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Analysis of *In-Situ* Bioremediation of PAH Contaminated Sediments using Hollow Fiber Membranes

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Abstract

Sediment contamination is a global environmental issue and there are no treatment technologies that can be readily applied except dredging, which is very expensive and time consuming. In this thesis, a computer model has been developed and applied to in-situ bioremediation of contaminated sediments. The mathematical model has been applied to experimental data that was obtained previously using a bench-scale system using sediments contaminated with polycyclic aromatic hydrocarbons (PAHs). The use of hollow fiber membranes offers advantages of cost-effectively supplying and controlling the availability of oxygen (air), nutrients or other electron acceptors, such as nitrate and sulfate to the contaminated sediments, without significant loss to the water column. The biokinetic and transport parameters in the mathematical model were fitted to the bench-scale experimental data to achieve a low average error between the experimental and model values. The fitted model was used to calculate the design of the hollow fiber system, such as distance between the fibers.

The WASP-6 computer program, developed previously for calculating dissolved oxygen levels in natural water bodies, was used to simulate the impact of contaminated sediments and the effect of using the membrane system to preserve the dissolved oxygen levels. Results of this study have shown that controlled delivery of oxygen from air is a feasible technique to achieve accelerated bioremediation rates of PAH contaminated sediments and improved water quality in rivers and lakes adversely impacted by these contaminated sediments.
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Nomenclature

**Parameters:**

\( C_{\text{org}}^\alpha \): Organic Matter in soil or sediment. (mg/Kg)

\( D_0 \): Diffusivity of oxygen in sediment. (cm\(^2\)/h)

\( K_1 \): PAH kinetics Parameter (mg/Kg.day\(^{-1}\))

\( K_2 \): Binding Constant. ((mg/Kg)\(^\alpha\) day\(^{-1}\))

\( K_2' \): \( K_2.C_{\text{org}}^\alpha\) (day\(^{-1}\))

\( K_c \): Half Saturation Constant for PAH. (mg/Kg)

\( K_0 \): Half Saturation Constant for electron acceptor. (mg/Kg)

\( SOD \): Sediment Oxygen Demand. (gm/m\(^2\).day\(^{-1}\))

\( \mu_{\text{max}} \): Maximum Biomass Growth. (day\(^{-1}\))

\( Y_e \): Yield Coefficient for Enzyme. (mg/mg)

\( Y_h \): Yield Coefficient for PAH. (mg/mg)

\( Y_o \): Yield Coefficient for electron acceptor. (mg/mg)

**Variables:**

\( \bar{A} \): Average Quantity over the area. (Applied for O and PAHs). (mg/Kg)

\( C \): PAH Concentration. (mg/Kg)

\( C_B \): Bound PAH concentration. (mg/Kg)

\( C_H \): PAH-Diol Concentration. (mg/Kg)

\( E \): Enzyme Concentration. (mg/Kg)

\( O \): Electron Acceptor Concentration. (mg/Kg)

\( X \): Biomass concentration (mg/Kg)
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Introduction

Pollutants from industry, mining, agriculture and other sources have contaminated sediments in many surface water bodies. (Renhold J, 1998) International concerns about contaminated sediments are increasing, mainly since sediments are viewed as long-term pollutant sinks for compounds, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl compounds (PCBs), and other hazardous chemicals. Now there is overwhelming support for the theory that toxics trapped in sediments can adversely impact human health and the environment for a long period of time. In September 1997, EPA completed its National Sediment Quality Survey, which was developed in response to a mandate by Congress. It is part of a three-document series titled “The Incidence and Severity of Sediment Contamination in Surface Waters of the United States,” which takes a comprehensive look at the severity of contaminated sediments in the United States. This survey uncovered that sediment contamination exists in every region and state of the country and there are 96 watersheds of probable concern. It concludes that approximately 10% of the sediment, underlying surface waters in the United States, is sufficiently contaminated with toxic pollutants that pose potential risks to fish, humans and wildlife that eat fish. One of the four goals that were established in this survey was to reduce the volume of existing contaminated sediment.

In EPA’s 1998 National Quality Survey, the most frequent chemical indicators for the highest level of sediment contamination were PCBs, mercury, organochlorine pesticides, and PAHs. These chemicals are very toxic and tend to bioaccumulate in fatty tissues. (Renhold J, 1998) Out of these toxic chemicals, PAHs are the ubiquitous contaminants of aquatic and terrestrial ecosystem. (MacGillivray et al. 1994) There are
over 100 different PAH compounds. PAHs originate in part from natural processes but their concentrations are elevated in many coastal ecosystems as a direct result of human activities. (MacGillivray et al 1994) PAH migrate to the sediments in aquatic ecosystems due to their hydrophobic nature and low water solubility and readily adsorb to the particulate matter. (Cerniglia et al 1994) Direct human exposure to PAHs in bottom sediment is minimal; however, due to the tendency of PAHs to accumulate in the food chain, their release during dredging operations, episodes of high hydraulic scouring, or leaching from confined disposal facilities, poses a threat to aquatic ecosystems. (Hughes et al 1997) There is no known use for most of these chemicals except for research purposes. A few PAHs are used in medicines and to make dyes, plastics and pesticides. Based on animal testing, PAHs are suspected of being carcinogenic. (White et al 1998) The Department of Health and Human Services (DHHS), International Agency for Research on Cancer (IARC), Department of health and family services (DHFS) and Environmental Protection Agency (EPA) has determined that some PAHs are known animal and suspected human carcinogens. In the Great Lakes Region, a large area of sediment accumulation, contaminated sediments pose a severe threat to human health and the environment. This has caused an increased interest in treating these facilities and to make it benign for the human exposure.

Previous attempts to treat contaminated sediments have mainly involved dredging followed by long-term storage (capping) or ex-situ treatment or in-situ treatment, using injection of nutrients, adapted microorganisms, chemicals, etc. While ex-situ treatment are very expensive, most of the in-situ methods suffer from losses of the additives to the overlying water column, competition from indigenous microorganisms and difficulty in
controlling environmental conditions, such as pH, temperature, alkalinity, etc. Luthy et al suggested through their findings that bioremediation could be the technically and economically feasible process for a realistic solution to the needs of contaminant removal both in in-situ and ex-situ operations. (Talley, Luthy and Ghosh et al 2001) The work being presented with the membrane promises a process, which can be used to enhance the rate of bioremediation, and control environmental conditions. Membranes being the part of biological systems’ separations mechanisms provide a promise of long sought after feasible solution to the environmental problems. The studies done previously gave positive results for complete mineralization. Various studies have identified specific organisms capable of degrading PAH compounds (Heitkamp, M.A. et al 1989; Cerniglia, C.E. 1984). Information on aerobic pathways is generally limited to two-and three-ring PAH compounds including naphthalene (Fredrickson, J.K et al 1991), acenaphthene, and phenanthrene (Fredrickson, J.K et al 1991), (Brodkorb, T.S. et al 1992). Biodegradation of PAHs under anaerobic and sulfate reducing conditions have also been discussed (Young, L. 1999). The genotoxicity and mutagenicity of PAH and their dead-end metabolites in case of oxygen limiting condition has been a cause of concern. (Haeseler et al 2001).

In the present work bench scale experiments of a novel method for in-situ bioremediation of contaminated sediments using membrane is simulated and analyzed. The method allows in-situ biodegradation of PAHs in contaminated sediments while preventing the membranes from fouling. The proposed novel approach involves the use of specially designed gaseous, inorganic, and organic nutrient bearing hollow fiber polymeric membranes for controlling the redox potential in contaminated sediments. A
review study was done to analyze the past work done in the area of in-situ bioremediation of contaminated sediments. A mathematical model was developed to represent the process. The parameters were fitted to it with reference to the bench scale experiments conducted in the previous studies conducted in Dr Rakesh Govind’s research group (Appendix 1). Further the kinetic parameters and the environment were used to find out the distance between the fibers as against the probable optimization parameters membrane efficiency, frequency of back-flush and days of treatment. This data can be used for an initial estimate of the pilot scale experiments. Natural attenuation approach was simulated and analyzed as the bottom line of remediation time. WASP-6 model is used to analyze the superiority of the technique in terms of preserving the DO of water, over the other having similar impact in sediment. Simulation data will be presented on biotransformation rates of 18 PAHs (2 ring to 6 ring compounds) as a function of time using PAH-contaminated New York Harbor sediment.
Background

Sediment treatment options include: (1) Source control, (2) Dredging and *ex situ* treatment, (3) Natural Attenuation, and (4) *In-situ* treatment. *In-situ* treatment includes: (a) Physical and chemical capping, (b) Waterway confinement (*in situ*). (c) *In-situ* sediment chemical treatment, and (d) *In-situ* sediment biological treatment. (Murphy TP *et al* 1999; Jon Reinhold 1998)

1. *Source Control*

When the future contamination is the main cause of concern and present contamination is not of alarming amount then one should use source control, as an alternative. Without proper source control we can miscalculate the treatment so source control has to be implemented when conducting test onsite. But the condition of having a site with only current contamination is highly idealistic and might not often be met. Hence there has to be some form of treatment that should be considered in the strategy to be complemented by the source control. It at first requires the fingerprinting of compound and matching them to the sources and then a plan to control the hydrological loading variables to be within the range of environmentally acceptable endpoints. Garbaciak Jr. Stephen *et al.* suggest that with adequate source control natural attenuation can take ten years to reach the desired concentrations. (Garbaciak Jr, Stephean *et al* 1998) This time frame is a bit too long for the critically contaminated sites. Hence, source control is definitely an option for low contamination sites, as a preventive measure, but not for highly contaminated one, as recognizing the source might not be possible for highly
contaminated site. Moreover the control may not always be possible. (Murphy TP et al 1999)

2. Dredging

Dredging is done in many ports to clear the port. One of the benefits of dredging is reducing the algae growth. (Murphy TP et al 1999) This is a highly costly process and this hinders the spread of this technology. Sediment most of the times are not dredged to the accuracy desired and leaves behind a pile of the contamination. This pile breaks off and contaminates the sediment again. Moreover the re-suspension of the sediments is another issue with the dredging. If dredged to accuracy the problem of disposing is real big and has to be dealt with, taking in mind the societal concerns from different aspects from personal (NIMBY – Not in My Backyard), legal to economical. Murphy et al. predict that dredging will cost, for parts of Hamilton Harbour, about USD 70/m², ex situ biological treatment (cheaper technology) of the organic contamination can be US$350/m², and some incineration strategies exceed USD500/m². (Murphy TP et al 1999) Thibodeaux, Louis J. et al conducted study of three sites in Louisiana, New York, and Michigan. Models and measurements were used to examine increased water concentrations, post-dredging sediment concentrations, effects on biota (mainly fish), contaminant losses, etc., for dredging primarily, but including the natural-recovery and capping remediation options. The effectiveness was evaluated by quantitatively analyzing enhanced contaminant release during dredging, short-term on the aquatic environment and long-term impacts on the aquatic environment. They found that existing technologies provide the means to extract large volumes of contaminated bed-sediment. Targeted removals of greater than 95 percent are achievable. However, 100 percent removal was
not possible, so that significant contaminants remained. The surficial-sediment concentrations remained high, with reduction in the 50 to 75 percent range being typical. (Thibodeaux, Louis J et al 2001) The impact on fish in the short term was nearly always negative. During dredging, significant contaminants entered the water column in both soluble and particulate form. The long-term impact of dredging could not be determined because of the limited data storage resource available. (Thibodeaux, Louis J et al 2001) Even after investing the huge amount in the dredging storage and ex-situ treatments, dredging has many technical disadvantages, and hence proves to be an unreliable option to be considered for the sites.

3. Natural Attenuation

With microorganisms in the site and hence enzymes present natural attenuation is most probable to occur in any site for all biodegradable and bioavailable compounds. Luthy et al. did a micro scale characterization and desorption analysis for the sediments with the objective of finding the surface effect of sediments on the contaminant adsorption, possible desorption of the PAHs from the sediment using extraction, mechanism governing sequestration, effect of such processes on bioavailability and toxicity limit assessment and nature of PAH association that leads to their unavailability. They concluded that surface to bulk ratio is directly proportional to the sorbed PAH concentration. They further concluded that the lighter coal and wood derived fraction of sediments have more PAH fraction then the abundant silica particles in sediment but they did not differentiate between different forms of organic carbon like humic matter particle, humic matter sorbed on mineral surfaces etc. They found that there were available and unavailable fractions present in the sediment. It was attributed to the sorption. (Luthy et
This is evident that aging is the factor, which governs the sorption, but Govind et al. hypothesized the interactions with humic matter to be a chemical binding. These bindings explain the high bioremediation rate observed. A combined model of biodegradation and chemical binding was proposed and fitted to be found appropriate with the experimental data and literature. (Govind et al 2001) Weber et al investigated oxidative coupling of hydroxylated aromatic compounds by natural geosorbent. (Weber et al 2003). Moreover, they showed that in order to form a biopolymer the presence of hydroxylated aromatics is required. Perminova et al. and Rice et al. attributed the detoxification of the PAHs in presence of humics to the chemical binding in their findings (Perminova et al. 2001, Rice et al. 2004). Rice et al. further found that bound residue formation for the metabolites PAH-diols are 5 to 20 times higher than the respective PAH (Rice et al. 2004). Pathways of sorption, chemical binding and biodegradation, and hence bioavailability and bioconcentration are complex and an area of curious research. Natural attenuation is believed to involve the combined effect of biodegradation under oxygen deficient condition and the chemical binding and sorption to the organics in the sediment. (Govind et al 2001) Bioavailability is a major factor to be considered before deciding the biodegradability of a soil or sediment. Semple et al. did a study with HPCD (hydroxypropyl-β-cyclodextrin) to find the bioavailability. Bioavailability they found depends on the soil structure (particle size matter and organic matter content), compound’s physico-chemical properties (Kow, mol size, solubility and vapor pressure) and intra soil processes (sorption, diffusion and entrapment). (Semple et al 1999) Rockne et al. further researched on the relationship of the size and density with the sequestration of PAH and found that the sequestration is both the function of density
of sediment and PAH structure. They found that majority of PAHs are associated with low density particles (<1.9 g/ml) for larger size classes of sediment particle which are the remains of terrestrial and marine tissues that have accumulated in the sediment but as the size decreases there is a reversal in these associations. (Rockne K J et al 1999) Hence we see natural attenuation is a complex process and is difficult to measure. Ignoring Natural attenuation in reporting would result in faulty predictions. This process is natural and hence thermodynamically favored. The problem on relying completely on this process is that it is a very slow process with no control and hence the time taken is going to be much more than desired in most cases. It can take decades for a site to clean up naturally. Huesemann M. H. et al. investigated the biodegradation and the desorption of PAH and concluded that if the biodegradation is the rate controlling process than even after a long time of wait we can expect incomplete treatment. (Huesemann M. H. et al. 2001). In case of the natural remediation it is expected to be rate limiting, as sediments are oxygen deficient and hence even a long wait with Natural Attenuation is going to be insufficient and inappropriate. Hence, while observing it for measurement accuracy, other remedial techniques should also be incorporated.

4. In-situ Treatment

a. In-situ capping (ISC)

In-Situ capping involves covering a contaminated sediment site with a clean isolating material in sub aqueous environment. In late 90s Azcue, Jose M. et al and Palermo et al suggested that the capping is economical and effective. (Azcue Jose M et al 1998, Palermo et al 1998)
i. **In-situ physical capping:** In physical capping a layer of chemically and biologically inert clean isolating material, which has no effect on sediment and it’s environment, except that of physical isolation of the contaminated sediment, preventing resuspension and transport to the other sites and trying not to let the sediment contamination affect the overlying water column by reducing the flux of dissolved contaminants into the water column. The first capping project was done in 1978 by Bocuniewicz *et al.* Later Azcue, Jose M *et al.* studied Hamilton Harbor, Lake Ontario, Canada 1998. They laid a sand 35 cm thick in 1995. They found a significant reduction in the flux of contaminants to the water column. They showed that the pore water concentration was significantly high than the overlying water. *(Azcue Jose M et al 1998)* There are many problems associated with capping. First of all as Azcue, Jose M *et al.* found, that new layer of sediment were formed on the cap, it is hard to determine how soon we can expect this layer to form. Moreover propeller of ships and storms can pose a threat to cap. Cost of this whole operation of putting a cap and that too clean is high. It contains a combined project of dredging a clean material and capping the subsurface sediment. *(Murphy TP et al 1999)* So, it is very hard to cap a site and it is even harder to maintain that capped till the time the contamination is over as natural attenuation as already discussed is a time taking process.
ii. **In-situ chemical capping (Active Barrier System ABS):** *In situ* chemical capping is a chemically reactive cover, which acts as a barrier for the contaminants without affecting the hydraulic interactions of the sediment and water column. (*Murphy TP et al 1999*) It involves adding chemicals such as zeolites, lime and iron, which deposits a new reactive layer on the sediment surface. This method is aimed at depositing the particles in precipitates formed by the chemicals added to form a cap. The problem is same as that of physical capping, that it is containment not a treatment of chemicals. Moreover zeolites need to be treated with surfactants or modified in order to prohibit non-polar chemicals. (*Jacobs et al 1999*) Environmental effects like ice jam (*Quadrini et al 2003*), which can make sediment and cap both move and hence make it difficult to contain the contamination, and manual interference, during several activities required to run the ships in the area, can spoil the capping. Moreover adding a chemical may not be a welcome idea for the society. These chemicals, which are being tried, may end up in food chain or increased toxicity in the sediment and disturbance in ecology of the sub surface.

*b. Denitrifying Condition*

MacRae JD *et al* suggested that in *Denitrifying Condition* PAH could be degraded in the marine sediment as long as nutrient is not limiting. (*MacRae JD, Hall KJ. 1998*) They further illustrated that nitrate is more attractive as compared to oxygen as it is 10000 times more soluble than the oxygen, yields almost same free energy, and the gaseous
products of the products do not accumulate in the system. The experiments conducted
gave half-lives of PAHs to be 33-88 days and half-lives of higher molecular weight PAHs
to be 143-812 days. (MacRae JD et al 1998) The half-lives of PAH under denitrifying
conditions are generally longer or fall in the upper end of the aerobic degradation ranges.
The denitrifying condition can be induced through various innovative process designs.

c. In-situ treatment by injection

With in-situ treatment by injection method chemicals or bacteria can be directly
injected into sediments for the following purposes; odor control, nutrient inactivation,
bioresidiation of some organic contaminants and other habitat improvement. (Murphy
TP et al 1999) Reducing algae formation by the injection of iron or nitrate into sediment
decreases the availability of P in the sediment by means of which the back flux to water
column is stopped. (Murphy TP et al 1999) The Limnofix In-Situ Sediment Treatment
Technology (LIST) uses an underwater harrow towed behind a boat to till the
contaminated sediment and inject it with a chemical oxidant, usually calcium nitrate.
Since calcium nitrate is also a nutrient, it must be injected deep into the sediment to
prevent it from escaping into the water column and boosting the growth of algae. Here
this is not specified how much deep is this to be injected so as to get no loss to the water.
Moreover going too deep will deviate us from the target surface contamination.

