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Advanced biological treatment and separation of hazardous constituents from petrochemical sludges*

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Abstract

A highly carcinogenic nature, low allowable release concentrations, and ongoing accumulation in land/water ecosystems all contribute to the fact that many sites on the National Priorities List (NPL) established by EPA name polynuclear aromatics (PNAs) as contaminants. High costs and deficient available capacity associated with incineration technology motivates investigation of bioremediation as a treatment alternative. Biodegradation of benzo [a] pyrene found in oil refinery and petrochemical plant sludges has been studied using a continuous flow stirred tank reactor. Evaluation of microbial growth showed that the Monod growth model was most appropriate with kinetic coefficients indicating microbial populations are capable of performing similar to that found in conventional suspended growth waste treatment systems.

Introduction

The application of biological processes for the treatment of organic sludges and contaminated soils is a promising new technology which offers an alternative to incineration as a method of destroying or altering hazardous constituents. The process also reduces the toxicity and migration potential of many organic compounds present in petrochemical and other industrial wastes. The development of alternative technologies for treatment of petrochemical wastes is necessary for several reasons, including the Resource Conservation and Re-

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covery Act, which regulates the management of hazardous wastes and requires that land disposal for several waste streams cease after given dates unless treatment standards for the wastes have been met. Similarly, the amendments to the National Contingency Plan (the "Superfund" directives) mandate that the remedial action alternative chosen at cleanup sites reduce the "volume, toxicity and mobility" of the wastes, and also that the alternative be cost-effective, permanent, and acceptable to the public, to the maximum extent possible.

The scope of this research is to study the biodegradation and partitioning of polynuclear aromatics (PNAs) contained in petrochemical sludges treated in continuous flow stirred tank reactor (CSTR) systems. Benzo([a]pyrene is targeted as a key PNA of interest due to its highly carcinogenic nature and its extremely low allowable release concentrations in sludges. The goal is to develop engineering parameters for design of treatment systems which will be more effective than existing alternative technologies in reducing accumulations of persistent hazardous compounds at waste disposal and Superfund sites.

Background

Deposition rates of PNAs from all sources are exceeding the natural destruction rates by microbial decomposition and photo-oxidation, and accumulations of these compounds in the land/water ecosystems are ongoing [1]. The majority of the accumulations are from anthropogenic sources and contain the semi-volatile condensed 4 and 5 aromatic ring compounds. Five of these PNA's are considered by the Environmental Protection Agency (EPA) to be carcinogens and include: benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[a]pyrene (BaP), chrysene, and dibenzo[a,h]fluoranthene. Benzo[a]pyrene is considered strongly carcinogenic based on cancers induced in small animal laboratory experimentation [2]. These compounds are typically solids at ambient temperatures, and are characterized by their high organic partition coefficients, very low aqueous solubility, low vapor pressures and tendency to bioaccumulate in the natural environment.

The Environmental Protection Agency has developed a listing of national sites containing hazardous materials and has established an order of priority for cleanup of these sites — the National Priorities List (NPL). Many of these sites are contaminated with PNAs. The EPA Office of Emergency and Remedial Response (OERR) has the responsibility for developing treatment strategies which can be applied to these sites. Three basic treatment mechanisms are favored by EPA [3]. The treatment options include: (a) destruction of the contaminant through chemical alteration to less toxic compounds (thermal destruction, dechlorination, and bioremediation); (b) transfer of the contaminants to other waste streams for subsequent treatment (low temperature thermal desorption, chemical extraction, and soil washing); and (c) contaminant

bonding to waste media (immobilization). The current preferred methodology is thermal combustion (incineration), but costs are high and available capacity falls far short of the accumulated and projected industrial production of hazardous wastes. The second choice is bioremediation where cost factors are low but biodegradation times are comparatively long. A bioremediation solution must insure that the contaminated soils or sludges are detoxified to permit safe release to the environment, and that all other products associated with the process such as recovered oils, surface scums, aqueous discharges, and decontaminated solids also meet current disposal regulations or are directed to further treatment.

