-BS (Tyagi et al., 1995; Blais et al., 2004)), two chemical oxidation processes (METIX-AC (Mercier et al., 2002; Blais et al., 2005) and STABIOX (Blais et al., 2003)) and one electrochemical process ((ELEC-STAB) (Drogui et al., 2005)) were investigated for PAH degradation. The effect of a nonionic surfactant (Tween 80 (Tw80)) on the solubilization and PAH removal in sewage sludge was also explored.

[1] 11 PAHs: acenaphthene (ACN), phenanthrene (PHE), fluorene (FLU), fluoranthrene (FLR), pyrene (PYR), benzo(b,j,k)fluoranthene (BJK), benzo(a)pyrene (BAP), indeno(1.2.3-cd)pyrene (INP) and benzo(ghi)perylene (BPR).

2. Materials and methods

2.1. Sewage sludge sampling and characteristics

Biological sewage sludge (from sequential batch reactor) was collected from the municipal wastewater treatment plant of Haute-Bécancour (Black Lake, QC, Canada) in May 2005, and stored in a polypropylene container at 4 °C. Total solids (TS) content of the sludge was adjusted to 18.0 or 30.0 g l^{-1} for all experiments. Eleven main PAH concentractions (mg kg^{-1} DM) in the sewage sludge ranged as follows: ACN (0.057 ± 0.002), FLU (0.062 ± 0.002), PHE (0.228 ± 0.012), FLR (0.529 ± 0.034), PYR (0.557 ± 0.044), BJK (1.223 ± 0.102), BAP (0.428 ± 0.050), INP (0.643 ± 0.042), BPR (0.568 ± 0.027), total 11 PAHs (4.294 ± 0.292). These PAH levels were less than the limitation of EU. Therefore, the doped sludges were used in this study.

2.2. Procedure of sludge PAH-spiking

Before experiments, the sludge was spiked with 5.5 mg kg^{-1} DM of each of 11 PAHs by adding standard solutions Mix 44 (1000 mg l^{-1} in CH_2Cl_2–benzene) and benzo(*j*)fluorantene (2000 mg l^{-1} in CH_2Cl_2–benzene). The sludge was successively mixed by being vigorously stirred (Mechanical shaker, Lab-Line Environ-Shaker, model 3528) for at least 1 h at room temperature (r.t., 20 ± 2 °C) and then kept at 4 °C for 24 h.

2.3. Sludge treatments

During and after treatment processes, sludge samples (300–600 ml) were taken and separated by centrifugation (2050 *g* for 30 min, Beckman Coulter Inc., modèle Allegra™ 6 centrifuge) or vacuum filtration (Whatman no. 4 membrane, pore size: 15–20 μm) into solid and liquid phases. PAH extraction and purification steps were carried out in triplicate on each solid and liquid phase.

2.3.1. Control assays

At first, to illustrate the PAH removal efficiency by different treatments, two control tests were carried out using 2 vol. of approximately 2 l of sludge. The first control was prepared by using the prealably doped but no treated sludge (DOC). A second control was prepared using sterilized (autoclaving under 103 kPa at 121 °C for 15 min) sludge (DAC). The sterilized sludge was averaged poored over four 1 l Erlenmeyer flasks and was aseptically doped according to the procedure previously described. The doped sludge in one flask (DAC-0) was separated into solid and liquid phases by centrifugation. Both phases were used for PAH extraction and analysis. The other three flasks were kept at r.t. for 7, 14 and 21 d (DAC-7, DAC-14 and DAC-21), respectively before separation into solid and liquid phases. Each treatment and PAH extraction and purification on