Following are the examples of some of the projects done (Jon Renhold 1998; LIST 1995)
Hamilton Harbor (Dofasco Boatslip), Canada was identified in the Great Lakes Region
because of environmental concerns. The harbor is contaminated with metals, sulfides,
oils, and a variety of organic compounds, especially PAHs. (Jon Renhold 1998) This area
has not only concerns related to historical contamination but the current run offs and
contaminations from other sources. The cost of dredging is almost in five billion dollar range. With dredging already a failure in the area and the cost factor so high, National Water Research Institute of the Environment Canada was prompted to decide to conduct several pilot-scale studies to remediate the contaminated sediments in Hamilton Harbor. The objective of the in situ treatment in the Dofasco Boatslip area was to stimulate anaerobic bioremediation with the natural microorganisms in the sediment using chemical injection of oxidants and/or nutrients. The Gander of The Department of Fisheries and Ocean was equipped with an 8 m wide injection boom to inject the chemicals into the sediment. (Jon Renhold 1998) During the first three treatments, only farm grade calcium nitrate was injected into the sediments: 3.6 tons on July 28, 1992; 3.89 tons on September 15-17, 1992; and 6 tons on April 27, 1993. On September 22, 1993, five tons of calcium nitrate along with five tons of organic amendment was injected again. (Jon Renhold 1998) Samples were monitored for the loss of PAHs to bioremediation. The air was monitored for the cross contamination issues. The laboratory studies on the sediments from Dofasco Boatslip indicated that the microorganisms biodegraded approximately 78% of the oils and 68% of the PAHs in 197 days. (Jon Renhold 1998) The high molecular weight compounds were degraded along with the low molecular weight compounds. In 1 – 2 years time frame around 1992-94 there was a significant degradation observed which tells that the biostimulation is a successful remedy. PAHs don’t pose a threat of release into the air so that was not a concern anyway. But there were certain problems with this approach. The treatment efficiency was less in areas with steep slopes and areas with logs because the injection equipment tended to jump or slip in these areas. Moreover when the chemical injection was
performed, diffusion of nitrate into deeper sediments caused methane to be released to the surface, where it competed with the contaminant for the nitrate oxidant. Therefore, to increase PAH degradation, a higher dose of oxidant was required to overcome its use by in fluxing methane. (Murphy TP et al 1999; Jon Renhold 1998)

*St. Mary’s River, Canada,* is contaminated with a large amount of organic waste. Prior to the treatment in Hamilton Harbor, Environment Canada conducted a pilot-scale study of in-situ chemical injection in sediments. The sediment was indirectly treated for organic compound by stabilizing the sulfide. The results were promising but it might be because of the oxidant added to stimulate the remediation. (Jon Renhold 1998)

*Salem, Massachusetts,* is contaminated with the PAHs from a manufacturing gas plant site. A full-scale treatment of this zone was done by Limnoflix Inc. to enhance the biodegradation of organic contaminants. The treatment was done by using injection of calcium nitrate to stimulate biodegradation of the PAHs, much like what was conducted at Hamilton Harbor. PAHs degraded to 90% in a year. (Jon Renhold 1998)

d. *Encapsulating or entrapping microorganisms*

Bioaugmentation is another way of enhancing the bioremediation. There has been little success to back the use of bioaugmentation as a strategy for in-situ treatment. The problem in bioaugmentation is the inability to support its growth and activity after the introduction in the new environment. This problem persists because of the competition with the stronger and already acclimatized bacteria and other species. The solution proposed is immobilization or encapsulation. It not only reduces competitions but also improves survival rate. Encapsulation involves the packaging of specific bacterial or fungal cells in a porous polymeric material such that Microorganisms can be stored for a
considerable period. Moreover from time to time we can introduce viable and active cells into the environment. Here we can selectively feed the nutrients to the population of organisms present. Now the problem is another limitation by mass transfer. But the mass transfer can be enhanced by the use of adsorbent in the immobilized matrix. These adsorbed PAHs can be more exposed to the immobilized bacteria. Co immobilized nitrogen and Phosphorus support extensive biodegradation though it was slower than the externally supplied nutrient system. Encapsulation also helps in reducing the exposure to the highly toxic atmosphere and controls the effect of the toxicity on the microorganisms.

We can use variety of microorganisms together in the augmentation. Agarose, alginate, carrageenan and polyacrylamide gels have been used as encapsulating matrices, but insufficient mechanical and chemical activity has limited their application. Porous Polyurethane foam has proven to be more durable and effective immobilization matrix. Vermiculite is another option. (Levinson William E. et al 1994; Lin J E et al 1995; Murphy TP et al 1999) We can use bioaugmentation when we see that the nature of the waste is very complex such that it can not be treated by resident bacteria, when we have no acclimatization period and we need the job to go as fast as it can. Moreover using the augmentation gives us the confidence as the consortia is of confidence. Sometimes the cost of testing a site is reasonably higher than the total cost of augmentation then we practice this option. (Forsyth J V 1995) Environmental factors like Temperature, pH, nutrient and moisture levels, and relative number of contaminant degrading microorganisms and the type and concentration of contaminant also play an important role in the consideration of the option. (Forsyth J V 1995) Crawford et al found that the best-worked and reproducible method was bacterial cells entrapped in a microbead
containing of an agarose matrix. These are concentrated and then coated with polyurethane by a controlled surface reaction. The coated microbead was washed free of oil and then used for analysis. (Crawford et al. 1993) Technology Resources Inc., SBP Technologies Inc., and the U.S. EPA Environmental Research Laboratory in Gulf Breeze, Florida conducted a test of the encapsulation and found that the reduction in viability of immobilized organisms was minimal and the degradation rates were promising in soil slurry as well as moist packed soil. (Jon Renhold 1998) This presents to us a further scope of the encapsulation as a potential treatment method. The problem still remains to be solved, is the mass transfer limitation of this process for which research is going on.

e. **Genetically modified microencapsulated microorganisms (GEMS)**

This class of encapsulation can be classified as a potential bioaugmentation technique as oxigenases of bacteria can be modified by directed evolution to target specifically PAHs. Other tricks can be applied in order to treat other contaminants too. (Furukawa K. et al. 2003) This technique has the basic problem that the genetic modifications have. The potential threat of introducing a new gene in the system and transferring the genetic information to the indigenous gene consortium is a possibility that is hard to ignore.

f. **Biological Carpet**

Immobilized bacteria can degrade in a very effective way. Heitkamp et al of Monsanto Company developed a novel technique to immobilize the bacteria in a nylon biocarrier. (Heitkamp, Michael A et al. 1996) Packed bed study showed promising results in the laboratory. Hap Pritchard proposed a design to attach the biocarrier to the
geotextile fiber and lay it on the surface upside down. Later this carpet can be used as a cap, as it won’t biodegrade. (Jon Renhold 1998)

g. Anaerobic PAH degrading enrichment culture under methanogenic condition

Holoman et al. discovered that PAHs could be degraded under methanogenic conditions with enrichment cultures. (Holoman et al 2001) They conducted a test for a year and found that Phenanthrene and Naphthalene are completely degraded though Pyrene did not degrade to that extent. They however, did not consider the irreversible chemical binding of the PAHs to the sediments, which can be the cause misinterpretations of results obtained. Moreover Pyrene and hence higher ring PAH seem to be recalcitrant in the specified condition even with enrichments.

h. Surfactant addition

Surfactants decrease the capillary forces and increase solubility of a solute. It is used in the sediment matrix where the concentration is above the critical micelle concentration. (Hughes JB et al. 1997) By increasing the solubility the surfactant increase the amount of soluble compound and hence the bioavailability. This increased solubility can be observed by the increased concentration gradient at the interface of sediment-water created by the high partitioning of the hydrophobic compounds at the interface. Yeom et al. suggested two mechanisms for this increased bioavailability of PAHs: increase of concentration gradient of soil-water interface and the swelling of the organic soil matrix, which causes the increase in diffusivity. From their model and the experiments they concluded that the penetration of the surfactant molecules into the soil matrix causing them to swell, caused the increase in diffusivity, which in turn was responsible for the increase in the PAHs release to the water. (Yeom IT et al. 1996;
Hughes JB et al. 1997) The prince William Alaska studies and the Exxon Valdez studies with the fertilizers show promising results. These results can be attributed to not only the nutrients, as they can already be there in the real environment, but to the surface activity of that fertilizer added. Churchill discovered non-ionic surfactants improved the biodegradability of phenanthrene. (Churchill PF et al. 1995) The direct mass transfer from the micelle to the bacterial cell was decreased with the increase in the micellar concentration. (Guha S et al. 1996) It also depends on the bacterial culture and the type of surfactant. (Guha S et al. 1996) So it is not certain that adding a surfactant will always increase bioavailability, it may act otherwise too. Moreover large partitioning of surfactant itself can also be a concern. Since bioavailability is dependent on the fact that the critical micellar concentration is overcome, after sorption on the sediment. This has economic viability issues involved. (Hughes JB et al. 1997) The bacteria excreted biosurfactant causes the dispersion / solubilization of the substrate. (Wick et al 2001) Addition of biosurfactant has recently been found by Amezcua-Vega et al to have an effect on the phenanthrene desorption and hence making it bioavailable to be degraded. The advantage with the biosurfactant over the synthetic is that they have higher biodegradability, less relative toxicity and high efficiency at higher concentration. (Amezcua-Vega et al. 2001) The problem to consider is high cost involved in this process.

i. Sulfate Reducing Condition

Lovely et al. using sulfate reducing condition, have demonstrated to have a stimulus response from the bacteria for the freshly added contaminant, like freshly added $^{14}$C-labeled PAHs. (Rothermich M M,. Hayes LA, Lovely DR. 2002) When the sediment is aged there is a significant reduction in the biodegradation possibly because of the lesser
bioavailability. In any case sediments have shown positive affects to sulfate amendments. (Rothermich M M et al 2002) Degradation might vary greatly based on the sediment type and the source of contaminant. Similar to denitrifying conditions sulfate reducing condition can also be induced through innovative process designs. The problem is that it is less preferred electron acceptor and losses to water column can be foreseen.

**j. Oxygen Addition**

At French Limited Superfund site in Harris County, Texas, a full-scale system was used to remediate the lagoon sediments containing a mixture of organic contaminants including PAHs and PCBs. Nutrients and oxygen were supplied to stimulate the remediation. It was successful as compared to more traditional technologies and the cost saving were around 50 % of the traditional ones. (Hughes JB et al. 1997)

**k. Oxygen and Hydrogen Release Compound**

Oxygen release compounds in presence of the required catalyst release the oxygen. ORC® marketed by the Regenesis Bioremediation is made of intercalated magnesium peroxide. (Koenigsberg et al 2001) The ORC® is insoluble and releases its oxygen while being converted to magnesium hydroxide, which again is insoluble. This oxygen is in turn provided to stimulate the microorganisms. (Kao C M et al 2003) The time-release component in the ORC® was because of the fact that they were intercalated in the food grade phosphate ion. (Koenigsberg et al 2001) There are other ways to get the time-release functionality in ORC, which have been explored. The Oregon facility was remediated using ORC for groundwater treatment contaminated with different chemicals along with Naphthalene. Naphthalene was treated from 220 ppb to Non-detectable levels. (Koenigsberg et al 2001) Schmidtke T et al. predicted that breakdown
of ORC will be a limiting factor for the process. (Schmidtke T. et al 1999) The problem with this system was that nearly half the oxygen produced was lost to the environment. (Schmidtke T. et al 1999) Temperature and time (history of the sample of ORC) too have an impact on oxygen release. (Schmidtke T. et al 1999; Otsuka-Yao-Matsuo Shinya et al 2003) Similarly, Hydrogen release compounds are also known to accelerate the bioremediation as electron donors for compounds like PCBs that need to be dechlorinated in order to get biodegraded. (Vigue Bryan W et al 2002) But in case of PAHs hydrogen release compounds are not known to be effective as Hydrogen acts as an electron donor.
<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Technology</th>
<th>Description</th>
<th>Issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>2001</td>
<td>Thibodeaux, Louis J et al</td>
<td>Dredging</td>
<td>Existing technologies provide the means to extract large volumes of contaminated bed-sediment. Targeted removals of greater than 95 percent are achievable.</td>
<td>1. Significant contaminants remained. 2. The surficial-sediment concentrations remained high, with reduction in the 50 to 75 percent range being typical. 3. Significant contaminants entered the water column in both soluble and particulate form. 4. Cost of the operation is very high.</td>
</tr>
<tr>
<td>1998</td>
<td>Azcue Jose M et al</td>
<td>In Situ Physical Capping</td>
<td>Significant reduction in the flux of contaminants to the water column.</td>
<td>1. New layer of sediment were formed on the cap. 2. propeller of ships and storms can pose a threat to cap. 3. Cost of putting a clean cap is high.</td>
</tr>
<tr>
<td>1999</td>
<td>Jacobs et al</td>
<td>In Situ Chemical Capping</td>
<td>Involves adding chemicals such as zeolites, lime and iron, which deposits a new reactive layer on the sediment surface.</td>
<td>1. Environmental effects and manual interference, during several activities required to run the ships in the area, can spoil the capping. 2. Chemicals, which are being tried, may end up in food chain or increased toxicity in the sediment and disturbance in ecology of the sub surface.</td>
</tr>
<tr>
<td>1998</td>
<td>MacRae JD et al</td>
<td>Denitrifying Condition</td>
<td>Nitrate is attractive as it is highly soluble with high free energy.</td>
<td>1. The half-lives of PAH under denitrifying conditions are generally longer or fall in the upper end of the aerobic degradation rages.</td>
</tr>
<tr>
<td>1999</td>
<td>Murphy TP et al</td>
<td>In situ Injection of nitrate</td>
<td>Chemicals or bacteria directly injected into sediments for odor control, nutrient inactivation, bioremediation of some organic contaminants.</td>
<td>1. Calcium nitrate is also a nutrient and must be injected deep into the sediment to prevent it from escaping into the water column and boosting the growth of algae. This depth is uncertain.</td>
</tr>
<tr>
<td>Year</td>
<td>Authors</td>
<td>Technique</td>
<td>Description</td>
<td>Challenges</td>
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<tr>
<td>1993</td>
<td>Crawford et al.</td>
<td>Encapsulation of microorganisms</td>
<td>Reduces competitions and improves survival rate. Selectively feeding the nutrients to the population of organisms is an added luxury. Helps in reducing the exposure to the highly toxic atmosphere and controls the effect of the toxicity on the microorganisms.</td>
<td>1. Added limitation by mass transfer for aged sediments.</td>
</tr>
<tr>
<td>2003</td>
<td>Furukawa K. et al.</td>
<td>Genetically modified microencapsulated microorganisms</td>
<td>Potential bioaugmentation technique as oxigenases of bacteria can be modified by directed evolution to target specifically PAHs.</td>
<td>1. Apart from mass transfers issue the potential threat of introducing a new gene in the system and transferring the genetic information to the indigenous gene consortium is a possibility that is hard to ignore.</td>
</tr>
<tr>
<td>1996</td>
<td>Heitkamp, Michael A et al.</td>
<td>Biological Carpet</td>
<td>Novel technique to immobilize the bacteria in a nylon biocarrier.</td>
<td>1. Storms and geological activity pose a threat to this. 2. Manual interference is also a threat to this approach.</td>
</tr>
<tr>
<td>1995</td>
<td>Churchill PF et al., Yeom IT et al., Guha S et al</td>
<td>Surfactant addition</td>
<td>Non-ionic surfactants improved the biodegradability of phenanthrene. Penetration of the surfactant molecules into the soil matrix causing them to swell, caused the increase in diffusivity, which in turn was responsible for the increase in the PAHs release to the water and Increase of concentration gradient of soil-water interface</td>
<td>1. The direct mass transfer from the micelle to the bacterial cell was decreased with the increase in the micellar concentration. 2. It also depends on the bacterial culture and the type of surfactant. 3. It is not certain that adding a surfactant will always increase bioavailability; it may act otherwise too. 4. Economic viability issues involves the fact that the critical micellar concentration is to be overcome</td>
</tr>
<tr>
<td>2001</td>
<td>Amezquita-Vega et al.</td>
<td>Biosurfactant Addition</td>
<td>Addition of biosurfactant was found to make phenanthrene bioavailable.</td>
<td>1. The cost involved in the process is high. 2. It also depends on the bacterial culture and the type of surfactant.</td>
</tr>
<tr>
<td>Year</td>
<td>Authors</td>
<td>Method/Condition</td>
<td>Summary</td>
<td>Findings</td>
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<td>-------</td>
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<td>------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------</td>
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<tr>
<td>2002</td>
<td>Rothermich M M et al</td>
<td>Sulfate Reducing Condition</td>
<td>Sediments have shown positive affects to sulfate amendments.</td>
<td>1. Degradation might vary greatly based on the sediment type and the source of contaminant.</td>
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<td>1999</td>
<td>Schmidtke T. et al, Koenigsberg et al</td>
<td>Oxygen Release Compounds</td>
<td>Naphthalene was treated from 220 ppb to Non-detectable levels.</td>
<td>1. Breakdown of ORC will be a limiting factor for the process. 2. Nearly half the oxygen produced was lost to the environment. 3. Temperature and time too have an impact on oxygen release.</td>
</tr>
<tr>
<td>2001</td>
<td>Breuer et al</td>
<td>Aeration combined with oxidizing agent</td>
<td>Research work is going on. No data published yet.</td>
<td>1. Aeration disturbs the sediment which in turn leads to the buried PAH containing sediment to come on surface. Pollutions mobilization is the issue.</td>
</tr>
<tr>
<td>2005</td>
<td>Federica et al</td>
<td>Aerobic indigenous Microflora</td>
<td>Degradation ranging from 55% to 95%.</td>
<td>1. No control over remediation. 2. Slow process. 3. Aerobic indigenous microflora are capable of degrading PAHs</td>
</tr>
<tr>
<td>2005</td>
<td>Quantin C. et al</td>
<td>Aerobic and anaerobic degradation</td>
<td>Iron and Sulfate based additives are way too slow as compared to aerobic degradation.</td>
<td>1. Batch analysis done can be scaled up for ex situ which is costly.</td>
</tr>
<tr>
<td>2005</td>
<td>Boyd T.J et al</td>
<td>Dissolved oxygen analysis</td>
<td>Dissolved oxygen in estuaries does affect the biodegradation.</td>
<td>1. The analysis puts light onto the need of oxygen in sediments for PAH degradation.</td>
</tr>
</tbody>
</table>
Research Objectives

The objectives of this study were as follows:

1. Conduct a detailed literature study of the methods for treating contaminated sediments;
2. Develop a mathematical model of the proposed hollow fiber membrane reactor system that had been experimentally applied at the bench-scale;
3. Develop a computer program which solves the model equations and minimizes the error between the model calculations and the experimental data to determine the best-fit values of the biokinetic and transport parameters in the model equations;
4. Use the fitted mathematical model to derive the design parameters such as the distance between the fibers;
5. Compare the bioremediation rates obtained using membranes with no membranes or natural attenuation conditions; and
6. Use the WASP-6 program to calculate the impact of contaminated sediments on water quality.
Biokinetic Analysis of the Bench Scale Experimental Data

1. *Technical Background*

- *Biodegradation*

Bioremediation is defined as the use of microorganisms or their metabolic products to mediate the transformation of hazardous chemicals to less toxic and environmentally acceptable compounds. Biodegradation is nature's way of recycling wastes, or breaking down organic matter into nutrients that can be used by other organisms. "Degradation" means decay, and the "bio-" prefix means that the decay is carried out by a huge assortment of bacteria, fungi, insects, worms, and other organisms that eat dead material and recycle it into new forms. In nature, there is no waste because everything gets recycled. The waste products from one organism become the food for others, providing nutrients and energy while breaking down the waste organic matter. Some organic materials will break down much faster than others, but all will eventually decay. By harnessing these natural forces of biodegradation, people can reduce wastes and clean up some types of environmental contaminants.

"Remediate" means to solve a problem, and "bio-remediate" means to use biological organisms to solve an environmental problem such as contaminated soil or groundwater. In a non-polluted environment, bacteria, fungi, protists, and other microorganisms are constantly at work breaking down organic matter. What would occur if an organic pollutant such as oil contaminated this environment? Some of the microorganisms would die, while others capable of eating the organic pollution would survive. Bioremediation works by providing these pollution-eating organisms with fertilizer, oxygen, and other conditions that encourage their rapid growth. These
organisms would then be able to break down the organic pollutant at a correspondingly faster rate. In fact, bioremediation is often used to help clean up oil spills.

Bioremediation of a contaminated site typically works in one of two ways. In the case described above, ways are found to enhance the growth of whatever pollution-eating microbes might already be living at the contaminated site. In the second, less common case, specialized microbes are added to degrade the contaminants. Bioremediation provides a good cleanup strategy for some types of pollution, but as you might expect, it will not work for all. For example, bioremediation may not provide a feasible strategy at sites with high concentrations of chemicals that are toxic to most microorganisms. These chemicals include metals such as cadmium or lead, and salts such as sodium chloride.