Constraints on biodegradation and partitioning of BaP

Microbial populations which contain the genetic material to produce the necessary extracellular enzymes, will proceed to biodegrade some PNAs to phenols [4]. The biodegradation of the simpler aromatic compounds usually proceeds by: removal and hydrolysis of side chains, cleavage of the aromatic ring and, finally, degradation of the aliphatic side products. The strong bioresistance of BaP is attributed to the alignment of the condensed ring structure [5]. The bay region metabolic steps for BaP have been described by Dipple and are shown on Figure 1. The metabolic pathway proceeds through intermediate epoxide and dihydrodiol steps and the carcinogenic potential is expressed in the dihydrodiol epoxide. It is reported that no microorganism has been isolated that will grow exclusively on BaP, but both procaryotic and eukaryotic organisms will biodegrade low concentrations in the presence of a common growth substrate [6]. Unpublished data from EPA (OERR) showed that all reported successful biodegradation attempts used initial BaP substrate concentrations of < 20 mg/L.

The highest concentrations of BaP in waste accumulations typically are dissolved in organic solvents present in these wastes, with partitioning occurring

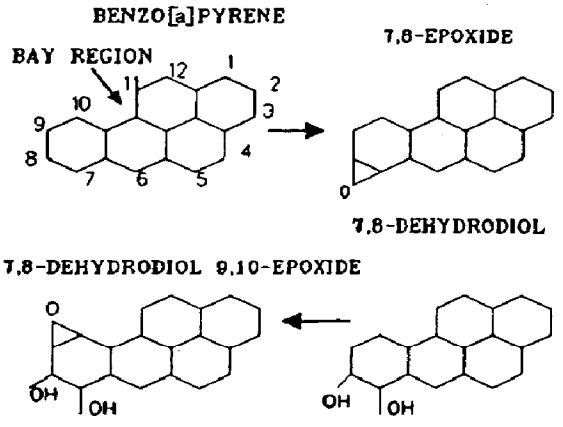

Fig. 1. Metabolism route for benzo[a]pyrene [5].

TABLE 1

Chemical properties of key polynuclear compounds[a]

Compound	Molecular weight (g/mol)	BP (°C)	MP (°C)	Density (kg/L)	Aqueous solubility (mg/L)	State (298 K, 1 bar)
Benzo[a]anthracene	252	437	162	1.274	0.014	Solid
Benzo[b]fluoranthene	252	–	168	–	0.014	Solid
Toluene	92	110	−95	0.87	515	Liquid
Benzo[a]pyrene	252	495	179	1.35	0.003	Solid
Dibenzo[a,h]anthracene	278	524	269	1.28	0.005	Solid
Pyrene	202	393	156	1.27	0.16	Solid
Naphthalene	128	218	81	1.16	30–134	Solid

[a]BP is boiling point at 1 bar; MP is melting point at 1 bar.

between the organic solvent phase, soil, and/or other solid particles present in sludges. The strong hydrophobicity of BaP prevents partitioning into aqueous solutions; solubility of BaP in water is reported at only 0.003 mg/L. The very low aqueous solubility of BaP reduces access of this complex molecule to microbial attack. A listing of the chemical properties of some key PNAs are shown on Table 1. The octanol–water partition coefficient (K_{ow}) is reported as 6.06; the organic carbon partition coefficient (K_{oc}) is reported as 5,500,000 mL/g [7].

Materials and methods

Characterization of oil refinery and petrochemical plant sludges

The two hazardous wastes selected for this study are sludges from American Petroleum Institute (API) separators. The first sludge was obtained from one of 16 API separators from a fully integrated crude oil refinery while the second sludge was obtained from an API separator in a petrochemical complex. The key properties of the two hazardous sludges used in the program are listed in Table 2.

TABLE 2

Properties of hazardous waste sludges (K051)

Property	Refining sludge	Petrochemical sludge
Density	1.87 g/mL	1.073 g/mL
Oil content	6.4% v/v	27.5% v/v
Oil density	0.85 g/mL	0.76 g/mL
Solids	30.1% w/w	10.5% w/w

The high solids (30% w/w) of the refinery sludge consists of granular sands. The oil concentration (6.4% v/v) is relatively low and the oil can be readily separated from the solids fraction. The petrochemical sludge, however, is characterized by a relatively high oil content (27.5% v/v). The solids content (10% w/w) is much lower in the petrochemical sludge than in the refinery sludge and exhibits a clayey consistency. Both sludges are from currently operating API separators and significant weathering has not occurred; thus, the oil densities are in the 0.76–0.84 g/ml range.