○ Monod Model

Monod came up with a model which in most cases fits all the unrestricted biological degradation in 1942. The model was based on the different phases involved in the bioremediation process – (1) Lag phase – when microorganisms are initially exposed to a chemical, it takes them some time to get acclimated to the environment in which the chemical is present. (2) Acceleration phase – in this phase, when cells has just adjusted to the environment and starts to propagate, the microbes synthesize the growth factors and enzymes required for the degradation. (3) Exponential phase – Both the cell concentration curve and the cell mass concentration-time curve depict an exponential function. This exponential relationship results from the basic fact that the growth occurs by cell division, called binary fission. (4) Declining phase – In this phase the growth starts retarding, which is mainly due to the fact that the chemical used for the growth has been depleted or the metabolic products are inhibiting further growth. (5) Stationary
phase – Cell propagation is balanced by the cell decay. The cell concentration reaches a plateau. (6) Decay phase – the cell decay is higher than the propagation rate. (7) Exponential death phase – The number of living cells decrease exponentially, when cell growth or propagation has completely ceased.

- **Double Monod Model**

  In 1972 the Monod model changed its form to Double Monod for electron acceptor limited degradations. This model introduces another saturation factor to take care of the concentration variation of electron acceptors. It tells us that though the degradation of PAH is dependant upon the concentration of PAH but it is also a monotonically increasing but saturating function of the electron acceptor concentration. Equations are listed in Mathematical Model presented in this section.

**Equation 1: Double Monod Model**

\[
\mu = \mu_{\text{max}} X \left( \frac{S}{K_s + S} \right) \left( \frac{O}{K_o + O} \right)
\]

Where,

- \(\mu\) = Biomass specific growth rate.
- \(\mu_{\text{max}}\) = Biomass maximum specific growth rate
- \(K_s\) = Monod half saturation constant for the contaminants.
- \(K_o\) = Monod half saturation constant for the electron acceptors.
- \(S\) = Substrate (contaminant) concentration.
- \(O\) = Oxygen concentration.
- \(X\) = Local biomass concentration.
Chemical Binding (Sequestration)

Luthy et al. did a micro scale characterization and desorption analysis for the sediments with the objective of finding the surface effect of sediments on the contaminant adsorption, possible desorption of the PAHs from the sediment using extraction, mechanism governing sequestration, effect of such processes on bioavailability and toxicity limit assessment and nature of PAH association that leads to their unavailability. (Ghoshal S, Luthy R G 1998) They concluded that surface to bulk ratio is directly proportional to the sorbed PAH concentration. They further concluded that the lighter coal and wood derived fraction of sediments have more PAH fraction then the abundant silica particles in sediment but they did not differentiate between different forms of organic carbon like humic matter particle, humic matter sorbed on mineral surfaces etc. They found that there were available and unavailable fractions present in the sediment. It was attributed to the sorption. (Luthy et al 2000) This is evident that aging is the factor, which governs the sorption, but Govind et al. hypothesized the interactions with humic matter to be a chemical binding. These bindings explain the high bioremediation rate observed. A combined model of biodegradation and chemical binding was proposed and fitted to be found appropriate with the experimental data and literature. (Govind et al 2001) Weber et al investigated oxidative coupling of hydroxylated aromatic compounds by natural geosorbent. (Weber et al 2003). Moreover, they showed that in order to form a biopolymer the presence of hydroxylated aromatics is required. Perminova et al. and Rice et al. attributed the detoxification of the PAHs in presence of humics to the chemical binding in their findings (Perminova et al. 2001, Rice et al 2004). Rice et al further found that bound residue formation for the metabolites
PAH-diols are 5 to 20 times higher than the respective PAH (Rice et al 2004). Pathways of sorption, chemical binding and biodegradation, and hence bioavailability and bioconcentration are complex and an area of curious research.

- Finite difference method

It is well known that almost all phenomena in nature involving reactive flows, combustion, gas dynamics, and many other processes can be described with the aid of the laws of physics in terms of algebraic, differential, integral equations, or combinations of them, relating different quantities of interest. The solution of such equations in an exact way is, in most cases, not possible. It thus becomes necessary to find methods for approximating the solutions to these equations. Approximate solution techniques like finite element, finite difference, finite volume, and collocation are among the most often used methods. These techniques are used to go from continuous models to discrete models. Perhaps the most traditional way to solve partial differential equations is Finite difference method. By this process, the equations referred to above are replaced by linear or non-linear systems of algebraic equations whose solutions approximate the solutions of the original equations. The finite Different Method (FDM) consists of transforming the partial derivatives in difference equations over a small interval. After substituting the derivatives approximations over the PDE, PDE is converted into a set of finite difference equations that can be solved either by explicit or implicit method. Explicit method allows evaluating the unknown value directly from the subsequent known future. It can be done because we have proper boundary conditions that always set any values at the termination date. It can be viewed as a dynamic programming backward procedure. Nonetheless, explicit method has to be carefully employed for stability of the equation.
• **Relative Residue Error**

After the application of Finite difference method and Runge Kutta method it is needed to check the accuracy of the solution against the experimental values. For a specific time we take the difference of the experimental to simulated value of PAH and divide by the experimental value. Then we add the square the value of all the time we have recorded this difference for and add them. Then we take the square root of these values and divide that by the number of events to get the RRE. The equation is as follows:

\[
RRE = \sqrt{\frac{\sum_{i=0}^{m} (q(t_i) - q^{\text{exp}}(t_i))^2}{q^{\text{exp}}(t_i)}}
\]

**Equation 2: Relative Residue error**

• **Method of Boxes**

To solve the parameters of the equation we use the method of boxes. It involves assuming a range to which the solution might belong. We divide the ranges of all the parameters into equal parts. Now for all parts we solve the equations as an objective function which in our case is RRE (relative residue error). The solution range for all the parameters gives us a new set of box boundaries to be divided and then solved for. We continue this until we find the most optimum objective function solution.
• Simulation Environment

For these simulations of the numerical method we chose MATLAB 7.0 (The Mathworks, Inc) Matlab has a great capability of flexible programming which lead to the use of it as an independent compiler for the above mentioned algorithms.

2. Chemical Reactions

Chemical reactions governing the bioremediation and sequestration are as follows:

Equation 3: PAH transformation and degradation kinetic equations
• First Order decay of PAH in presence of Enzymes to PAH-dihydrodiols
  \[
  \text{PAH} + \text{E} \quad \xrightarrow{K_1} \quad \text{PAH-OH} \quad (3.1)
  \]

• Chemical Binding (Sequestration) with the Soil Humic Matters
  \[
  \text{PAH-OH} + \alpha \text{SOM} \quad \xrightarrow{K_2} \quad \text{PAH-SOM} \quad (3.2)
  \]

• Biodegradation of PAH diols
  \[
  \text{PAH-OH} \quad \xrightarrow{\mu, K, K} \quad \text{yCO}_2 + \text{zH}_2\text{O} + \text{Biomass (x)} \quad (3.3)
  \]

3. Mathematical Model

• Assumptions

The model is based on following assumptions:

Biomass, PAHs and oxygen are always uniformly distributed with regards to membrane bio-reactor radius.

Initially biomass, PAHs and oxygen are uniform throughout the membrane bio-reactor.

The whole process can be divided into following parts:
•**Hollow fiber membranes supplying the electron acceptors**

Hollow fiber membranes will be supplying the electron acceptors by forming a meniscus at the interface which will be just sufficient to form a non bubbling interface at the time of pulsing and hence no convection. This will provide the boundary condition with the equilibrium condition satisfied at the gas liquid interface (in case of oxygen as electron acceptor) hence concentration of the interface being equal to the saturation concentration. Further in the case of other electron acceptors diffusion from the boundary will be the cause of the electron acceptor transport from the membrane fibers. Hence the boundary condition will correspond to the concentration of the electron acceptor in the medium.

•**Diffusion and consumption of electron acceptor in the sediment**

Diffusion reaction equation will govern the concentration of the electron acceptor in the sediment. Here the electron acceptor will start to move from the membrane and in turn will be consumed according to the kinetics of the biodegradation.

•**Sediment Oxygen Demand**

Dead organic material accumulated on the bed of a lake, reservoir or wetland often provides the substrate for substantial microbial activity as well as chemical processes that withdraw dissolved oxygen (DO) from the water column. A model to estimate the actual DO profile and the “sediment oxygen demand (SOD)” must specify the rate of microbial or chemical activity in the sediment as well as the diffusive supply of DO from the water column through the diffusive boundary layer into the sediment. Sediment oxygen demand is the generally accepted biological demand of electron acceptors to degrade the organic matters other than the targeted contaminant in the clean
sediment. The superimposition of the SOD will give us the real utilization of electron acceptor for the degradation process.

- **Hypothesis of the PAH Degradation**

  There is enough evidence to support the theory that PAH can not be directly transformed / biodegraded. They first take a much amenable form of the PAH-Diols following a first order kinetics with the help of enzymes formed by the microbes. The mechanism and the existence of PAH-diol are well documented (Cerniglia, C.E. *et al* 1984) and supported by many researchers now and are out of the scope of the present work. (Weber *et al*, 2003) It is further assumed and found to be experimentally close to the assumption that PAH here undergoes a first order kinetic degradation into the diols. (Weber *et al*, 2003)

- **Hypothesis of the PAH-Diol Transformation / Degradation**

  Biological species indulge themselves into the biological transformation (biopolymerization) and biodegradation when they come in contact with the species to be consumed as electron donor (the contaminant). Based on this we could hypothesize that a chemical binding phenomenon which will convert the PAHs into the diols and then into the bound organic matter which can not be traced as PAHs but has a potential to come out if loosely bound under certain change in environmental condition, exists parallel to the degradation of PAHs. Hence PAH-diols undergo a biodegradation by following biokinetics model (assumed to be Double Monod Model) and a first order conversion to the Humic Matter by chemical binding to the humic matter. There is enough evidence now in the literature which helps us prove the hypothesis to be correct. (Weber *et al*, 2003)
• **Biomass growth modeling**

The biomass growth is modeled as the double Monod with inclusion of electron acceptors and contaminants concentration to be driving forces. (Equation 1: Double Monod Model)

• **Enzyme Concentration**

Enzyme concentration is dependent on the production of the enzymes from the biomass and consumption in the first order kinetics for PAH conversion to diols.

• **Initial conditions** –

Initial conditions for the biokinetic analysis (at time $t = 0$) of PAHs are as follows:

**Equation 4: Initial conditions for the simulation for biokinetics analysis**

$$O(r, 0) = O_0,$$  \hspace{1cm} (4.1)

*Where,*

$O$ = electron acceptor concentration at time $t = 0$.

$$C(r, 0) = C_0,$$  \hspace{1cm} (4.2)

*Where,*

$C$ = PAH concentration at time $t = 0$.

$$E(r, 0) = 0,$$  \hspace{1cm} (4.3)

*Where,*

$E$ = Enzyme concentration at time $t = 0$.

$$C_b(r, 0) = 0,$$  \hspace{1cm} (4.4)

*Where,*

$C_b$ = Bound PAH concentration at time $t = 0$.

$$X(r, 0) = x_0,$$  \hspace{1cm} (4.5)

*Where,*
x = Biomass concentration at time t = 0

- **Boundary Condition** –

Equation 5: Boundary Conditions for the simulation of biokinetic analysis

\[ O(R, t) = O_0 \quad r = R \]  \hspace{1cm} (5.1)

Where,

\( O \) = electron acceptor concentration at distance \( r = R \)

\[ \frac{\partial O(r, t)}{\partial t} = 0 \quad r = R^* \]  \hspace{1cm} (5.2)

Where,

\( O \) = electron acceptor concentration at distance \( r = R^* \)

- **Mathematical Model** -
Table 2: Mathematical Model for bioremediation using membrane

<table>
<thead>
<tr>
<th>Eqn No.</th>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
</table>
| 1. | \[
\frac{\partial O(r,t)}{\partial t} = D_o \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial O(r,t)}{\partial r} \right) - \frac{1}{Y_o} \frac{\mu_{\text{max}} x(r,t) C_H(r,t)}{K_e + C_H(r,t) - K_o + O(r,t)} \right) - \text{SOD}
\] | Oxygen Diffusion with Consumption |
| 2. | \[- \frac{\partial C(r,t)}{\partial t} = K_1 C(r,t) E(r,t)\] | PAH Consumption |
| 3. | \[\frac{\partial C_H(r,t)}{\partial t} = \frac{1}{Y_e} \frac{\mu_{\text{max}} x(r,t) C_H(r,t)}{K_e + C_H(r,t) - K_o + O(r,t)} O(r,t) + K_1 C_H(r,t) E(r,t) - K_2 C_{org} C_H\] | PAH-diol Consumption |
| 4. | \[\frac{\partial x(r,t)}{\partial t} = \frac{\mu_{\text{max}} x(r,t) C_H(r,t)}{K_e + C_H(r,t) - K_o + O(r,t)} O(r,t)\] | Biomass Growth Rate |
| 5. | \[\frac{\partial E(r,t)}{\partial t} = - \frac{1}{Y_e} \frac{\mu_{\text{max}} x(r,t) C_H(r,t)}{K_e + C_H(r,t) - K_o + O(r,t)} O(r,t) - K_1 C(r,t) E(r,t)\] | Enzyme Concentration |
| 6. | \[\frac{\partial C_B(r,t)}{\partial t} = K_2 C_{org} C_H(r,t)\] | Bound Contaminant |
| 7. | \[\bar{O} = \frac{\int_0^2 O(r,t) r dr}{(R^2 - r^2)}\] | Oxygen Uptake |
| 8. | \[\bar{C} = \frac{\int_0^2 C(r,t) r dr}{(R^2 - r^2)}\] | Average PAH in sediment |
Equation 6: Mathematical Model for bioremediation using membrane

- **Oxygen Diffusion with Consumption**

\[ \frac{\partial O(r,t)}{\partial t} = D_o \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial O(r,t)}{\partial r} - \frac{1}{Y_o} \frac{\mu_{max}}{K_c + C_H(r,t)} \frac{\mu_{max}}{K_o + O(r,t)} \ - SOD \tag{6.1} \]

Where,

- \(O\) = electron acceptor concentration
- \(r\) = distance from the fiber
- \(t\) = time elapsed
- \(D_o\) = diffusivity of electron acceptor in the system
- \(Y_o\) = Biomass yield factor of oxygen
- \(\mu_{max}\) = Biomass maximum specific growth rate
- \(K_c\) = Monod half saturation constant for the contaminants.
- \(K_o\) = Monod half saturation constant for the electron acceptors.
- \(C_h\) = Substrate (PAH-dihydrodiol) concentration.
- \(O\) = Oxygen concentration.
- \(x\) = Local biomass concentration.
- \(SOD\) = Sediment Oxygen Demand

- **PAH Consumption**

\[ - \frac{\partial C(r,t)}{\partial t} = K_1 C(r,t) E(r,t) \tag{6.2} \]

Where,

- \(r\) = distance from the fiber
- \(t\) = time elapsed
\( C \) = Local PAH concentration.

\( E \) = Local Enzyme concentration

\( K_1 \) = rate constant for the initial reaction.

**PAH-diol Consumption**

\[
\frac{\partial C_H(r,t)}{\partial t} = -\frac{1}{Y_H} \mu_{\text{max}} x(r,t) C_H(r,t) \times \frac{O(r,t)}{K_o + O(r,t)} + K_1 C_H(r,t) E(r,t) - K_2 C^{\alpha}_{\text{org}} C_H \tag{6.3}
\]

Where,

\( C_H \) = PAH-diol concentration

\( r \) = distance from the fiber

\( t \) = time elapsed

\( Y_H \) = Biomass yield factor of the hydrolyzed contaminants

\( \mu_{\text{max}} \) = Biomass maximum specific growth rate

\( K_c \) = Monod half saturation constant for the contaminants.

\( K_o \) = Monod half saturation constant for the electron acceptors.

\( E \) = Local Enzyme concentration

\( O \) = Oxygen concentration.

\( x \) = Local biomass concentration.

\( K_1 \) = rate constant for the initial reaction.

\( K_2 \) = rate constant for the chemical binding reaction

\( C^{\alpha}_{\text{org}} \) = Humic matter concentration

\( C_B \) = Bound PAH concentration

**Biomass Growth Rate**
\[
\frac{\partial x(r,t)}{\partial t} = \frac{\mu_{\text{max}} x(r,t) C_H (r,t)}{K_e + C_H (r,t)} \frac{O(r,t)}{K_o + O(r,t)} \tag{6.4}
\]

Where,

- \( C_H \) = PAH-diol concentration
- \( r \) = distance from the fiber
- \( t \) = time elapsed
- \( \mu_{\text{max}} \) = Biomass maximum specific growth rate
- \( K_e \) = Monod half saturation constant for the contaminants.
- \( K_o \) = Monod half saturation constant for the electron acceptors.
- \( O \) = Oxygen concentration.
- \( x \) = Local biomass concentration.

**Enzyme Concentration**

\[
\frac{\partial E(r,t)}{\partial t} = -\frac{1}{Y_e} \frac{\mu_{\text{max}} x(r,t) C_H (r,t)}{K_e + C_H (r,t)} \frac{O(r,t)}{K_o + O(r,t)} - K_1 C(r,t) E(r,t) \tag{6.5}
\]

Where,

- \( r \) = distance from the fiber
- \( t \) = time elapsed
- \( C \) = Local PAH concentration.
- \( E \) = Local Enzyme concentration
- \( K_1 \) = rate constant for the initial reaction.
- \( Y_e \) = Enzyme yield factor of the hydrolyzed contaminants
- \( \mu_{\text{max}} \) = Biomass maximum specific growth rate
- \( K_e \) = Monod half saturation constant for the contaminants.
- \( K_o \) = Monod half saturation constant for the electron acceptors.
\[ \hat{C}_B (r, t) = K_2 C_{\text{org}} \alpha \]  

Where,

- \( C_H \) = PAH-diol concentration
- \( r \) = distance from the fiber
- \( t \) = time elapsed
- \( K_2 \) = rate constant for the chemical binding reaction
- \( C_{\text{org}}^\alpha \) = Humic matter concentration
- \( C_B \) = Bound PAH concentration

4. Oxygen Uptake

\[ \bar{O} = \frac{2 \int 2\kappa' O(r,t) rdr}{\kappa (R^2 - R^*)} \]  

Where,

- \( O \) = Local Oxygen concentration
- \( r \) = distance from the fiber
- \( t \) = time elapsed
- \( R \) = radius of membrane fiber
- \( R^* \) = boundary of the domain
- \( \bar{O} \) = average oxygen concentration

5. Average PAH in sediment
\[
\overline{C} = \frac{2 \int_{R}^{R^*} C(r, t) r dr}{(R^*^2 - R^2)}
\]  

(6.8)

Where,

\( C \) = Total local contaminant concentration

\( r \) = distance from the fiber

\( t \) = time elapsed

\( R \) = radius of membrane fiber

\( R^* \) = boundary of the domain

\( \overline{C} \) = average contaminant concentration

4. **Simulation Method**

Simulation involved programming the PDEs in MATLAB® using numerical techniques. Here the PDEs specified are highly coupled and nonlinear which makes the analytical results hard to achieve. Hence the numerical approach was taken into account and solved following certain well established methods. These methods are already explained in the technical background so here we would just take a moment to appreciate their role in the simulation.

- **Finite difference method**

All the PDEs were converted into the ODEs. All the equations were broken into the space and time domain to form the algebraic equation. The results were some simultaneous equations which were again solved using the numerical method explicitly. Here the boundary conditions are taken at the boundary of the membrane and the reactor.
• **Runge – Kutta method**

In order to compare the result of the data spread over space and time we had to integrate the output contamination in space and then compare using the RRE optimization for the optimum solution.