Experimental design for testwork in continuous reactors

The schematic design for the sealed continuous flow stirred tank reactor is shown in Fig. 2. The reactor consisted of a 2 liter capacity sealed reaction kettle where all joints were either teflon or ground glass. The reactor volume was maintained at one liter air headspace and one liter solid–liquid volume. Feed sludge, inorganic nutrients, and makeup water were added on a uniform chronological basis. Laboratory air was scrubbed to remove carbon dioxide (CO_2) and was pumped into the vapor space above the stirred liquid. A mixed liquor suspended solids (MLSS) recycle system permitted biomass recycle. An outlet foam trap ensured capture of any escaping organic compounds of interest. Uniform stirring was maintained throughout the testing period. The design shape of the reactor and designated mixing intensity, resulted in a relatively uniform distribution of the solids, and guaranteed that aerobic conditions prevailed throughout the liquid phase. The culture, however, has demonstrated a facultative capability, but biodegradation rates as expected have been much slower under anaerobic conditions. One of the four entry ports in the reactor cover was used for sampling of the reactor head space and the MLSS in the liquid/solids suspended growth system. When a continuous flow reactor system was determined to be in a state of equilibrium during a specific experiment, the reactor was completely disassembled and all vapor, liquid and solid phases in the reactor or downstream systems were tested quantitatively for BaP and other PNAs of interest.

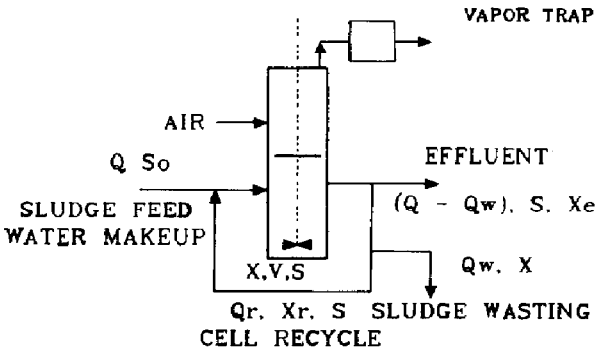

Fig. 2. Schematic of the experimental setup used in this study.

TABLE 3

Experimental design for testwork with refinery and petrochemical sludges

Parameter	Refinery	Petrochemical
Feed range, g/d	10–25	10–25
Sludge recycle, %	0– 0	0–15
Hydraulic detention, d	5–10	5–10
Mean cell residence time, d	5–15	5–15
MLSS, mg/L	5,000–10,000	10,000–15,000

The refinery sludge was used initially as feedstock in the first phase of the testwork and the petrochemical sludge was used in the second phase. The key reactor operating conditions are listed in Table 3 .

Feed rate variations were designed to incorporate changes of 100–250% v/v on the lowest rates and thus represent a meaningful change. The mean cell residence time (MCRT) for both test phases was set within the ranges for conventional activated sludge treatment plants (5–15 days), but the desired operational MCRT was 5–10 days, which is intended to emulate the performance of the high rate conventional treatment plants. Biomass recycle was not initiated on the refinery sludge reactors due to the low oil content in the feed but 5–10% cell recycle was used in the second phase.

The sampling programs undertaken on the suspended growth systems were designed to capture all of the PNAs present in any location in the sealed reactor systems. The polyurethane foam trap was designed to recover any PNAs escaping in the reactor vapor system. All clingage on the reactor walls, covers, and stirbars were carefully washed with methylene chloride solvent. The settleable solids consisting of the microbial culture and other solids were thoroughly extracted and then tested for the presence of PNAs. The sample recovery and analytical testing methods utilized EPA procedures (U.S. EPA 1986).

Microbial population stability

Microbial succession and effectiveness were evaluated using continuous flow complete mix reactors utilizing the sludges as feedstocks and monitoring the microbial population for any change in species composition and substrate removal effectiveness. Detailed methodologies for microorganism identification and enumeration, and metabolic activity have been presented elsewhere [9].

Results and discussion

The measurement of specific growth rates and substrate utilization rates were made during previous research activities [10,11] to describe critical microbial kinetic coefficients required for bench-scale reactor design. These in-

cluded the determination of specific growth rates, yield coefficients and half saturation constants. Evaluation of the microbial growth observed revealed that the Monod growth model was most appropriate of those examined. The kinetic coefficients revealed that the microbial populations are capable of performing similar to that required in conventional suspended growth waste treatment systems (i.e., activated sludge and its various modifications). Of particular importance is the maximum specific growth rate (7 per day at 20°C) which indicates that portions of, or all of, the microbial populations present can survive in conventional systems [10]. A half saturation constant of 14,000 mg/L indicates that attainment of low concentrations in the effluent streams should be difficult. As will be shown, this difficulty is not supported by continuous flow stirred reactor studies.

Microbial stability in terms of species present and numbers were described previously over the timeframe of one month [12]. No microbial species changes were observed after one month of continuous loading. Microbial stability was assessed over an eight-month operating period using pour plate techniques. Figure 3 shows that both the refinery sludge culture and petrochemical sludge culture possessed similar growth potential after eight months. Similar data are presented for colonies grown on their specific substrate. As can be seen in Fig. 4, petrochemical sludge microorganisms have developed a greater growth potential with time than the refinery sludge microorganisms, which show no change. The ability of the refinery sludge culture to grow on phenanthrene, benzo[a]anthracene and benzo[a]pyrene is presented in Fig. 5; the petrochemical sludge culture growth potential is presented in Fig. 6. The microor-

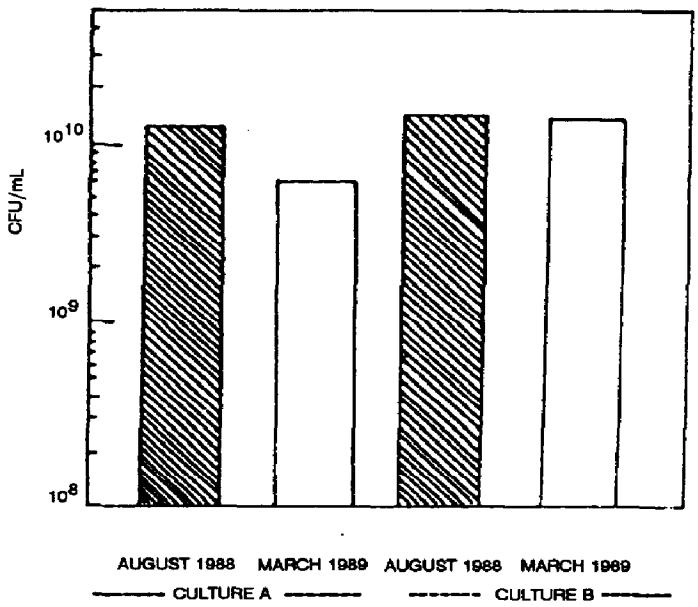

Fig. 3. Growth of refining (A) and petrochemical (B) cultures on nutrient agar with time.