• **Method of Boxes**

In order to optimize the data over the objective function of RRE to be least we used the method of boxes. The initial parameter range was assumed to be large enough and the data converged successfully showing RRE less than 0.05.

5. **Simulation Results and Discussion**

The PAH Degradation data for the reactor were divided into groups of 2, 3, 4, 5 and 6 rings and their results were discussed by group. The initial concentration of PAH was taken from the data table of Mukundan Ramani and Dr Rakesh Govind previous experiments (Appendix 1). Table 3: Initial PAH Concentration for the simulation represents the data for the initial condition

**Table 3: Initial PAH Concentration for the simulation**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (mg/Kg) (Percentage of Total PAHs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>3.8 (12.3)</td>
</tr>
<tr>
<td>2-Methylnaphthalene</td>
<td>2.6 (6.23)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>7.8 (20.3)</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>2.8 (7.82)</td>
</tr>
<tr>
<td>Anthracene</td>
<td>3.2 (8.23)</td>
</tr>
<tr>
<td>Fluorene</td>
<td>1.8 (4.27)</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>6.4 (14.5)</td>
</tr>
<tr>
<td>Pyrene</td>
<td>3.9 (6.67)</td>
</tr>
<tr>
<td>Benzo [a] anthracene</td>
<td>2.1 (3.46)</td>
</tr>
<tr>
<td>Chrysene</td>
<td>2.7 (4.78)</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>2.1 (3.19)</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>1.7 (2.15)</td>
</tr>
<tr>
<td>Benzo[ghi]perylene</td>
<td>0.8 (1.54)</td>
</tr>
<tr>
<td>TPAH</td>
<td>46.8 (98.6)</td>
</tr>
</tbody>
</table>
• **Aerobic:**

For aerobic simulation the electron acceptor is Oxygen. The fiber is used to keep the environment around it to the saturated level of oxygen concentration hence providing us with the boundary condition. The other boundary condition is the wall of the reactor which gives us the no flux condition across it. The initial condition of the PAHs is taken out of the Table 3: Initial PAH Concentration for the simulation for all the rings of PAHs. Experimental data, boundary and initial conditions were taken from the Appendix 1 (Govind, R. and Ramani M. 2001) and thesis (Govind, R. and Ramani M. 2000). Following figures and tables reflect the curve fits of the model described in Equation 6: Mathematical Model for bioremediation using membrane.

- **2 Ring PAHs**

  Initial Condition:
  
  \[
  \begin{align*}
  \text{PAH} & = 3.2 \text{ mg/Kg}.
  
  \text{PAHdiol} & = 3.2 \text{ mg/Kg}.
  
  \text{PAHbound} & = 0 \text{ mg/Kg}.
  
  \text{Biomass} & = 10 \text{ mg/Kg}.
  
  \text{Enzyme} & = 0 \text{ mg/Kg}.
  
  \text{Oxygen} & = 8 \text{ mg/Kg}.
  \end{align*}
  \]

  Boundary Condition:
  
  \[O(R, t) = O_o \quad r=R\]

  Where,
  
  \[O = \text{electron acceptor concentration at distance } r = R\]
\[
\frac{\partial O(r,t)}{\partial t} = 0 \quad \text{where} \quad r = R^*
\]

Where,

\[O = \text{electron acceptor concentration at distance } r = R^* \quad (R^* = 1 \text{ cms.})\]

Figure 1: Aerobic degradation of 2 Ring PAHs

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.05. Following curve shows Bound PAH –
Figure 2: Bound PAH for 2 Ring PAH simulation

3 Ring PAHs

Initial Condition:

- PAH = 7.0 mg/Kg.
- PAHdiol = 8.6 mg/Kg.
- PAHbound = 0 mg/Kg.
- Biomass = 10 mg/Kg.
- Enzyme = 0 mg/Kg.
- Oxygen = 8 mg/Kg.

Boundary Condition:

\[ O(R, t) = O_o \quad r = R \]

Where,

\[ O = \text{electron acceptor concentration at distance } r = R \]

\[ \frac{\partial O(r,t)}{\partial t} = 0 \quad r = R^* \]
Where,

\[ O = \text{electron acceptor concentration at distance } r = R^* \text{ (R}^* = 1 \text{ cms.)} \]

Figure 3: Aerobic degradation of 3 Ring PAHs

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.03. Following curve shows 3 ring bound PAH

Figure 4: Bound PAH for 3 Ring simulation
**4 Ring PAHs**

**Initial Condition:**

- \( \text{PAH} = 7.0 \text{ mg/Kg.} \)
- \( \text{PAHdiol} = 8.6 \text{ mg/Kg.} \)
- \( \text{PAHbound} = 0 \text{ mg/Kg.} \)
- \( \text{Biomass} = 10 \text{ mg/Kg.} \)
- \( \text{Enzyme} = 0 \text{ mg/Kg.} \)
- \( \text{Oxygen} = 8 \text{ mg/Kg.} \)

**Boundary Condition:**

\[ O(R, t) = O_o \quad r = R \]

Where,

\[ O = \text{electron acceptor concentration at distance } r = R \]

\[ \frac{\partial O(r,t)}{\partial t} = 0 \quad r = R^* \]

Where,

\[ O = \text{electron acceptor concentration at distance } r = R^* (R^* = 1 \text{ cms.}) \]
Figure 5: Aerobic degradation of 4 Ring PAHs

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.02. Following curve shows 4 ring bound PAH.

Figure 6: Bound PAH for 4 ring aerobic simulation

5 Ring PAHs
Initial Condition:

PAH = 1.8 mg/Kg.
PAHdiol = 2.0 mg/Kg.
PAHbound = 0 mg/Kg.
Biomass = 10 mg/Kg.
Enzyme = 0 mg/Kg.
Oxygen = 8 mg/Kg.

Boundary Condition:

\[ O(R, t) = O_o \quad r = R \]

Where,

\[ O = \text{electron acceptor concentration at distance } r = R \]

\[ \frac{\partial O(r, t)}{\partial t} = 0 \quad r = R^* \]

Where,

\[ O = \text{electron acceptor concentration at distance } r = R^* \quad (R^* = 1 \text{ cms.}) \]

Figure 7: Aerobic degradation of 5 Ring PAHs
The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.02. Following curve shows the bound PAH for 5 ring PAHs

![Graph showing bound PAH for 5 ring PAH simulation](image)

**Figure 8: Bound PAH for 5 ring PAH simulation**

- **6 Ring PAHs**

**Initial Condition:**

- PAH = 0.4 mg/Kg.
- PAHdiol = 0.4 mg/Kg.
- PAHbound = 0 mg/Kg.
- Biomass = 10 mg/Kg.
- Enzyme = 0 mg/Kg.
- Oxygen = 8 mg/Kg.

**Boundary Condition:**

\[ O(R, t) = O_o \quad r=R \]

Where,
\[ O = \text{electron acceptor concentration at distance } r = R \]

\[ \frac{\partial O(r,t)}{\partial t} = 0 \quad r = R^* \]

Where,

\[ O = \text{electron acceptor concentration at distance } r = R^* \ (R^* = 1 \text{ cms.}) \]

Figure 9: Aerobic degradation of 6 Ring PAHs

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.02. Following curve shows the bound PAH for 6 ring PAH simulation.
Figure 10: Bound PAH for 6 ring simulation
Kinetic Parameters obtained for Aerobic condition

Table 4: Kinetic Parameters obtained for Aerobic condition simulation

<table>
<thead>
<tr>
<th>Ring Size</th>
<th>Parameter</th>
<th>K1 (mg/kg. day⁻¹)</th>
<th>K2 (day⁻¹)</th>
<th>D₀ (cm²/h)</th>
<th>μ (day⁻¹)</th>
<th>Kc (mg/Kg)</th>
<th>Ko (mg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Rings</td>
<td></td>
<td>0.021 ± 0.001</td>
<td>0.0095 ± 0.0001</td>
<td>0.24158 ± 0.0004</td>
<td>9.72929 ± 0.0001</td>
<td>5.83757 ± 0.00180</td>
<td></td>
</tr>
<tr>
<td>3 Rings</td>
<td></td>
<td>0.005 ± 0.001</td>
<td>0.00958 ± 0.00001</td>
<td>0.1995 ± 0.0001</td>
<td>13.0654 ± 0.00400</td>
<td>4.39313 ± 0.000001</td>
<td></td>
</tr>
<tr>
<td>4 Rings</td>
<td></td>
<td>0.005 ± 0.001</td>
<td>0.00958 ± 0.0001</td>
<td>0.3596 ± 0.0001</td>
<td>14.612 ± 0.0032</td>
<td>5.83371 ± 0.00045</td>
<td></td>
</tr>
<tr>
<td>5 Rings</td>
<td></td>
<td>0.001 ± 0.001</td>
<td>0.00958 ± 0.00004</td>
<td>0.19854 ± 0.003210</td>
<td>24.8980 ± 0.003200</td>
<td>5.99035 ± 0.00351</td>
<td></td>
</tr>
<tr>
<td>6 Rings</td>
<td></td>
<td>0.001 ± 0.0001</td>
<td>0.00958 ± 0.00001</td>
<td>0.20047 ± 0.003200</td>
<td>29.8630 ± 0.003200</td>
<td>5.77276 ± 0.003200</td>
<td></td>
</tr>
<tr>
<td>Parameter</td>
<td>Ye (mg/Kg)</td>
<td>Yh (mg/Kg)</td>
<td>Yo (mg/Kg)</td>
<td>RRE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>------------</td>
<td>------------</td>
<td>------------</td>
<td>-----</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Ring Size</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Rings</td>
<td>2.49806±0.00001</td>
<td>0.3506±0.0001</td>
<td>0.0708±0.0001</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 Rings</td>
<td>2.61984±0.00021</td>
<td>1.2167±0.0001</td>
<td>0.9444±0.0003</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 Rings</td>
<td>2.5534±0.0002</td>
<td>2.6183±0.0004</td>
<td>0.5047±0.0003</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 Rings</td>
<td>2.22015±0.00015</td>
<td>2.4979±0.0002</td>
<td>0.7221±0.0006</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 Rings</td>
<td>2.22015±0.0002</td>
<td>2.0754±0.0007</td>
<td>2.422±0.0006</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Denitrifying Condition

For denitrifying condition simulation the electron acceptor is sodium nitrate. The fiber is used to keep the environment around it to the nitrate concentration inside the fiber hence providing us with the boundary condition. The other boundary condition is the wall of the reactor which gives us the no flux condition across it. The initial condition of the PAHs is taken out of the Table 3: Initial PAH Concentration for the simulation for all the rings of PAHs. Experimental data, boundary and initial conditions were taken from the Appendix 1 (Govind, R. and Ramani M. 2001) and thesis (Govind, R. and Ramani M. 2000). Following figures and tables reflect the curve fits of the model described in Equation 6: Mathematical Model for bioremediation using membrane.

2 Ring PAHs

Initial Condition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAH</td>
<td>3.2 mg/Kg.</td>
<td></td>
</tr>
<tr>
<td>PAHdiol</td>
<td>3.2 mg/Kg.</td>
<td></td>
</tr>
<tr>
<td>PAHbound</td>
<td>0 mg/Kg.</td>
<td></td>
</tr>
<tr>
<td>Biomass</td>
<td>10 mg/Kg.</td>
<td></td>
</tr>
<tr>
<td>Enzyme</td>
<td>0 mg/Kg.</td>
<td></td>
</tr>
<tr>
<td>Sodium Nitrate</td>
<td>15 mg/Kg.</td>
<td></td>
</tr>
</tbody>
</table>

Boundary Condition:

\[ O(R, t) = O_0 \quad r = R \]

Where,

\[ O = electron \, acceptor \, concentration \, at \, distance \, r = R \]

\[ \frac{\partial O(r,t)}{\partial t} = 0 \quad r = R^* \]
Where,

\[ O = \text{electron acceptor concentration at distance } r = R^* \ (R^* = 1 \text{ cms.}) \]

Figure 11: degradation of 2 Ring PAHs under Denitrifying Condition

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.06.

- **3 Ring PAHs**

Initial Condition:

- PAH = 7.0 mg/Kg.
- PAHdiol = 8.6 mg/Kg.
- PAHbound = 0 mg/Kg.
- Biomass = 10 mg/Kg.
- Enzyme = 0 mg/Kg.
- Sodium Nitrate = 15 mg/Kg.

Boundary Condition:

\[ O(R, t) = O_o \quad r = R \]
Where,

\[ O = \text{electron acceptor concentration at distance } r = R \]

\[ \frac{\partial O(r,t)}{\partial t} = 0 \quad r = R^* \]

Where,

\[ O = \text{electron acceptor concentration at distance } r = R^* \ (R^* = 1 \text{ cms.}) \]

**Figure 12: degradation of 3 Ring PAHs under Denitrifying Condition**

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.04.

- **4 Ring PAHs**

Initial Condition:

- PAH = 7.0 mg/Kg.
- PAHdiol = 8.6 mg/Kg.
- PAHbound = 0 mg/Kg.
- Biomass = 10 mg/Kg.
Enzyme = 0 mg/Kg.

Sodium Nitrate = 15 mg/Kg.

Boundary Condition:

\[ O(R, t) = O_o \quad r = R \]

Where,

\[ O = \text{electron acceptor concentration at distance } r = R \]

\[ \frac{\partial O(r, t)}{\partial t} = 0 \quad r = R^* \]

Where,

\[ O = \text{electron acceptor concentration at distance } r = R^* \quad (R^* = 1 \text{ cms.}) \]

Figure 13: degradation of 4 Ring PAHs under Denitrifying Condition

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.03.

- 5 Ring PAHs

Initial Condition:
PAH = 1.8 mg/Kg.
PAHdiol = 2.0 mg/Kg.
PAHbound = 0 mg/Kg.
Biomass = 10 mg/Kg.
Enzyme = 0 mg/Kg.
Sodium Nitrate = 15 mg/Kg.

Boundary Condition:
\[ O(R, t) = O_o \quad r = R \]

Where,
\[ O = \text{electron acceptor concentration at distance } r = R \]

\[ \frac{\partial O(r, t)}{\partial t} = 0 \quad r = R^* \]

Where,
\[ O = \text{electron acceptor concentration at distance } r = R^* \quad (R^* = 1 \text{ cms.}) \]

Figure 14: degradation of 5 Ring PAHs under Denitrifying Condition
The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.03.

- **6 Ring PAHs**

**Initial Condition:**

- PAH = 7.0 mg/Kg.
- PAHdiol = 8.6 mg/Kg.
- PAHbound = 0 mg/Kg.
- Biomass = 10 mg/Kg.
- Enzyme = 0 mg/Kg.
- Sodium Nitrate = 15 mg/Kg.

**Boundary Condition:**

$$O(R, t) = O_o \quad r=R$$

Where,

$$O = electron\ acceptor\ concentration\ at\ distance\ r = R$$

$$\frac{\partial O(r,t)}{\partial t} = 0 \quad r=R^*$$

Where,

$$O = electron\ acceptor\ concentration\ at\ distance\ r = R^* \quad (R^* = 1\ cms.)$$
Figure 15: degradation of 6 Ring PAHs under Denitrifying Condition

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.01.
**Kinetic Parameters obtained for Denitrifying condition**

Table 5: Kinetic Parameters obtained for denitrifying condition simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ring Size</th>
<th>$K1$ (mg/kg. day$^{-1}$)</th>
<th>$K2$ (day$^{-1}$)</th>
<th>$D_0$ (cm$^2$/h)</th>
<th>$\mu$ (day$^{-1}$)</th>
<th>$Kc$ (mg/Kg)</th>
<th>$Ko$ (mg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 Rings</td>
<td>13 ± 2</td>
<td>0.001 ± 0.001</td>
<td>0.009 ± 0.0001</td>
<td>0.264 ± 0.0007</td>
<td>12.6666 ± 0.0001</td>
<td>59.8958 ± 0.0001</td>
</tr>
<tr>
<td></td>
<td>3 Rings</td>
<td>13 ± 2</td>
<td>0.001 ± 0.001</td>
<td>0.009 ± 0.0001</td>
<td>0.1525 ± 0.0002</td>
<td>12.0599 ± 0.0035</td>
<td>56.9444 ± 0.0035</td>
</tr>
<tr>
<td></td>
<td>4 Rings</td>
<td>13 ± 2</td>
<td>0.001 ± 0.001</td>
<td>0.009 ± 0.0001</td>
<td>0.1575 ± 0.0006</td>
<td>16.167 ± 0.0003</td>
<td>41.8333 ± 0.00037</td>
</tr>
<tr>
<td></td>
<td>5 Rings</td>
<td>13 ± 2</td>
<td>0.001 ± 0.001</td>
<td>0.0099 ± 0.0001</td>
<td>0.1865 ± 0.0001</td>
<td>17.8298 ± 0.00001</td>
<td>60.0244 ± 0.00001</td>
</tr>
<tr>
<td></td>
<td>6 Rings</td>
<td>13 ± 2</td>
<td>0.001 ± 0.001</td>
<td>0.0099 ± 0.0001</td>
<td>0.1853 ± 0.0001</td>
<td>22.9745 ± 0.00010</td>
<td>41.8333 ± 0.0001</td>
</tr>
</tbody>
</table>

63
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ye (mg/Kg)</th>
<th>Yh (mg/Kg)</th>
<th>Yo (mg/Kg)</th>
<th>RRE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring Size</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Rings</td>
<td>2.5534 ± 0.002</td>
<td>1.66243 ± 0.0003</td>
<td>2.49890 ± 0.0003</td>
<td>0.06</td>
</tr>
<tr>
<td>3 Rings</td>
<td>0.3975 ± 0.0002</td>
<td>1.18400 ± 0.00024</td>
<td>0.93968 ± 0.0002</td>
<td>0.04</td>
</tr>
<tr>
<td>4 Rings</td>
<td>2.2201 ± 0.0002</td>
<td>1.66058 ± 0.0002</td>
<td>1.36597 ± 0.00031</td>
<td>0.03</td>
</tr>
<tr>
<td>5 Rings</td>
<td>0.9478 ± 0.0001</td>
<td>1.58666 ± 0.00032</td>
<td>2.18334 ± 0.01890</td>
<td>0.03</td>
</tr>
<tr>
<td>6 Rings</td>
<td>2.6198 ± 0.0001</td>
<td>1.56459 ± 0.00025</td>
<td>2.49890 ± 0.000015</td>
<td>0.01</td>
</tr>
</tbody>
</table>
For sulfate reducing simulation the electron acceptor is sodium sulfate. The fiber is used to keep the environment around it to the sulfate concentration inside the fiber hence providing us with the boundary condition. The other boundary condition is the wall of the reactor which gives us the no flux condition across it. The initial condition of the PAHs is taken out of the Table 3: Initial PAH Concentration for the simulation for all the rings of PAHs. Experimental data, boundary and initial conditions were taken from the Appendix 1 (Govind, R. and Ramani M. 2001) and thesis (Govind, R. and Ramani M. 2000). Following figures and tables reflect the curve fits of the model described in Equation 6: Mathematical Model for bioremediation using membrane.

2 Ring PAHs

Initial Condition:

- PAH = 3.2 mg/Kg.
- PAHdiol = 3.2 mg/Kg.
- PAHbound = 0 mg/Kg.
- Biomass = 10 mg/Kg.
- Enzyme = 0 mg/Kg.
- Sodium Sulfate = 12 mg/Kg.

Boundary Condition:

\[ O(R, t) = O_0 \quad r = R \]

Where,

\[ O = electron \, acceptor \, concentration \, at \, distance \, r = R \]

\[ \frac{\partial O(r, t)}{\partial t} = 0 \quad r = R^* \]
Where,

\[ O = \text{electron acceptor concentration at distance } r = R^* \ (R^* = 1 \text{ cms.}) \]

Figure 16: degradation of 2 Ring PAHs under Sulfate reducing Condition

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.01.

- **3 Ring PAHs**

Initial Condition:

- PAH = 7.0 mg/Kg.
- PAHdiol = 8.6 mg/Kg.
- PAHbound = 0 mg/Kg.
- Biomass = 10 mg/Kg.
- Enzyme = 0 mg/Kg.
- Sodium Sulfate = 12 mg/Kg.