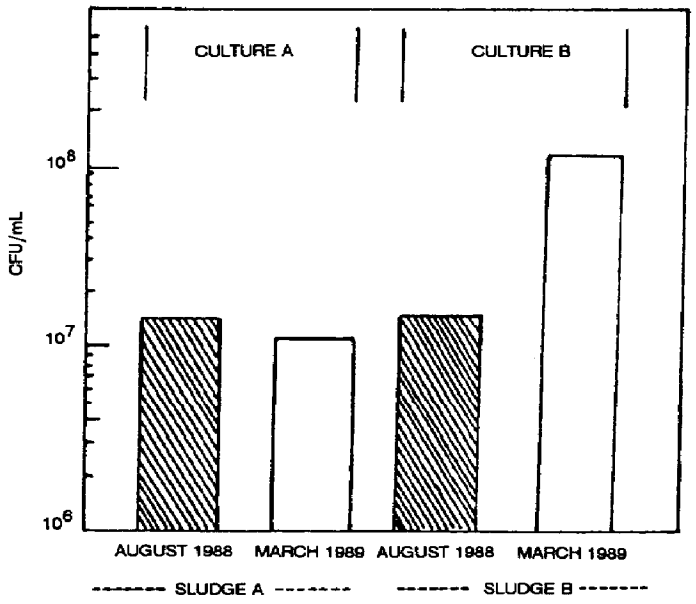

Fig. 4. Growth of refinery (A) and petrochemical (B) cultures on their specific substrate with time.

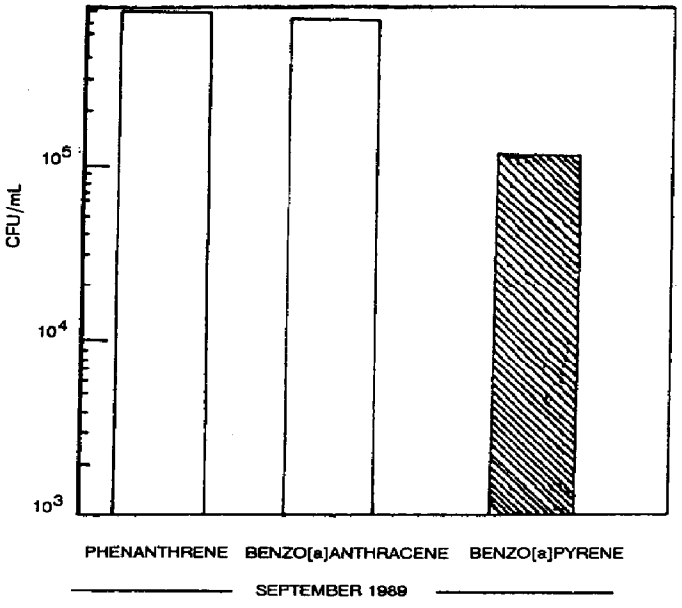

Fig. 5. Growth of refining (A) culture on selected PNAs.

ganisms cultivated on refinery sludge possess near equal growth potential on each of the three PNA substrates, with benzo[a]pyrene being the least supportive in terms of growth. The petrochemical sludge culture shows reduced capability of growth on benzo[a]pyrene compared to the other substrates and compared to the refinery sludge culture.

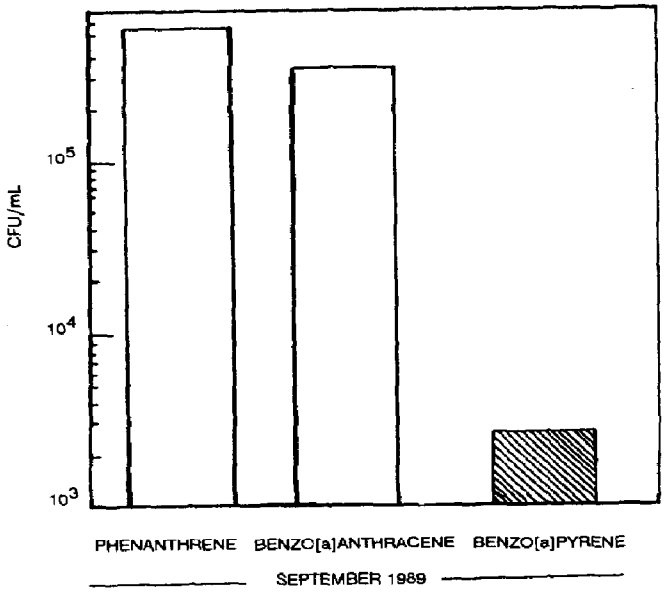

Fig. 6. Growth of petrochemical (B) culture on selected PNAs.