Boundary Condition:

\[ O(R, t) = O_o \quad r=R \]
Where,

\[ O = \text{electron acceptor concentration at distance } r = R \]

\[ \frac{\partial O(r,t)}{\partial t} = 0 \quad r = R^* \]

Where,

\[ O = \text{electron acceptor concentration at distance } r = R^* \quad (R^* = 1 \text{ cms.}) \]

**Figure 17: degradation of 3 Ring PAHs under Sulfate reducing Condition**

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.01.

**4 Ring PAHs**

Initial Condition:

\[
\begin{align*}
\text{PAH} &= 7.0 \text{ mg/Kg.} \\
\text{PAHdiol} &= 8.6 \text{ mg/Kg.} \\
\text{PAHbound} &= 0 \text{ mg/Kg.} \\
\text{Biomass} &= 10 \text{ mg/Kg.}
\end{align*}
\]
Enzyme $= 0 \text{ mg/Kg.}$

Sodium Sulfate $= 12 \text{ mg/Kg.}$

Boundary Condition:

$$O(R, t) = O_o \quad r=R$$

Where,

$$O = \text{electron acceptor concentration at distance } r = R$$

$$\frac{\partial O(r,t)}{\partial t} = 0 \quad r=R^*$$

Where,

$$O = \text{electron acceptor concentration at distance } r = R^* (R^* = 1 \text{ cms.})$$

Figure 18: degradation of 4 Ring PAHs under Sulfate reducing Condition

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.02.

○ 5 Ring PAHs

Initial Condition:
PAH = 1.8 mg/Kg.
PAHdiol = 2.0 mg/Kg.
PAHbound = 0 mg/Kg.
Biomass = 10 mg/Kg.
Enzyme = 0 mg/Kg.
Sodium Sulfate = 12 mg/Kg.

Boundary Condition:
\[ O(R, t) = O_0 \quad r = R \]

Where,
\[ O = \text{electron acceptor concentration at distance } r = R \]
\[ \frac{\partial O(r,t)}{\partial t} = 0 \quad r = R^* \]

Where,
\[ O = \text{electron acceptor concentration at distance } r = R^* \quad (R^* = 1 \text{ cms.}) \]

Figure 19: degradation of 5 Ring PAHs under Sulfate reducing Condition
The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.03.

6 Ring PAHs

Initial Condition:

\[
\begin{align*}
\text{PAH} &= 7.0 \text{ mg/Kg.} \\
\text{PAHdiol} &= 8.6 \text{ mg/Kg.} \\
\text{PAHbound} &= 0 \text{ mg/Kg.} \\
\text{Biomass} &= 10 \text{ mg/Kg.} \\
\text{Enzyme} &= 0 \text{ mg/Kg.} \\
\text{Sodium Sulfate} &= 12 \text{ mg/Kg.}
\end{align*}
\]

Boundary Condition:

\[
O(R, t) = O_o \quad r = R
\]

Where,

\[
O = \text{electron acceptor concentration at distance } r = R
\]

\[
\frac{\partial O(r,t)}{\partial t} = 0 \quad r = R^*
\]

Where,

\[
O = \text{electron acceptor concentration at distance } r = R^* (R^* = 1 \text{ cms.})
\]
Figure 20: degradation of 6 Ring PAHs under Sulfate reducing Condition

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.02.
**Kinetic Parameters obtained for Sulfate reducing condition**

Table 6: Kinetic Parameters obtained for sulfate reducing condition simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>K1 (mg/kg . day$^{-1}$)</th>
<th>K2 (day$^{-1}$)</th>
<th>D0 (cm$^2$/h)</th>
<th>µ (day$^{-1}$)</th>
<th>Kc (mg/Kg)</th>
<th>Ko (mg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Rings</td>
<td>13 ± 2</td>
<td>0.008 ± 0.002</td>
<td>0.0049 ± 0.0001</td>
<td>0.0001 ± 0.00001</td>
<td>49.9 ± 0.01</td>
<td>49.9978 ± 0.0022</td>
</tr>
<tr>
<td>3 Rings</td>
<td>13 ± 2</td>
<td>0.008 ± 0.002</td>
<td>0.0049 ± 0.0001</td>
<td>0.00005 ± 0.00001</td>
<td>49.9 ± 0.00</td>
<td>49.9965 ± 0.00035</td>
</tr>
<tr>
<td>4 Rings</td>
<td>13 ± 2</td>
<td>0.008 ± 0.002</td>
<td>0.004 ± 0.0001</td>
<td>0.00005 ± 0.00001</td>
<td>49.9 ± 0.00</td>
<td>49.9965 ± 0.00344</td>
</tr>
<tr>
<td>5 Rings</td>
<td>13 ± 2</td>
<td>0.008 ± 0.002</td>
<td>0.004 ± 0.0001</td>
<td>0.00003 ± 0.00001</td>
<td>49.9 ± 0.01</td>
<td>49.9965 ± 0.00348</td>
</tr>
<tr>
<td>6 Rings</td>
<td>13 ± 2</td>
<td>0.008 ± 0.002</td>
<td>0.0043 ± 0.0001</td>
<td>0.00003 ± 0.00001</td>
<td>49.9 ± 0.02</td>
<td>49.9965 ± 0.00035</td>
</tr>
<tr>
<td>Parameter</td>
<td>Ye (mg/Kg)</td>
<td>Yh (mg/Kg)</td>
<td>Yo (mg/Kg)</td>
<td>RRE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>------------</td>
<td>------------</td>
<td>------------</td>
<td>------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Rings</td>
<td>1.619845 ± 0.000245</td>
<td>1.619845 ± 0.000245</td>
<td>0.040586 ± 0.001000</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 Rings</td>
<td>1.619845 ± 0.000246</td>
<td>1.619845 ± 0.000246</td>
<td>0.040010 ± 0.000020</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 Rings</td>
<td>1.619845 ± 0.000245</td>
<td>1.619845 ± 0.000245</td>
<td>0.040030 ± 0.000031</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 Rings</td>
<td>2.619717 ± 0.000293</td>
<td>2.619717 ± 0.000293</td>
<td>0.040030 ± 0.000030</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 Rings</td>
<td>3.019665 ± 0.000334</td>
<td>3.019665 ± 0.000334</td>
<td>0.040030 ± 0.000031</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
•  **Anaerobic Condition**

For anaerobic simulation there is no electron acceptor. The Boundary conditions are not needed as PAHs being bulky and sticky are assumed to be non-moving. The initial condition of the PAHs is taken out of the Table 3: Initial PAH Concentration for the simulation for all the rings of PAHs. Experimental data and initial conditions were taken from the Appendix 1 (Govind, R. and Ramani M. 2001) and thesis (Govind, R. and Ramani M. 2000). Following figures and tables reflect the curve fits of the model described in Equation 6: Mathematical Model for bioremediation using membrane except for the changes - diffusion reaction equation for electron acceptor and the double Monod becomes a classical Monod model equation.

**2 Ring PAHs**

Initial Condition:

\[
\begin{align*}
\text{PAH} & = 3.2 \text{ mg/Kg.} \\
\text{PAHdiol} & = 3.2 \text{ mg/Kg.} \\
\text{PAHbound} & = 0 \text{ mg/Kg.} \\
\text{Biomass} & = 10 \text{ mg/Kg.} \\
\text{Enzyme} & = 0 \text{ mg/Kg.}
\end{align*}
\]
Figure 21: degradation of 2 Ring PAHs under Anaerobic Condition

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.01.

3 Ring PAHs

Initial Condition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAH</td>
<td>7.0</td>
</tr>
<tr>
<td>PAHdiol</td>
<td>8.6</td>
</tr>
<tr>
<td>PAHbound</td>
<td>0</td>
</tr>
<tr>
<td>Biomass</td>
<td>10</td>
</tr>
<tr>
<td>Enzyme</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 22: degradation of 3 Ring PAHs under Anaerobic Condition

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.009.

- 4 Ring PAHs

Initial Condition:

- PAH = 7.0 mg/Kg.
- PAHdiol = 8.6 mg/Kg.
- PAHbound = 0 mg/Kg.
- Biomass = 10 mg/Kg.
- Enzyme = 0 mg/Kg.
Figure 23: degradation of 4 Ring PAHs under Anaerobic Condition

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.01.

- **5 Ring PAHs**

Initial Condition:

- \( \text{PAH} \) = 1.8 mg/Kg.
- \( \text{PAHdiol} \) = 2.0 mg/Kg.
- \( \text{PAHbound} \) = 0 mg/Kg.
- \( \text{Biomass} \) = 10 mg/Kg.
- \( \text{Enzyme} \) = 0 mg/Kg.
Figure 24: degradation of 5 Ring PAHs under Anaerobic Condition

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.009.

6 Ring PAHs

Initial Condition:

- PAH = 7.0 mg/Kg.
- PAHdiol = 8.6 mg/Kg.
- PAHbound = 0 mg/Kg.
- Biomass = 10 mg/Kg.
- Enzyme = 0 mg/Kg.
Figure 25: degradation of 6 Ring PAHs under Anaerobic Condition

The curve here shows the simulation result and the points shown are the experimental data. The RRE for the simulation was found to be 0.009.
**Kinetic Parameters obtained for Anaerobic condition**

Table 7: Kinetic Parameters obtained for anaerobic condition simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ring Size</th>
<th>( K_1 ) (mg/kg-day(^{-1}))</th>
<th>( K_2 ) (day(^{-1}))</th>
<th>( D_0 ) (cm(^2)/h)</th>
<th>( \mu ) (day(^{-1}))</th>
<th>( K_c ) (mg/Kg)</th>
<th>( K_o ) (mg/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Rings</td>
<td>13 ± 2</td>
<td>0.001 ± 0.001</td>
<td>N/A</td>
<td>0.00299 ± 0.00001</td>
<td>17.4800 ± 0.00212</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>3 Rings</td>
<td>13 ± 2</td>
<td>0.001 ± 0.001</td>
<td>N/A</td>
<td>0.00288 ± 0.00001</td>
<td>19.1004 ± 0.0111</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>4 Rings</td>
<td>13 ± 2</td>
<td>0.001 ± 0.001</td>
<td>N/A</td>
<td>0.00289 ± 0.00001</td>
<td>16.8859 ± 0.00312</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>5 Rings</td>
<td>13 ± 2</td>
<td>0.001 ± 0.001</td>
<td>N/A</td>
<td>0.00259 ± 0.00001</td>
<td>19.8611 ± 0.00286</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>6 Rings</td>
<td>13 ± 2</td>
<td>0.001 ± 0.001</td>
<td>N/A</td>
<td>0.00231 ± 0.00001</td>
<td>19.8611 ± 0.0034</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Parameter</td>
<td>Ye (mg/Kg)</td>
<td>Yh (mg/Kg)</td>
<td>Yo (mg/Kg)</td>
<td>RRE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>------------</td>
<td>------------</td>
<td>------------</td>
<td>-----</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Rings</td>
<td>0.00418 ± 0.0166</td>
<td>0.28679 ± 0.01666</td>
<td>N/A</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 Rings</td>
<td>0.56459 ± 0.00015</td>
<td>1.61984 ± 0.00024</td>
<td>N/A</td>
<td>0.007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 Rings</td>
<td>0.00418 ± 0.00024</td>
<td>0.61257 ± 0.00024</td>
<td>N/A</td>
<td>0.007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 Rings</td>
<td>0.00418 ± 0.00024</td>
<td>0.86915 ± 0.00024</td>
<td>N/A</td>
<td>0.007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 Rings</td>
<td>0.16151 ± 0.00026</td>
<td>0.79048 ± 0.00024</td>
<td>N/A</td>
<td>0.009</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
• Comparative Analysis
  
  2 Ring PAHs

![Graph of Comparative Analysis for 2 Ring PAHs](image)

Figure 26: Comparative simulation analysis for the 2 Ring PAH compounds

• 3 Ring PAHs

![Graph of Comparative Analysis for 3 Ring PAHs](image)

Figure 27: Comparative simulation analysis for the 3 Ring PAH compounds
4 Ring PAHs

Figure 28: Comparative simulation analysis for the 4 Ring PAH compounds

5 Ring PAHs

Figure 29: Comparative simulation analysis for the 5 Ring PAH compounds
6 Ring PAHs

Figure 30: Comparative simulation analysis for the 6 Ring PAH compounds

First order growth kinetics comparison for PAHs

Figure 31: First order growth rate comparison of the different electron acceptor conditions
First order Degradation kinetics comparison for PAHs

According to the published literature (Capone D G, Bauer J E, 1985; Ghoshal S, Luthy R G 1998; Smith K, Cutright T, Qammar H 2000; Lotfabad S K, Gray M R 2002; Knightes C D, Peters C 2000; Ahn I S, Lion L W, Shuler M L 1996; Poeton T S, Stensel H D, Strand S E 1998) the values of $K_a$ varies from 0.52 to 444. The value of $\mu$ varies from the 0.01 to 30.6 and value of $Y$ is published as 0.2 to 0.95. In all the values we are found to be in range of the values found earlier.
Simulation of Full-Scale System

Technical Background

Distance of the fiber was assumed and then the calculation of the day of the treatment will be evaluated using the flux coming out of the membrane bundles. This flux can be manipulated with the three different parameters. The efficiency of the geotechnical fiber to retain the microbes free atmosphere by filtering the microbes will indirectly affect the oxygen flux by making the inner mixing of the water and oxygen without degradation more effective. The distance between the fibers will govern directly the amount that is transported in an area. The back flushing frequency of the fiber will make the boundary condition to change back to fresh water and hence the flux to increase.

- Efficiency of membrane

Efficiency of the membrane is defined as the ability to retain the micro organism free environment inside the fiber assembly. The efficiency would affect the degradation by governing the flux coming out of the membrane assembly.

- Back flushing

Back flushing is a long established technique for flushing the meshes or membranes to free them from blockages. This back flushing would refresh the membranes and membranes would effectively work as a new one for practical purposes. This is associated with the cost so this parameter is taken into account for the cost – efficiency trade offs optimization scenario.

1. Chemical Reactions

Chemical reactions governing the bioremediation and sequestration are as follows:
Equation 7: PAH transformation and degradation kinetic equations

- **First Order decay of PAH in presence of Enzymes to PAH-dihydrodiols**
  \[ \text{PAH} + E \xrightarrow{K_1} \text{PAH-OH} \]  
  \[ (8.1) \]

- **Chemical Binding (Sequestration) with the Soil Humic Matters**
  \[ \text{PAH-OH} + \alpha \text{SOM} \xrightarrow{K_2} \text{PAH-SOM} \]  
  \[ (8.2) \]

- **Biodegradation of PAH diols**
  \[ \text{PAH-OH} \xrightarrow{\mu, K_o, K_c} y\text{CO}_2 + z\text{H}_2\text{O} + \text{Biomass (x)} \]  
  \[ (8.3) \]

2. **Mathematical Model**

- **Assumptions**

  The model is based on following assumptions:

  Biomass, PAHs and oxygen are always uniformly distributed with regards to membrane bio-reactor radius.

  Initially biomass, PAHs and oxygen are uniform throughout the membrane bio-reactor.

  Biomass, PAHs and Oxygen are always uniformly distributed with regards to depth of sediment.

  Initially biomass, PAHs and Oxygen are uniform throughout the depth being considered of the sediment.

  The Schematics of the process is as follows:

  ![Figure 33: Schematic of design of the membrane module](image URL)
The whole process can be divided into following parts:

- **Hollow fiber membranes supplying the electron acceptors**

  Hollow fiber membranes will be supplying the electron acceptors by forming a meniscus at the interface which will be just sufficient to form a non bubbling interface at the time of pulsing and hence no convection. This will provide the boundary condition with the equilibrium condition satisfied at the gas liquid interface (in case of oxygen as electron acceptor) hence concentration of the interface being equal to the saturation concentration. Hence the boundary condition will correspond to the concentration of the electron acceptor in the medium which is Oxygen in the considered solution.

- **Diffusion and consumption of electron acceptor in the sediment**

  Diffusion reaction equation will govern the concentration of the electron acceptor in the membrane assembly inside the geotextile fiber. Here the electron acceptor will start to move from the membrane and in turn will be consumed according to the kinetics of the biodegradation.

- **Hypothesis of the PAH Degradation**

  There is enough evidence to support the theory that PAH can not be directly transformed / biodegraded. They first take a much amenable form of the PAH-Diols following a first order kinetics with the help of enzymes formed by the microbes. The mechanism and the existence of PAH-diol are well documented (Cerniglia, C.E. et al 1984) and supported by many researchers now and are out of the scope of the present work. (Weber et al, 2003) It is further assumed and found to be experimentally close to the assumption that PAH here undergoes a first order kinetic degradation into the diols. (Weber et al, 2003)
• **Hypothesis of the PAH-Diol Transformation / Degradation**

Biological species indulge themselves into the biological transformation (biopolymerization) and biodegradation when they come in contact with the species to be consumed as electron donor (the contaminant). PAH-diols undergo a biodegradation by following biokinetics model (assumed to be Double Monod Model) and a first order conversion to the Humic Matter by chemical binding to the humic matter.

• **Biomass growth modeling**

   The biomass growth is modeled as the double Monod with inclusion of electron acceptors and contaminants concentration to be driving forces. (Equation 1: Double Monod Model)

• **Enzyme Concentration**

   Enzyme concentration is dependent on the production of the enzymes from the biomass and consumption in the first order kinetics for PAH conversion to diols.

• **Oxygen Flux from the membrane reactor assembly to sediment**

   The flux of oxygen being supplied from the membrane bioreactor assembly goes to the sediment oxygen demand and the bioremediation and biotransformation.

• **Diffusion and consumption of electron acceptor in the sediment**

   Diffusion reaction equation will govern the concentration of the electron acceptor in the sediment. Here the electron acceptor will start to move from the water column and in turn will be consumed according to the kinetics of the biodegradation.

• **Sediment Oxygen Demand**

   Dead organic material accumulated on the bed of a lake, reservoir or wetland often provides the substrate for substantial microbial activity as well as chemical
processes that withdraw dissolved oxygen (DO) from the water column. A model to estimate the actual DO profile and the “sediment oxygen demand (SOD)” must specify the rate of microbial or chemical activity in the sediment as well as the diffusive supply of DO from the water column through the diffusive boundary layer into the sediment. Sediment oxygen demand is the generally accepted biological demand of electron acceptors to degrade the organic matters other than the targeted contaminant in the clean sediment. The superimposition of the SOD will give us the real utilization of electron acceptor for the degradation process.

- **Hypothesis of the PAH Degradation**

  There is enough evidence to support the theory that PAH can not be directly transformed / biodegraded. They first take a much amenable form of the PAH-Diols following a first order kinetics with the help of enzymes formed by the microbes. The mechanism and the existence of PAH-diol are well documented (Cerniglia, C.E. et al 1984) and supported by many researchers now and are out of the scope of the present work. (Weber et al, 2003) It is further assumed and found to be experimentally close to the assumption that PAH here undergoes a first order kinetic degradation into the diols. (Weber et al, 2003)

- **Hypothesis of the PAH-Diol Transformation / Degradation**

  Biological species indulge themselves into the biological transformation (biopolymerization) and biodegradation when they come in contact with the species to be consumed as electron donor (the contaminant). Based on this we could hypothesize that a chemical binding phenomenon which will convert the PAHs into the diols and then into the bound organic matter which can not be traced as PAHs but has a potential to come
out if loosely bound under certain change in environmental condition, exists parallel to
the degradation of PAHs. Hence PAH-diols undergo a biodegradation by following
biokinetics model (assumed to be Double Monod Model) and a first order conversion to
the Humic Matter by chemical binding to the humic matter. There is enough evidence
now in the literature which helps us prove the hypothesis to be correct. (Weber et al,
2003)

- **Biomass growth modeling**

  The biomass growth is modeled as the double Monod with inclusion of electron
acceptors and contaminants concentration to be driving forces. (Equation 1: Double
Monod Model)

- **Enzyme Concentration**

  Enzyme concentration is dependent on the production of the enzymes from the
biomass and consumption in the first order kinetics for PAH conversion to diols.