Tables 4 and 5 list the performance data collected on the CSTR systems fed API separator sludges from refinery and petrochemical operations, respectively. The loading rates, effluent concentrations and 1986 Constituent Concentration Levels (CCL) for PNAs are included in each Table. Seven of the

TABLE 4

PNA removal efficiencies in continuous loaded reactor treating refinery sludge

PNA	Feed rate (mg/kg)	Effluent (mg/kg)	(Percentage removed)	1986 CCL[a] (mg/kg)	1990 CCL[a] (mg/kg)
Naphthalene	48.0	0.24	(99.5)	(Reserved)	42
Fluorene	48.4	0.2	(99.6)	–	–
Phenanthrene	17.2	1.2	(93)	7.7	34
Anthracene	2.6	0.2	(92)	6.2	28
Fluoranthrene	2.2	0.32	(85)	–	–
Pyrene	19.8	2.48	(87)	2.0	36
Benzo[a]anthracene	13.8	0.96	(93)	1.4	20
Chrysene	27.8	2.52	(91)	2.2	15
Benzo[k]fluoranthene	12.3	0.92	(93)	–	–
Benzo[g,h,i]perylene	5.3	0.08	(99)	–	–
Benzo[a]pyrene	35.0	2.28	(93)	0.84	12

[a]Constituent Concentration Level — Concentrations of the associated hazardous constituents of K-51 wastes that may not be exceeded by the waste or treatment residual for allowable land disposal of the waste or residual.

TABLE 5

PNA removal efficiencies in continuous loaded reactor treating petrochemical sludge

PNA	Feed rate (mg/kg)	Effluent (mg/kg)	1986 CCL[a] (mg/kg)	1990 CCL[a] (mg/kg)
Naphthalene	41.3	7.3	(Reserved)	42
Fluorene	8.3	2.9	-	-
Phenanthrene	13.1	3.5	7.7	34
Anthracene	11.8	1.7	6.2	28
Fluoranthrene	2.7	0.1	-	-
Pyrene	4.4	1.4	2.0	36
Benzo[a]anthracene	2.5	2.5	1.4	20
Chrysene	5.2	0.1	2.2	15
Benzo[a]pyrene	3.0	0.7	0.84	12

[a]Constituent Concentration Level — Concentrations of the associated hazardous constituents of K051 wastes that may not be exceeded by the waste or treatment residual for allowable land disposal of the waste or residual.

eleven PNAs detected in the refinery sludge were decreased to below the 1986 CCL requirement for release of the sludge to land for disposal. All detected PNAs were reduced to below 1986 CCL requirements for the petrochemical sludge.

In June 1990 the EPA raised the CCL requirements for K051 non-wastewaters by approximately a factor of five to ten for the constituents listed in Tables 4 and 5 and established levels for naphthalene which was not previously determined. The test results determined in this study demonstrate that for the refinery and petrochemical sludges treated at bench scale, the more protective CCLs can be achieved.

The data indicate that the average PNA removal rate for the refinery sludge was greater than 93%; the petrochemical sludge average PNA removal was approximately 74%. This compares with a total oil and grease removal of 73% for the refinery sludge; 75% oil and grease reduction was achieved for the petrochemical sludge. Comparing the two types of sludge treated, lesser PNA removals were achieved for the petrochemical sludge because of the lower attendant PNA feed concentrations. It is anticipated that greater PNA concentrations in the petrochemical sludge can be treated while still achieving the CCL requirements for this test condition.

Typical test run mass balance

To properly assess the biological degradation component to overall removals within the system, a mass balance must be performed around the reactor. Many of the components are very poorly soluble in water and will adsorb onto float-

ing solids, biological solids, settling solids and scum on the walls of the reactor; volatile portions will be lost during the aeration process, and water soluble components will leave in the liquid stream. The results of a typical test run are

TABLE 6

Process control variables for test T1R3 (typical testrun)

Parameter	Value
BaP loading rate, (mg/kg solids)	287
Dry solids loading rate, (g/d)	1.3
Oil and grease loading rate, (g/d)	1.8
Reactor volume (L)	1.0
Mean cell residence time, (d)	8.7
Hydraulic residence time, (d)	4.3
Recycle, (%)	9
BaP degradation, (%)	98
BaP in solids effluent, (mg/kg solids)	5.9