**Equation 8: Mathematical Model for bioremediation using membrane in sediment**

- **Inside membrane reactor assembly:**

- **Oxygen Diffusion with Consumption**

\[
\frac{\partial O(r,t)}{\partial t} = D_o \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial O(r,t)}{\partial r} - \frac{1}{Y_o} \frac{\mu_{\text{max}} x(r,t) O(r,t)}{K_o + O(r,t)}
\]  

(8.1)

Where,

- **O** = electron acceptor concentration

- **r** = distance from the fiber

- **t** = time elapsed

- **D_o** = diffusivity of electron acceptor in the system
$Y_o$ = Biomass yield factor of oxygen

$\mu_{max}$ = Biomass maximum specific growth rate

$K_o$ = Monod half saturation constant for the electron acceptors.

$O$ = Oxygen concentration.

$x$ = Local biomass concentration.

**Biomass Growth Rate**

$$\frac{\partial x(r,t)}{\partial t} = \frac{\mu_{max} x(r,t)O(r,t)}{K_o + O(r,t)}$$ (8.2)

Where,

$r$ = distance from the fiber

$t$ = time elapsed

$\mu_{max}$ = Biomass maximum specific growth rate

$K_o$ = Monod half saturation constant for the electron acceptors.

$O$ = Oxygen concentration.

$x$ = Local biomass concentration.

**Enzyme Concentration**

$$\frac{\partial E(r,t)}{\partial t} = -\frac{1}{Y_E} \frac{\mu_{max} x(r,t)O(r,t)}{K_o + O(r,t)}$$ (8.3)

Where,

$r$ = distance from the fiber

$t$ = time elapsed

$E$ = Local Enzyme concentration

$Y_E$ = Enzyme yield factor of the hydrolyzed contaminants

$\mu_{max}$ = Biomass maximum specific growth rate
\[ K_o = \text{Monod half saturation constant for the electron acceptors.} \]

\[ O = \text{Oxygen concentration.} \]

\[ x = \text{Local biomass concentration.} \]

- **Oxygen Uptake**

\[
\bar{O} = \frac{2 \int O(r,t)rdr}{k} \quad (8.4)
\]

- **Outside membrane assembly inside sediment:**

- **Oxygen Diffusion with Consumption**

\[
\frac{\partial O(r,t)}{\partial t} = D_o \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial O(r,t)}{\partial r} \right) - \frac{1}{Y_o} \frac{\mu_{\text{max}} x(r,t) C_{\text{H}}(r,t)}{K_c + C_{\text{H}}(r,t)} \frac{O(r,t)}{K_o + O(r,t)} - \text{SOD} \quad (8.5)
\]

Where,

- \[ O = \text{electron acceptor concentration} \]
- \[ r = \text{distance from the surface of sediment water interface} \]
- \[ t = \text{time elapsed} \]
- \[ D_o = \text{diffusivity of electron acceptor in the system} \]
- \[ Y_o = \text{Biomass yield factor of oxygen} \]
- \[ \mu_{\text{max}} = \text{Biomass maximum specific growth rate} \]
- \[ K_c = \text{Monod half saturation constant for the contaminants.} \]
- \[ K_o = \text{Monod half saturation constant for the electron acceptors.} \]
- \[ C_{\text{H}} = \text{Substrate (PAH-dihydrodiol) concentration.} \]
- \[ O = \text{Oxygen concentration.} \]
- \[ x = \text{Local biomass concentration.} \]
- \[ \text{SOD} = \text{Sediment Oxygen Demand} \]
- **PAH Consumption**

\[ - \frac{\partial C(r, t)}{\partial t} = K_1 C(r, t) E(r, t) \]  \hspace{1cm} (8.6)

Where,

- \( r \) = distance from the surface of sediment water interface
- \( t \) = time elapsed
- \( C \) = Local PAH concentration.
- \( E \) = Local Enzyme concentration
- \( K_1 \) = rate constant for the initial reaction.

- **PAH-diol Consumption**

\[
\frac{\partial C_H(r,t)}{\partial t} = - \frac{1}{Y_H} \frac{\mu_{max} x(r,t) C_H(r,t)}{K_e + C_H(r,t)} \frac{O(r,t)}{K_o + O(r,t)} + K_i C_H(r,t) E(r,t) - K_w C_{wag} C_H \]  \hspace{1cm} (8.7)

Where,

- \( C_H \) = PAH-diol concentration
- \( r \) = distance from the surface of sediment water interface
- \( t \) = time elapsed
- \( Y_H \) = Biomass yield factor of the hydrolyzed contaminants
- \( \mu_{max} \) = Biomass maximum specific growth rate
- \( K_e \) = Monod half saturation constant for the contaminants.
- \( K_o \) = Monod half saturation constant for the electron acceptors.
- \( E \) = Local Enzyme concentration
- \( O \) = Oxygen concentration.
- \( x \) = Local biomass concentration.
\[ K_1 = \text{rate constant for the initial reaction.} \]
\[ K_2 = \text{rate constant for the chemical binding reaction} \]
\[ C^\alpha_{\text{org}} = \text{Humic matter concentration} \]
\[ C_B = \text{Bound PAH concentration} \]

- **Biomass Growth Rate**

\[
\frac{\partial x(r,t)}{\partial t} = \frac{\mu_{\text{max}} x(r,t) C_H(r,t)}{K_c + C_H(r,t)} \frac{O(r,t)}{K_o + O(r,t)} \tag{8.8}
\]

Where,

\[ C_H = \text{PAH-diol concentration} \]
\[ r = \text{distance from the surface of sediment water interface} \]
\[ t = \text{time elapsed} \]
\[ Y_H = \text{Biomass yield factor of the hydrolyzed contaminants} \]
\[ \mu_{\text{max}} = \text{Biomass maximum specific growth rate} \]
\[ K_c = \text{Monod half saturation constant for the contaminants.} \]
\[ K_o = \text{Monod half saturation constant for the electron acceptors.} \]
\[ O = \text{Oxygen concentration.} \]
\[ x = \text{Local biomass concentration.} \]

- **Enzyme Concentration**

\[
\frac{\partial E(r,t)}{\partial t} = -\frac{1}{Y_E} \frac{\mu_{\text{max}} x(r,t) C_H(r,t)}{K_c + C_H(r,t)} \frac{O(r,t)}{K_o + O(r,t)} - K_i C(r,t) E(r,t) \tag{8.9}
\]

Where,

\[ r = \text{distance from the surface of sediment water interface} \]
\[ t = \text{time elapsed} \]
\[ C = \text{Local PAH concentration.} \]
\( E \) = Local Enzyme concentration

\( K_1 \) = rate constant for the initial reaction.

\( Y_H \) = Biomass yield factor of the hydrolyzed contaminants

\( \mu_{\text{max}} \) = Biomass maximum specific growth rate

\( K_c \) = Monod half saturation constant for the contaminants.

\( K_o \) = Monod half saturation constant for the electron acceptors.

\( O \) = Oxygen concentration.

\( x \) = Local biomass concentration.

1. **Bound Contaminant**

\[
\frac{\partial C_H(r,t)}{\partial t} = K_2 C_{\text{org}} \alpha C_H(r,t)
\]

(8.10)

Where,

\( C_H \) = PAH-diol concentration

\( r \) = distance from the surface of sediment water interface

\( t \) = time elapsed

\( K_2 \) = rate constant for the chemical binding reaction

\( C_{\text{org}}^\alpha \) = Humic matter concentration

\( C_B \) = Bound PAH concentration

2. **Oxygen Uptake**

\[
\bar{\mathcal{O}} = \frac{2 \int_{r'} O(r,t) rdr}{R^2}
\]

(8.11)

Where,

\( O \) = Local Oxygen concentration

\( r \) = distance from the surface of sediment water interface
\[ t = \text{time elapsed} \]
\[ R^* = \text{boundary of the domain} \]
\[ \overline{O} = \text{average oxygen concentration} \]

- **Average PAH in sediment**

\[
\overline{C} = \frac{2 \int_{R}^{R^*} C(r, t) rdr}{(R^*)^2} \quad (8.12)
\]

Where,

- \( C \) = Total local contaminant concentration
- \( r \) = distance from the surface of sediment water interface
- \( t \) = time elapsed
- \( R^* \) = boundary of the domain
- \( \overline{C} \) = average contaminant concentration

3. **Simulation Method**

Simulation involved programming the PDEs in MATLAB® using numerical techniques. Here the PDEs specified are highly coupled and nonlinear which makes the analytical results hard to achieve. Hence the numerical approach was taken into account and solved following certain well established methods. These methods are already explained in the technical background so here we would just take a moment to appreciate their role in the simulation.

- **Finite difference method**

All the PDEs were converted into the ODEs. All the equations were broken into the space and time domain to form the algebraic equation. The results
were some simultaneous equations which were again solved using the numerical method explicitly.

- **Runge – Kutta method**

In order to compare the result of the data spread over space and time we had to integrate the output contamination in space and then compare using the RRE optimization for the optimum solution.

4. **Simulation Results and Discussion**

The PAH Degradation data for the reactor were divided into groups of 2, 3, 4, 5 and 6 rings and their results were discussed by group. The initial concentration of PAH was taken from the data table of Mukundan Ramani and Dr Rakesh Govind previous experiments (Appendix 1).

- **Aerobic**:

For aerobic simulation the electron acceptor is Oxygen. The fiber and then membrane assembly is used to keep the environment around it to the saturated level of oxygen concentration hence providing us with the boundary condition. The other boundary condition is the wall of the reactor which gives us the no flux condition across it. The initial condition of the PAHs is taken out of the Table 3: Initial PAH Concentration for the simulation for all the rings of PAHs. Experimental data, boundary and initial conditions were taken from the Appendix 1 (Govind, R. and Ramani M. 2001) and thesis (Govind, R. and Ramani M. 2000). Following figures and tables reflect the curve
fits of the model described in Equation 8: Mathematical Model for bioremediation using
membrane in sediment. The simulation works dynamically on the backflush period for
the back-flushing operation. Moreover it takes care of the efficiency of the membrane.

○ 2 Ring PAHs

Initial Condition (inside membrane assembly):

Biomass = 10*((100-efficiency of the membrane)/100) mg/Kg.
Enzyme = 0 mg/Kg.
Oxygen = 8 mg/Kg.

Initial Condition (inside sediment):

PAH = 3.2 mg/Kg.
PAHdiol = 3.2 mg/Kg.
PAHbound = 0 mg/Kg.
Biomass = 10 mg/Kg.
Enzyme = 0 mg/Kg.
Oxygen = 8 mg/Kg.

Boundary Condition:

○ Boundary Condition for membrane surface –

\[ O(R, t) = O_o \quad r = R \]

Where,

\( O = \text{electron acceptor concentration at distance } r = R \)

○ Boundary Condition for membrane asseembly–

\[ \frac{\partial O(r,t)}{\partial t} = 0 \quad r = \text{range in cms} \]

Range = distance between the fiber / 2
Boundary Condition for sediment assembly interface –

Flux of oxygen from membrane assembly = flux into the sediment

\[ D_w \left( \frac{\partial O(r,t)}{\partial r} \right) = D_s \left( \frac{\partial O(r,t)}{\partial r} \right) \]

Boundary condition at sediment depth 50 cms.

\[ \frac{\partial O(r,t)}{\partial t} = 0 \quad r=50 \text{ cms} \]

Where,

\[ O = \text{electron acceptor concentration at distance } r \text{ and time } t \]

Case 1:

Efficiency of membrane = 99.9

Frequency of Backflush = 90 days

Figure 34: Scale up simulation for the 99.9% Efficiency and 90 days backflush frequency
Case 2:

Efficiency of membrane = 99.9

Frequency of Backflush = 60 days

![Figure 35: Scale up simulation for the 99.9% Efficiency and 60 days backflush frequency](image)

Case 3:

Efficiency of membrane = 99.9

Frequency of Backflush = 30 days

![Figure 36: Scale up simulation for the 99.9% Efficiency and 30 days backflush frequency](image)
Case 4:

Efficiency of membrane = 99

Frequency of Backflush = 90 days

Figure 37: Scale up simulation for the 99% Efficiency and 90 days backflush frequency

Case 5:

Efficiency of membrane = 99

Frequency of Backflush = 60 days

Figure 38: Scale up simulation for the 99% Efficiency and 60 days backflush frequency
Case 6:

Efficiency of membrane = 99
Frequency of Backflush = 30 days

Figure 39: Scale up simulation for the 99% Efficiency and 30 days backflush frequency

Case 7:

Efficiency of membrane = 95
Frequency of Backflush = 90 days

Figure 40: Scale up simulation for the 95% Efficiency and 90 days backflush frequency
Case 8:

Efficiency of membrane = 95
Frequency of Backflush = 60 days

Figure 41: Scale up simulation for the 95% Efficiency and 60 days backflush frequency

Case 9:

Efficiency of membrane = 95
Frequency of Backflush = 30 days

Figure 42: Scale up simulation for the 95% Efficiency and 30 days backflush frequency
Case 10:
Efficiency of membrane = 90
Frequency of Backflush = 90 days

Figure 43: Scale up simulation for the 90% Efficiency and 90 days backflush frequency

Case 11:
Efficiency of membrane = 90
Frequency of Backflush = 60 days

Figure 44: Scale up simulation for the 90% Efficiency and 60 days backflush frequency
Case 12:

Efficiency of membrane = 90

Frequency of Backflush = 30 days

Figure 45: Scale up simulation for the 90% Efficiency and 30 days backflush frequency
3 Ring PAHs

Initial Condition (inside membrane assembly):

- **Biomass** = $10 \times ((100 - \text{efficiency of the membrane})/100)$ mg/Kg.
- **Enzyme** = 0 mg/Kg.
- **Oxygen** = 8 mg/Kg.

Initial Condition (inside sediment):

- **PAH** = 7.0 mg/Kg.
- **PAHdiol** = 8.6 mg/Kg.
- **PAHbound** = 0 mg/Kg.
- **Biomass** = 10 mg/Kg.
- **Enzyme** = 0 mg/Kg.
- **Oxygen** = 8 mg/Kg.

Boundary Condition:

Boundary Condition:

- **Boundary Condition for membrane surface** –

  $$O(R, t) = O_o \quad r = R$$

  Where,

  $$O = \text{electron acceptor concentration at distance } r = R$$

- **Boundary Condition for membrane assembly**–

  $$\frac{\partial O(r,t)}{\partial t} = 0 \quad r = \text{range in cms}$$

  Range = distance between the fiber / 2

- **Boundary Condition for sediment assembly interface** –

  Flux of oxygen from membrane assembly = flux into the sediment
$$D_w \left( \frac{\partial O(r,t)}{\partial r} \right) = D_q \left( \frac{\partial O(r,t)}{\partial r} \right)$$

Boundary condition at sediment depth 50 cms.

$$\frac{\partial O(r,t)}{\partial t} = 0 \quad r = 50 \text{ cms}$$

Where,

$$O = \text{electron acceptor concentration at distance } r \text{ and time } t$$

Case 1:

Efficiency of membrane = 99.9

Frequency of Backflush = 90 days

Figure 46: Scale up simulation for the 99.9\% Efficiency and 90 days backflush frequency
Case 2:

Efficiency of membrane = 99.9
Frequency of Backflush = 60 days

Figure 47: Scale up simulation for the 99.9% Efficiency and 60 days backflush frequency

Case 3:

Efficiency of membrane = 99.9
Frequency of Backflush = 30 days

Figure 48: Scale up simulation for the 99.9% Efficiency and 30 days backflush frequency
Case 4:

Efficiency of membrane = 99

Frequency of Backflush = 90 days

Figure 49: Scale up simulation for the 99% Efficiency and 90 days backflush frequency

Case 5:

Efficiency of membrane = 99

Frequency of Backflush = 60 days

Figure 50: Scale up simulation for the 99% Efficiency and 60 days backflush frequency
Case 6:

Efficiency of membrane $= 99$
Frequency of Backflush $= 30$ days

Figure 51: Scale up simulation for the 99% Efficiency and 30 days backflush frequency

Case 7:

Efficiency of membrane $= 95$
Frequency of Backflush $= 90$ days

Figure 52: Scale up simulation for the 95% Efficiency and 90 days backflush frequency
Case 8:
Efficiency of membrane = 95
Frequency of Backflush = 60 days

Figure 53: Scale up simulation for the 95% Efficiency and 60 days backflush frequency

Case 9:
Efficiency of membrane = 95
Frequency of Backflush = 30 days

Figure 54: Scale up simulation for the 95% Efficiency and 30 days backflush frequency
Case 10:

Efficiency of membrane = 90
Frequency of Backflush = 90 days

Figure 55: Scale up simulation for the 90% Efficiency and 90 days backflush frequency

Case 11:

Efficiency of membrane = 90
Frequency of Backflush = 60 days

Figure 56: Scale up simulation for the 90% Efficiency and 60 days backflush frequency
Case 12:

Efficiency of membrane = 90
Frequency of Backflush = 30 days

Figure 57: Scale up simulation for the 90% Efficiency and 30 days backflush frequency

- 4 Ring PAHs

Initial Condition (inside membrane assembly):

Biomass = 10*((100-efficiency of the membrane)/100) mg/Kg.
Enzyme = 0 mg/Kg.
Oxygen = 8 mg/Kg.

Initial Condition (inside sediment):

PAH = 7.0 mg/Kg.
PAHdiol = 8.6 mg/Kg.
PAHbound = 0 mg/Kg.
Biomass = 10 mg/Kg.
Enzyme = 0 mg/Kg.

Oxygen = 8 mg/Kg.

Boundary Condition:

Boundary Condition:

○ *Boundary Condition for membrane surface* –

\[ O(R, t) = O_0 \]

Where,

\[ O = \text{electron acceptor concentration at distance } r = R \]

○ *Boundary Condition for membrane assembly* –

\[ \frac{\partial O(r, t)}{\partial t} = 0 \quad r = \text{range in cms} \]

Range = distance between the fiber / 2

○ *Boundary Condition for sediment assembly interface* –

Flux of oxygen from membrane assembly = flux into the sediment

\[ D_w \left( \frac{\partial O(r, t)}{\partial r} \right) = D_s \left( \frac{\partial O(r, t)}{\partial r} \right) \]

○ *Boundary condition at sediment depth 50 cms.*

\[ \frac{\partial O(r, t)}{\partial t} = 0 \quad r = 50 \text{ cms} \]

Where,

\[ O = \text{electron acceptor concentration at distance } r \text{ and time } t \]

Case 1:

Efficiency of membrane = 99.9

Frequency of Backflush = 90 days
Figure 58: Scale up simulation for the 99.9% Efficiency and 90 days backflush frequency

Case 2:

Efficiency of membrane = 99.9

Frequency of Backflush = 60 days

Figure 59: Scale up simulation for the 99.9% Efficiency and 60 days backflush frequency
Case 3:

Efficiency of membrane = 99.9

Frequency of Backflush = 30 days

Figure 60: Scale up simulation for the 99.9% Efficiency and 30 days backflush frequency

Case 4:

Efficiency of membrane = 99

Frequency of Backflush = 90 days

Figure 61: Scale up simulation for the 99% Efficiency and 90 days backflush frequency
Case 5:

Efficiency of membrane = 99

Frequency of Backflush = 60 days

Figure 62: Scale up simulation for the 99% Efficiency and 60 days backflush frequency

Case 6:

Efficiency of membrane = 99

Frequency of Backflush = 30 days

Figure 63: Scale up simulation for the 99% Efficiency and 30 days backflush frequency
Case 7:
Efficiency of membrane = 95
Frequency of Backflush = 90 days

Figure 64: Scale up simulation for the 95% Efficiency and 90 days backflush frequency

Case 8:
Efficiency of membrane = 95
Frequency of Backflush = 60 days

Figure 65: Scale up simulation for the 95% Efficiency and 60 days backflush frequency
Case 9:
Efficiency of membrane = 95
Frequency of Backflush = 30 days

Figure 66: Scale up simulation for the 95% Efficiency and 30 days backflush frequency

Case 10:
Efficiency of membrane = 90
Frequency of Backflush = 90 days

Figure 67: Scale up simulation for the 90% Efficiency and 90 days backflush frequency
Case 11:
Efficiency of membrane  = 90
Frequency of Backflush  = 60 days

Figure 68: Scale up simulation for the 90% Efficiency and 60 days backflush frequency

Case 12:
Efficiency of membrane  = 90
Frequency of Backflush  = 30 days
Figure 69: Scale up simulation for the 90% Efficiency and 60 days backflush frequency

5 Ring PAHs

Initial Condition (inside membrane assembly):

Biomass = 10*((100-efficiency of the membrane)/100) mg/Kg.
Enzyme = 0 mg/Kg.
Oxygen = 8 mg/Kg.