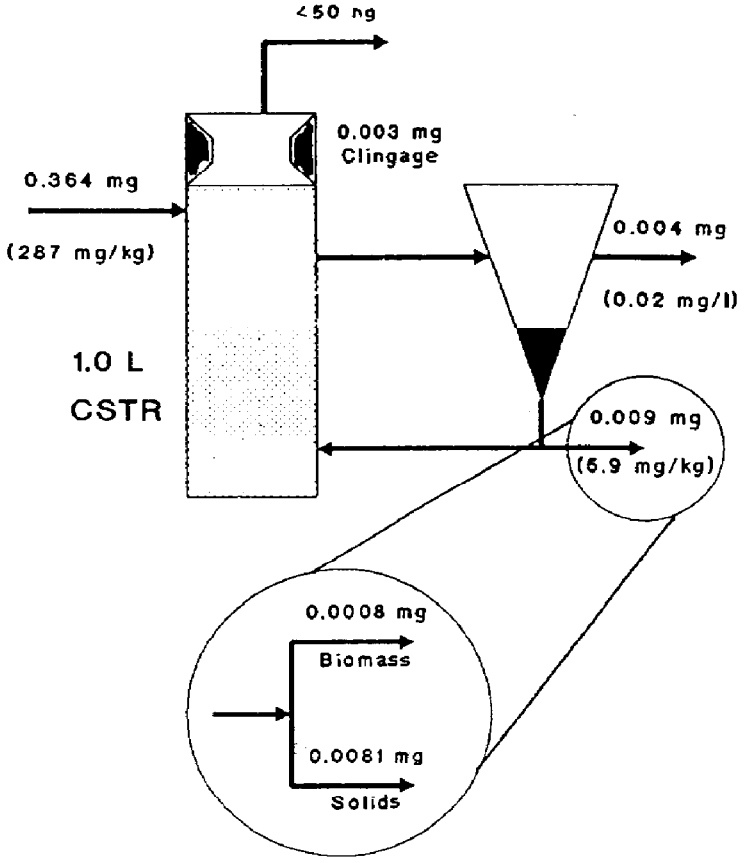

Fig. 7. Benzo[a]pyrene mass balance for the reactor of Fig. 2.

shown on Fig.7. This test used the petrochemical sludge as feed. The process operational parameters are listed in Table 6.

The mass balance depicted in Fig. 7 for BaP shows that the largest amount of BaP leaving the system is associated with the solids fraction. This is to be expected since BaP is very poorly soluble in water and is also nonvolatile. These two features are demonstrated by the very low concentrations of BaP in the liquid stream (0.02 mg/L) and absence of detectable concentrations (25–50 ng) in the vapor trap. Accumulations on the reactor walls amounted to less than one percent of the total BaP fed to the system; and are associated with the dried solids residues splashed on the sides during the mixing and aeration. All effluent fractions (solids, free liquid, and gases) meet the U.S. EPA constituent contaminant levels for release requirements for K051 wastewaters and non-wastewaters (40 CFR 268). The total removal of BaP from this reactor was 96.5%.

Benzo[a]pyrene accumulations associated with biomass in the system were measured by separation of the solids fractions based on settling velocities. As a result these observations are highly variable, but do indicate little accumulation in the biomass fraction.

The above experiment has been duplicated five times in the laboratory with removal efficiencies in the range of 96–99% for BaP for BaP feed concentrations of approximately 285 mg/kg. The lowest reactor performance resulted in effluent BaP concentrations of 12 mg/kg, and was achieved with solids loadings in the feed were as high as 10,000 mg/l, with hydraulic retention times as short as 3.5 days and solids retention times as short as 7 days. Best reactor performance 2.1 mg/kg BaP in the effluent, at solids loadings of 8400 mg/L, a hydraulic retention time of 5.7 days and a solids retention time of 12 days.

Based on the results obtained in this study, it can be concluded that biological treatment to reduce PNAs in refinery sludges and petrochemical sludges is a viable technology. This technology, when operated properly, can meet the Constituent Contaminant Levels set forth by the U.S. EPA consistently.

Acknowledgements

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