Initial Condition (inside sediment):

PAH = 1.8 mg/Kg.
PAHdiol = 2.0 mg/Kg.
PAHbound = 0 mg/Kg.
Biomass = 10 mg/Kg.
Enzyme = 0 mg/Kg.
Oxygen = 8 mg/Kg.

Boundary Condition:

Boundary Condition:

Boundary Condition for membrane surface –
\[ O(R, t) = O_o \quad r = R \]

Where,

\[ O = \text{electron acceptor concentration at distance } r = R \]

- **Boundary Condition for membrane assembly** –

\[ \frac{\partial O(r, t)}{\partial t} = 0 \quad r = \text{range in cms} \]

Range = distance between the fiber / 2

- **Boundary Condition for sediment assembly interface** –

Flux of oxygen from membrane assembly = flux into the sediment

\[ D_w \left( \frac{\partial O(r, t)}{\partial r} \right) = D_o \left( \frac{\partial O(r, t)}{\partial r} \right) \]

- **Boundary condition at sediment depth 50 cms.**

\[ \frac{\partial O(r, t)}{\partial t} = 0 \quad r = 50 \text{ cms} \]

Where,

\[ O = \text{electron acceptor concentration at distance } r \text{ and time } t \]

**Case 1:**

Efficiency of membrane = 99.9

Frequency of Backflush = 90 days
Case 2:

Efficiency of membrane = 99.9

Frequency of Backflush = 60 days
Case 3:

Efficiency of membrane = 99.9

Frequency of Backflush = 30 days

Figure 72: Scale up simulation for the 99.9% Efficiency and 30 days backflush frequency

Case 4:

Efficiency of membrane = 99

Frequency of Backflush = 90 days

Figure 73: Scale up simulation for the 99% Efficiency and 90 days backflush frequency
Case 5:

Efficiency of membrane = 99

Frequency of Backflush = 60 days

Figure 74: Scale up simulation for the 99% Efficiency and 60 days backflush frequency

Case 6:

Efficiency of membrane = 99

Frequency of Backflush = 30 days

Figure 75: Scale up simulation for the 99% Efficiency and 30 days backflush frequency
Case 7:

Efficiency of membrane = 95
Frequency of Backflush = 90 days

Figure 76: Scale up simulation for the 95% Efficiency and 90 days backflush frequency

Case 8:

Efficiency of membrane = 95
Frequency of Backflush = 60 days

Figure 77: Scale up simulation for the 95% Efficiency and 60 days backflush frequency
Case 9:

Efficiency of membrane = 95
Frequency of Backflush = 30 days

![Graph showing scale up simulation for 95% Efficiency and 30 days backflush frequency]

Figure 78: Scale up simulation for the 95% Efficiency and 30 days backflush frequency

Case 10:

Efficiency of membrane = 90
Frequency of Backflush = 90 days

![Graph showing scale up simulation for 90% Efficiency and 90 days backflush frequency]

Figure 79: Scale up simulation for the 90% Efficiency and 90 days backflush frequency
Case 11:

Efficiency of membrane = 90
Frequency of Backflush = 60 days

Figure 80: Scale up simulation for the 90% Efficiency and 60 days backflush frequency

Case 12:

Efficiency of membrane = 90
Frequency of Backflush = 30 days

Figure 81: Scale up simulation for the 90% Efficiency and 30 days backflush frequency
6 Ring PAHs

Initial Condition (inside membrane assembly):

Biomass = 10* ((100 - efficiency of the membrane)/100) mg/Kg.
Enzyme = 0 mg/Kg.
Oxygen = 8 mg/Kg.

Initial Condition (inside sediment):

PAH = 0.4 mg/Kg.
PAHdiol = 0.4 mg/Kg.
PAHbound = 0 mg/Kg.
Biomass = 10 mg/Kg.
Enzyme = 0 mg/Kg.
Oxygen = 8 mg/Kg.

Boundary Condition:

Boundary Condition for membrane surface –

\[ O(R, t) = O_0 \quad \text{r} = R \]

Where,

\[ O = \text{electron acceptor concentration at distance } r = R \]

Boundary Condition for membrane assembly –

\[ \frac{\partial O(r, t)}{\partial r} = 0 \quad \text{r = range in cms} \]

Range = distance between the fiber / 2

Boundary Condition for sediment assembly interface –

Flux of oxygen from membrane assembly = flux into the sediment
$$D_w \left( \frac{\partial O(r,t)}{\partial r} \right) = D_n \left( \frac{\partial O(r,t)}{\partial r} \right)$$

- Boundary condition at sediment depth 50 cms.

$$\frac{\partial O(r,t)}{\partial t} = 0 \quad r=50 \text{ cms}$$

Where,

$O = electron\ acceptor\ concentration\ at\ distance\ r\ and\ time\ t$

Case 1:

Efficiency of membrane $= 99.9$

Frequency of Backflush $= 90$ days

Figure 82: Scale up simulation for the 99.9% Efficiency and 90 days backflush frequency
Case 2:

Efficiency of membrane = 99.9
Frequency of Backflush = 60 days

![Graph showing scale up simulation for the 99.9% Efficiency and 60 days backflush frequency](image1)

Figure 83: Scale up simulation for the 99.9% Efficiency and 60 days backflush frequency

Case 3:

Efficiency of membrane = 99.9
Frequency of Backflush = 30 days

![Graph showing scale up simulation for the 99.9% Efficiency and 30 days backflush frequency](image2)

Figure 84: Scale up simulation for the 99.9% Efficiency and 30 days backflush frequency
Case 4:

Efficiency of membrane = 99

Frequency of Backflush = 90 days

Figure 85: Scale up simulation for the 99% Efficiency and 90 days backflush frequency

Case 5:

Efficiency of membrane = 99

Frequency of Backflush = 60 days

Figure 86: Scale up simulation for the 99% Efficiency and 60 days backflush frequency
Case 6:

Efficiency of membrane = 99
Frequency of Backflush = 30 days

Figure 87: Scale up simulation for the 99% Efficiency and 30 days backflush frequency

Case 7:

Efficiency of membrane = 95
Frequency of Backflush = 90 days

Figure 88: Scale up simulation for the 95% Efficiency and 90 days backflush frequency
Case 8:
Efficiency of membrane = 95
Frequency of Backflush = 60 days

Figure 89: Scale up simulation for the 95% Efficiency and 60 days backflush frequency

Case 9:
Efficiency of membrane = 95
Frequency of Backflush = 30 days

Figure 90: Scale up simulation for the 95% Efficiency and 30 days backflush frequency
Case 10:
Efficiency of membrane = 90
Frequency of Backflush = 90 days

Figure 91: Scale up simulation for the 90% Efficiency and 90 days backflush frequency

Case 11:
Efficiency of membrane = 90
Frequency of Backflush = 60 days

Figure 92: Scale up simulation for the 90% Efficiency and 60 days backflush frequency
Case 12:

Efficiency of membrane = 90

Frequency of Backflush = 30 days

Figure 93: Scale up simulation for the 90% Efficiency and 30 days backflush frequency
Natural attenuation Treatment

1. Technical Background

With microorganisms in the site and hence enzymes present natural attenuation is most probable to occur in any site for all biodegradable and bioavailable compounds. Luthy et al. did a micro scale characterization and desorption analysis for the sediments with the objective of finding the surface effect of sediments on the contaminant adsorption, possible desorption of the PAHs from the sediment using extraction, mechanism governing sequestration, effect of such processes on bioavailability and toxicity limit assessment and nature of PAH association that leads to their unavailability. They concluded that surface to bulk ratio is directly proportional to the sorbed PAH concentration. They further concluded that the lighter coal and wood derived fraction of sediments have more PAH fraction then the abundant silica particles in sediment but they did not differentiate between different forms of organic carbon like humic matter particle, humic matter sorbed on mineral surfaces etc. They found that there were available and unavailable fractions present in the sediment. It was attributed to the sorption. (Luthy et al 2000) This is evident that aging is the factor, which governs the sorption, but Govind et al. hypothesized the interactions with humic matter to be a chemical binding. These bindings explain the high bioremediation rate observed. A combined model of biodegradation and chemical binding was proposed and fitted to be found appropriate with the experimental data and literature. (Govind et al 2001) Weber et al investigated oxidative coupling of hydroxylated aromatic compounds by natural geosorbent. (Weber et al 2003). Moreover, they showed that in order to form a biopolymer the presence of hydroxylated aromatics is required. Perminova et al. and Rice et al. attributed the
detoxification of the PAHs in presence of humics to the chemical binding in their findings (Perminova et al. 2001, Rice et al 2004). Rice et al further found that bound residue formation for the metabolites PAH-diols are 5 to 20 times higher than the respective PAH (Rice et al 2004). Pathways of sorption, chemical binding and biodegradation, and hence bioavailability and bioconcentration are complex and an area of curious research. Natural attenuation is believed to involve the combined effect of biodegradation under oxygen deficient condition and the chemical binding and sorption to the organics in the sediment. (Govind et al 2001) Bioavailability is a major factor to be considered before deciding the biodegradability of a soil or sediment. Semple et al did a study with HPCD (hydroxypropyl-β-cyclodextrin) to find the bioavailability. Bioavailability they found depends on the soil structure (particle size matter and organic matter content), compound’s physico-chemical properties (Kow, mol size, solubility and vapor pressure) and intra soil processes (sorption, diffusion and entrapment). (Semple et al 1999) Rockne et al further researched on the relationship of the size and density with the sequestration of PAH and found that the sequestration is both the function of density of sediment and PAH structure. They found that majority of PAHs are associated with low density particles (<1.9 g/ml) for larger size classes of sediment particle which are the remains of terrestrial and marine tissues that have accumulated in the sediment but as the size decreases there is a reversal in these associations. (Rockne K J et al 1999) Hence we see natural attenuation is a complex process and is difficult to measure. Ignoring Natural attenuation, in reporting, results in faulty predictions. This process is natural and hence thermodynamically favored. The problem on relying completely on this process is that it is a very slow process with no control and hence the time taken is going to be much more
than desired in most cases. It can take decades for a site to clean up naturally. Huesemann M. H. et al. investigated the biodegradation and the desorption of PAH and concluded that if the biodegradation is the rate controlling process than even after a long time of wait we can expect incomplete treatment. (Huesemann M. H. et al. 2001).

2. **Chemical Reactions**

Chemical reactions governing the bioremediation and sequestration are as follows:

**Equation 9: PAH transformation and degradation kinetic equations**

- **First Order decay of PAH in presence of Enzymes to PAH-dihydrodiols**
  \[ \text{PAH} + E \xrightarrow{K_1} \text{PAH-OH} \quad (10.1) \]

- **Chemical Binding (Sequestration) with the Soil Humic Matters**
  \[ \text{PAH-OH} + \alpha \text{SOM} \xrightarrow{K_2} \text{PAH-SOM} \quad (10.2) \]

- **Biodegradation of PAH diols**
  \[ \text{PAH-OH} \xrightarrow{\mu \cdot K_c} y\text{CH}_4 + z\text{CO}_2 + \text{Biomass (x)} \quad (10.3) \]

3. **Mathematical Model**

- **Assumptions**

  The model is based on following assumptions:

  Biomass, PAHs and oxygen are always uniformly distributed with regards to depth.

  Initially biomass, PAHs and oxygen are uniform throughout the depth.

  Water is steady with no turbulence.

  Water has no oxidative reaction. Diffusion is the only parameter governing the oxygen transport in the water column.
The whole process can be divided into following parts:

- **Oxygen transfer from Water Air interface to Water**

  The electron acceptor is being supplied to the water through the air water interface. The water is at equilibrium at all the times during natural attenuation. So the water surface exposed to atmosphere is at saturated oxygen concentration at all times during natural attenuation. This gives us the boundary condition for the simulation.

- **Oxygen transport within the Water column**

  Oxygen transport is governed by the water diffusion through the water column. Here we assume that the diffusion at all time is going through in steady water column. There is no turbulence in the water. This gives us the transport equation to be a parabolic PDE.

- **Flux from the water column to the sediment**

  Sediment has the flux of oxygen coming through the water column. There is no loss assumed in between. This gives us the boundary condition for the simulation of the bioremediation of the contaminated sediments.

- **Diffusion and consumption of electron acceptor in the sediment**

  Diffusion reaction equation will govern the concentration of the electron acceptor in the sediment. Here the electron acceptor will start to move from the water column and in turn will be consumed according to the kinetics of the biodegradation.

- **Sediment Oxygen Demand**

  Dead organic material accumulated on the bed of a lake, reservoir or wetland often provides the substrate for substantial microbial activity as well as chemical processes that withdraw dissolved oxygen (DO) from the water column. A model to
estimate the actual DO profile and the “sediment oxygen demand (SOD)” must specify the rate of microbial or chemical activity in the sediment as well as the diffusive supply of DO from the water column through the diffusive boundary layer into the sediment. Sediment oxygen demand is the generally accepted biological demand of electron acceptors to degrade the organic matters other than the targeted contaminant in the clean sediment. The superimposition of the SOD will give us the real utilization of electron acceptor for the degradation process.

- **Hypothesis of the PAH Degradation**

There is enough evidence to support the theory that PAH can not be directly transformed / biodegraded. They first take a much amenable form of the PAH-Diols following a first order kinetics with the help of enzymes formed by the microbes. The mechanism and the existence of PAH-diol are well documented (Cerniglia, C.E. *et al* 1984) and supported by many researchers now and are out of the scope of the present work. (Weber *et al*, 2003) It is further assumed and found to be experimentally close to the assumption that PAH here undergoes a first order kinetic degradation into the diols. (Weber *et al*, 2003)

- **Hypothesis of the PAH-Diol Transformation / Degradation**

Biological species indulge themselves into the biological transformation (biopolymerization) and biodegradation when they come in contact with the species to be consumed as electron donor (the contaminant). Based on this we could hypothesize that a chemical binding phenomenon which will convert the PAHs into the diols and then into the bound organic matter which can not be traced as PAHs but has a potential to come out if loosely bound under certain change in environmental condition, exists parallel to
the degradation of PAHs. Hence PAH-diols undergo a biodegradation by following biokinetcs model (assumed to be Double Monod Model) and a first order conversion to the Humic Matter by chemical binding to the humic matter. There is enough evidence now in the literature which helps us prove the hypothesis to be correct. (Weber et al, 2003)

- *Biomass growth modeling*

  The biomass growth is modeled as the double Monod with inclusion of electron acceptors and contaminants concentration to be driving forces. (Equation 1: Double Monod Model)

- *Enzyme Concentration*

  Enzyme concentration is dependent on the production of the enzymes from the biomass and consumption in the first order kinetics for PAH conversion to diols.

- *Water Column and Sediment Parameters*

  Water depth =100 ft = 3048 cms.
  Sediment depth = 50 cms
  Days = 100

- *Initial Conditions*

  **Equation 10: Initial Conditions for the simulation of Natural attenuation**

  - *For Water column*
    
    Oxygen = 8
  
  - *For Sediment*
    
    Oxygen = 8
    PAH = 50
PAHdiol = 50
PAHbound = 0
Biomass = 10
Enzyme = 0

• Boundary Conditions -

Equation 11: Boundary Condition for the simulation of Natural attenuation

○ Oxygen Diffusion with Consumption

\[ O = 8 \text{ mg/L} \]

○ Boundary Condition for sediment water interface –

Flux of oxygen from water = flux into the sediment

\[ D_w \left( \frac{\partial O(r,t)}{\partial r} \right) = D_o \left( \frac{\partial O(r,t)}{\partial r} \right) \]

○ Boundary condition at sediment depth 50 cms.

\[ D_o \left( \frac{\partial O(r,t)}{\partial r} \right) = 0 \]

• Mathematical Model -

Equation 12: Mathematical Model for bioremediation using membrane

○ Water Column Equation

\[ \frac{\partial O(r,t)}{\partial t} = D_w \frac{\partial}{\partial r} \left( \frac{\partial O(r,t)}{\partial r} \right) \]

Where,

\[ O = \text{electron acceptor concentration} \]
\[ r = \text{distance from the surface of water column} \]
\[ t = \text{time elapsed} \]
\[ D_w = \text{diffusivity of oxygen in the water column} \]
Inside Sediment Equations -

Oxygen Diffusion with Consumption

\[ \frac{\partial O(r,t)}{\partial t} = D_0 \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial O(r,t)}{\partial r} - \frac{1}{Y_o} \frac{\mu_{\text{max}} x(r,t) C_h (r,t)}{K_c + C_h (r,t)} \frac{O(r,t)}{K_o + O(r,t)} - SOD \]

Where,

- \( O \) = electron acceptor concentration
- \( r \) = distance from the surface of sediment water interface
- \( t \) = time elapsed
- \( D_0 \) = diffusivity of electron acceptor in the system
- \( Y_o \) = Biomass yield factor of oxygen
- \( \mu_{\text{max}} \) = Biomass maximum specific growth rate
- \( K_c \) = Monod half saturation constant for the contaminants.
- \( K_o \) = Monod half saturation constant for the electron acceptors.
- \( C_h \) = Substrate (PAH-dihydrodiol) concentration.
- \( O \) = Oxygen concentration.
- \( x \) = Local biomass concentration.
- \( SOD \) = Sediment Oxygen Demand

**PAH Consumption**

\[ - \frac{\partial C (r,t)}{\partial t} = K_e C (r,t) E (r,t) \]

Where,

- \( r \) = distance from the surface of sediment water interface
- \( t \) = time elapsed
C = Local PAH concentration.
E = Local Enzyme concentration
K_1 = rate constant for the initial reaction.

- **PAH-diol Consumption**

\[
\frac{\partial C_H(r,t)}{\partial t} = -\frac{1}{Y_H} \frac{\mu_{\text{max}} x(r,t) C_H(r,t)}{K_c + C_H(r,t)} \frac{O(r,t)}{K_o + O(r,t)} + K_1 C_H(r,t) E(r,t) - K_2 C_{\text{org}}^\alpha C_H
\]

Where,

C_H = PAH-diol concentration
r = distance from the surface of sediment water interface
t = time elapsed
Y_H = Biomass yield factor of the hydrolyzed contaminants
\( \mu_{\text{max}} \) = Biomass maximum specific growth rate
K_c = Monod half saturation constant for the contaminants.
K_o = Monod half saturation constant for the electron acceptors.
E = Local Enzyme concentration
O = Oxygen concentration.
x = Local biomass concentration.
K_1 = rate constant for the initial reaction.
K_2 = rate constant for the chemical binding reaction
C_{\text{org}}^\alpha = Humic matter concentration
C_B = Bound PAH concentration

- **Biomass Growth Rate**
\[
\frac{\partial x(r, t)}{\partial t} = \frac{\mu_{\text{max}} x(r, t) C (r, t)}{K + C (r, t)} \frac{O (r, t)}{K_o + O (r, t)}
\]

Where,

\( C_H \) = PAH-diol concentration

\( r \) = distance from the surface of sediment water interface

\( t \) = time elapsed

\( Y_H \) = Biomass yield factor of the hydrolyzed contaminants

\( \mu_{\text{max}} \) = Biomass maximum specific growth rate

\( K_c \) = Monod half saturation constant for the contaminants.

\( K_o \) = Monod half saturation constant for the electron acceptors.

\( O \) = Oxygen concentration.

\( x \) = Local biomass concentration.

\( E \) = Local Enzyme concentration

\( K_i \) = rate constant for the initial reaction.

\( Y_H \) = Biomass yield factor of the hydrolyzed contaminants

\( \mu_{\text{max}} \) = Biomass maximum specific growth rate

\( K_c \) = Monod half saturation constant for the contaminants.
$K_o$ = Monod half saturation constant for the electron acceptors.

$O$ = Oxygen concentration.

$x$ = Local biomass concentration.

**Bound Contaminant**

$$\frac{\partial C_B(r,t)}{\partial t} = K_2 C^\alpha_{org} C_H(r,t)$$

Where,

$C_H$ = PAH-diol concentration

$r$ = distance from the surface of sediment water interface

$t$ = time elapsed

$K_2$ = rate constant for the chemical binding reaction

$C^\alpha_{org}$ = Humic matter concentration

$C_B$ = Bound PAH concentration

**Oxygen Uptake**

$$\bar{O} = \frac{2 \int_{R^*} O(r,t)rdr}{\int_{R^*}}$$

Where,

$\bar{O}$ = average oxygen concentration

$r$ = distance from the surface of sediment water interface

$t$ = time elapsed

$R^*$ = boundary of the domain

$O$ = Local Oxygen concentration

**Average PAH in sediment**
\[ \overline{C} = \frac{2 \int_{R^*}^{r^*} C(r, t) r dr}{(R^* + 2)} \]

Where,

- \( C \) = Total local contaminant concentration
- \( r \) = distance from the surface of sediment water interface
- \( t \) = time elapsed
- \( R^* \) = boundary of the domain
- \( \overline{C} \) = average contaminant concentration

4. **Simulation Method**

Simulation involved programming the PDEs in MATLAB® using numerical techniques. Here the PDEs specified are highly coupled and nonlinear which makes the analytical results hard to achieve. Hence the numerical approach was taken into account and solved following certain well established methods. These methods are already explained in the technical background so here we would just take a moment to appreciate their role in the simulation.

- **Finite difference method**

  All the PDEs were converted into the ODEs. All the equations were broken into the space and time domain to form the algebraic equation. The results were some simultaneous equations which were again solved using the numerical method explicitly.

- **Runge–Kutta method**
In order to compare the result of the data spread over space and time we had to integrate the output contamination in space and then compare using the RRE optimization for the optimum solution.

5. Simulation Results and Discussion

The PAH Degradation data for the reactor were divided into groups of 2, 3, 4, 5 and 6 rings and their results were discussed by group. The initial concentration of PAH was taken to be 100 mg / Kg.

- **2 Ring PAHs**

![Figure 94: Natural attenuation of 2 ring PAHs in sediment](image)

- **3 Ring PAHs**
Figure 95: Natural Attenuation for 3 Ring PAHs in river water

- 4 Ring PAHs

Figure 96: Natural Attenuation for 4 Ring PAHs in river water
5 Ring PAHs

Figure 97: Natural Attenuation for 5 Ring PAHs in river water

6 Ring PAHs

Figure 98: Natural Attenuation for 6 Ring PAHs in river water
Simulation of Water Quality

1. Technical Background

The Water Quality Analysis Simulation Program— (WASP6), an enhancement of the original WASP. This model helps users interpret and predict water quality responses to natural phenomena and man-made pollution for various pollution management decisions. WASP6 is a dynamic compartment-modeling program for aquatic systems, including both the water column and the underlying benthos. The time-varying processes of advection, dispersion, point and diffuse mass loading and boundary exchange are represented in the basic program.

The basic principle of both the hydrodynamics and water-quality program is the conservation of mass. The water volume and water-quality constituent masses being studied are tracked and accounted for over time and space using a series of mass balancing equations. The hydrodynamics program also conserves momentum, or energy, throughout time and space.

For the operational information the manual of WASP 6 can be easily downloaded from the EPA website.

- Environmental Parameters:

  These parameters define the basic model identity including the segmentation and control simulation. The parameters are categorized under Systems (CBOD And DO) and Segments (Water Surface, Water Subsurface and Sediment layer)

- Transport Parameters:

  This group of parameters defines the advective and dispersive transport of simulated variables. The parameters are categorized under Number of Flow fields(water column flow and
solid flow), *Particulate Transport* (time variable settling and resuspension rates for particulate BOD)

- **Boundary Parameters:**

  This group of parameters includes boundary concentrations (BOD and DO), Waste loads (municipal and waste water discharges and urban and agricultural runoffs), solid transport field (initial solid settling), initial conditions (BOD and DO initial conditions) and dissolved fraction (Dissolved fraction for DO and BOD).

- **Transformation Parameters:**

  This group of parameters includes spatially variable parameters, constants and kinetic time functions for the water quality constituents being simulated. The parameters are categorized as Water Temperature, Sediment Oxygen Demand, BOD Deoxygenation rate and reaeration rate.

  More details about the input parameters can be found in the manual given by EPA (EPA 2004). Following Figure describes the complexity this model is capable of handling:
Figure 99: Schematic of WASP 6 simulation
2. Chemical Reactions

Some chemical reactions which take part in DO change in Water column:

\[ C_xH_yO_z \rightarrow CO_2 + H_2O \]
\[ NH_3 + 2 O_2 \rightarrow NO_3 + H_2O + H^+ \]
\[ 5 CH_2O + 5 H_2O + 4 NO_3 + 4 H^+ \rightarrow 5CO_2 + 2N_2 + 12 H_2O \]
\[ 2NO_3 \rightarrow 2 NH_3 + 3 O_2 \]

Rest of the information can be found in the manual from EPA. (EPA 2004)

3. Simulation Method

Input screens:

![Parameters dialog box](image)

Figure 100: parameters setup for the wasp 6
Figure 101: Segments for the consideration of the DO in WASP 6

Figure 102: Initial concentration for the segments
Figure 103: System data for the system variables

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Figure 104: parameters for the simulation used with their scaling factors

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Figure 105: constant parameters for the simulation

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Figure 106: constant parameters for the simulation

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<td>✔️</td>
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<td>0.0000</td>
<td>0.0900</td>
</tr>
<tr>
<td>Denitrification Temperature Coefficient</td>
<td>✔️</td>
<td>1.04</td>
<td>0.0000</td>
<td>1.0400</td>
</tr>
<tr>
<td>Half Saturation: Denitrification Oxygen Limit</td>
<td>✔️</td>
<td>1</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>
Figure 107: constant parameters for the simulation

<table>
<thead>
<tr>
<th>Constant</th>
<th>Used</th>
<th>Value</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phytoplankton Maximum Growth Rate @20c</td>
<td>0</td>
<td></td>
<td>0.0000</td>
<td>3.0000</td>
</tr>
<tr>
<td>Phytoplankton Growth Temperature Coefficient</td>
<td>0</td>
<td>0.0000</td>
<td>1.0700</td>
<td></td>
</tr>
<tr>
<td>Phytoplankton Light Formulation Switch (1=DiTeno, 2=x)</td>
<td>0</td>
<td>1.0000</td>
<td>2.0000</td>
<td></td>
</tr>
<tr>
<td>Phytoplankton Maximum Quantum Yield Constant</td>
<td>0</td>
<td>0.0000</td>
<td>720.0000</td>
<td></td>
</tr>
<tr>
<td>Phytoplankton Self Shading Extinction</td>
<td>0</td>
<td>0.0000</td>
<td>0.0230</td>
<td></td>
</tr>
<tr>
<td>Phytoplankton Carbon:Chlorophyll Ratio</td>
<td>0</td>
<td>0.0000</td>
<td>200.0000</td>
<td></td>
</tr>
<tr>
<td>Phytoplankton Optimal Light Saturation</td>
<td>0</td>
<td>0.0000</td>
<td>350.0000</td>
<td></td>
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<tr>
<td>Phytoplankton Half-Saturation Constant for Nitrogen</td>
<td>0</td>
<td>0.0500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phytoplankton Half-Saturation Constant for Phosphorus</td>
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<td>0.0500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phytoplankton Endogenous Respiration Rate @20c</td>
<td>0</td>
<td>0.0000</td>
<td>0.5000</td>
<td></td>
</tr>
<tr>
<td>Phytoplankton Respiratory Temperature Coefficient</td>
<td>0</td>
<td>0.0000</td>
<td>1.0800</td>
<td></td>
</tr>
<tr>
<td>Phytoplankton Photosynthesis Potential</td>
<td>0</td>
<td>0.0000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 108: constant parameters for the simulation

<table>
<thead>
<tr>
<th>Constant</th>
<th>Used</th>
<th>Value</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD Decay Rate @20c</td>
<td>2E-1</td>
<td></td>
<td>0.0000</td>
</tr>
<tr>
<td>BOD Decay Rate Temperature Correction</td>
<td>1.04</td>
<td></td>
<td>0.0000</td>
</tr>
<tr>
<td>BOD Decay Rate in Sediments</td>
<td>1.2E-2</td>
<td></td>
<td>0.0000</td>
</tr>
<tr>
<td>BOD Decay Rate in Sediments Temperature Correction</td>
<td>1.04</td>
<td></td>
<td>0.0000</td>
</tr>
<tr>
<td>BOD Half Saturation Oxygen Limit</td>
<td>5E-1</td>
<td></td>
<td>0.0000</td>
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</tbody>
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Figure 109: constant parameters for the simulation

<table>
<thead>
<tr>
<th>Constant</th>
<th>Used</th>
<th>Value</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Waterbody Type Used for Wind Driven Reaeration Rate</td>
<td></td>
<td>0</td>
<td>0.0000</td>
</tr>
<tr>
<td>2 Oxygen: Carbon Stoichiometric Ratio</td>
<td></td>
<td>2.67</td>
<td>0.0000</td>
</tr>
<tr>
<td>3 Reaeration Rate Constant at 20°C, per day</td>
<td></td>
<td>1.23</td>
<td>0.0000</td>
</tr>
<tr>
<td>4 Reaeration Option (Same Wind and Hydraulic Kc)</td>
<td></td>
<td>0</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Figure 110: constant parameters for the simulation

<table>
<thead>
<tr>
<th>Constant</th>
<th>Used</th>
<th>Value</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Dissolved Organic Nitrogen Mineralization Rate @20°C</td>
<td></td>
<td>2.1E-1</td>
<td>0.0000</td>
</tr>
<tr>
<td>2 Dissolved Organic Nitrogen Mineralization Temperature</td>
<td></td>
<td>1.07</td>
<td>0.0000</td>
</tr>
<tr>
<td>3 Organic Nitrogen Decay in Sediments</td>
<td></td>
<td>0</td>
<td>0.0000</td>
</tr>
<tr>
<td>4 Organic Nitrogen Decay in Sediment Temperature Co</td>
<td></td>
<td>0</td>
<td>0.0000</td>
</tr>
<tr>
<td>5 Fraction of Phytoplankton Death Recycled to Organic</td>
<td></td>
<td>8E-1</td>
<td>0.0000</td>
</tr>
</tbody>
</table>
Figure 111: constant parameters for the simulation

<table>
<thead>
<tr>
<th>Constant</th>
<th>Used</th>
<th>Value</th>
<th>Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Mineralization Rate of Dissolved Organic Phosphorus</td>
<td></td>
<td>2.2E-1</td>
<td>0.0000</td>
</tr>
<tr>
<td>2 Dissolved Organic Phosphorus Mineralization Temperature</td>
<td></td>
<td>1.07</td>
<td>0.0000</td>
</tr>
<tr>
<td>3 Organic Phosphorus Decay Rate in Sediments</td>
<td></td>
<td>0</td>
<td>0.0000</td>
</tr>
<tr>
<td>4 Organic Phosphorus Decay in Sediments Temperature</td>
<td></td>
<td>0</td>
<td>0.0000</td>
</tr>
<tr>
<td>5 Fraction of Phytoplankton Death Recycled to Organic</td>
<td></td>
<td>8E-1</td>
<td>0.0000</td>
</tr>
</tbody>
</table>
Figure 112: boundary parameter for the uBOD

For more information on the parameters and simulation wasp 6 manual should be referred.

4. Simulation Results and Discussion

- Normal Condition
**Figure 113: DO for normal condition water body**

- *Sulfate Reducing Condition:*

**Figure 114: DO for the sulfate reducing condition**

- *Denitrifying Condition*
Figure 115: DO for denitrifying condition

- **Aerobic Condition**

Figure 116: DO for Aerobic Condition
Conclusions

• Biokinetics Analysis

  o A plausible reaction pathway along with the diffusion and background electron acceptor demand (SOD) was proposed in sediments. This proposed model seems to well comply with the prevalent theories around and the latest findings (Selig H, Keinath II T M, Weber W. J. 2003)

  o Experimental data obtained from the studies conducted by Ramani (Govind, R. and Ramani M. 2001) was modeled using the kinetic pathways based on the proposed kinetics model from Ramani (Govind, R. and Ramani M. 2000) combined with real time bioremediation model. (Srivastava P, Govind R, Tabak H H 2004) The relative residual error is lower than 0.05 for all ring sizes and electron acceptors, showing excellent fits to the model gives us a fair idea of the biokinetics parameters.

  o The first order degradation approximation ($\mu / (Y_{H}, K_o, K_o)$) of the kinetics analysis shows that the difference between the oxygen and rest of the electron acceptors in terms of the effectively treating the sediments is big and hence it can be concluded that the Oxygen is effectively treating the sediments. The efficiency is the most in the oxygen electron acceptor and it diminishes as we go from denitrifying to the sulfate reducing to the anaerobic remediation conditions. As per ring size there is a fair trend of the degradation of the PAHs similarly found in the literature. The value of the degradation constant reduces with the increasing ring size.
The first order growth simulation shows the similar trends. For the same electron acceptors the trend in the ring size is predictably decreasing with the increasing ring size except for the four ring size which was parallel to many findings in the literature showing the similar trends. So the growth kinetics tends to be biased towards oxygen electron acceptor and lower ring sizes.

• **Scale Up Analysis (Design Analysis)**

  o The data obtained shows that the range of the fibers is an effective way to achieve the treatment objectives. As the range changes the treatment is changed for all the compounds. For lower range the treatment is more effective though it is bound from the cost factor in the huge module build up we are expecting. So it is a good choice when we are considering the design parameters in real time. Since the range 4 cms and 7 cms are very close it would be definitely a big factor in optimization reducing cost of membranes to almost 50%.

  o Data obtained further shows that the membrane efficiency is an effective treatment parameter as this would ensure the treatment days along with the treatment percentage for a given time. More the efficiency more the treatment bound by the availability and the cost of the membrane as the 95 percent effective membrane is very close to 99.5 percent effective membrane but the 90 percent effective membrane falls way short of the treatment efficiency on the scale of the given treatment percentages.

  o The data shows that the back flushing operation which can be controlled is also one of the effective parameters in the design. The more we refresh the better the percentage of treatment in given time. Again it is upper bound by the cost
considerations of this operation. However it is asymptotically most effective at the continuous backflush though it might not be needed.

- **Natural Attenuation Simulation and Water Quality Analysis**
  - It is known that the natural attenuation approach is destined to leave some contamination even after a long wait. A year long simulation resulted in the confirmation of this.
  - Water quality analysis shows that the DO would go down as we treat the sediments without supplying them with the electron acceptors. So the techniques like bioaugmentation without a supporting biostimulation by electron acceptor supply is always going to lead to low DO levels.
  - We can conclude that controlled continuous oxygen supply definitely scores over the bioremediation techniques so far known.
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Appendix 1

IN-SITU BIORESTORATION OF CONTAMINATED SEDIMENTS USING MEMBRANES AND GEL BEADS

Henry H. Tabak (U.S. EPA, NRMRL, Cincinnati, OH)
Rakesh Govind, Mukundan Ramani
(Chemical Engineering Department, University of Cincinnati, Cincinnati, OH)

ABSTRACT: In this paper bench-scale evaluation of two novel methods for in-situ biorestoration of contaminated sediments is presented. The first method involves the use of specially designed gaseous, inorganic, and organic nutrient bearing hollow fiber polymeric membranes for controlling the redox potential in contaminated sediments. The method allows in-situ biodegradation of PAHs in contaminated sediments while preventing the membranes from fouling. Experimental data will be presented on biotransformation rates of 18 PAHs (2 ring to 6 ring compounds) as a function of redox potential using PAH-contaminated New York Harbor sediment. Another in-situ method, presented in his paper, for biorestoration of contaminated groundwater aquifer sediments, involves bioaugmentation and/or biostimulation using encapsulated acclimated selective bacterial cultures in specially formulated silica gel beads.

INTRODUCTION

Sediment contaminants can be broadly classified into three categories: (1) organics which biotransform under aerobic conditions but are relatively recalcitrant under anaerobic conditions, such as polycyclic aromatic hydrocarbons (PAHs); (2) contaminants which biotransform under anaerobic conditions but are relatively recalcitrant under aerobic conditions, such as highly chlorinated PCBs; and (3) compounds that undergo both aerobic and anaerobic biotransformations. Further, diffusion of contaminants within the sediment region is slow mainly due to retardation effects of sediment organic carbon and often poor aqueous solubility of the contaminants.

Previous attempts to treat contaminated sediments have mainly involved dredging followed by long-term storage (capping) or ex-situ treatment or in-situ treatment, using injection of nutrients, adapted microorganisms, chemicals, etc. Most of the in-situ methods suffer from losses of the additives to the overlying water, competition from indigenous microorganisms and difficulty in controlling environmental conditions, such as pH, temperature, alkalinity, etc.

Various studies have identified specific organisms capable of degrading PAH compounds (Heitkamp and Cerniglia, 1989; Cerniglia, 1984). Information on aerobic pathways is generally limited to two-and three-ring PAH compounds including naphthalene (Fredrickson et al., 1991), acenaphthene (Ellis et al., 1991), and phenanthrene (Fredrickson et al., 1991; Brodkorb and Legge, 1992). Biodegradation of PAHs under anaerobic and sulfate reducing conditions have also been discussed (Young, 1999).

Objectives. The main objectives of this study were to demonstrate the feasibility of using microporous membranes for manipulating the redox potential and deliver treatment
agents into PAH contaminated sediments and aquifers, thereby enhancing the rate and extent of in-situ bioremediation. Table 1 summarizes the PAHs accumulated in the New York-New Jersey Harbor sediment, which was used in our experimental studies.

**TABLE 1. Selected polycyclic aromatic hydrocarbons (PAHs) in NY/NJ sediment.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (mg/Kg) (Percentage of Total PAHs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>3.8 (12.3)</td>
</tr>
<tr>
<td>2-Methylnaphthalene</td>
<td>2.6 (6.23)</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>7.8 (20.3)</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>2.8 (7.82)</td>
</tr>
<tr>
<td>Anthracene</td>
<td>3.2 (8.23)</td>
</tr>
<tr>
<td>Fluorene</td>
<td>1.8 (4.27)</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>6.4 (14.5)</td>
</tr>
<tr>
<td>Pyrene</td>
<td>3.9 (6.67)</td>
</tr>
<tr>
<td>Benzo [a] anthracene</td>
<td>2.1 (3.46)</td>
</tr>
<tr>
<td>Chrysene</td>
<td>2.7 (4.78)</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>2.1 (3.19)</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>1.7 (2.15)</td>
</tr>
<tr>
<td>Benzo[ghi]perylene</td>
<td>0.8 (1.54)</td>
</tr>
<tr>
<td>TPAH</td>
<td>46.8 (98.6)</td>
</tr>
</tbody>
</table>

**MATERIALS AND METHODS**

**Membrane Reactor Studies**

Shaker vial extraction method (Huang et al. 1996) was used to analyze the soil concentration of each PAH. The extracts are analyzed using a Hewlett Packard Gas Chromatograph equipped with a flame ionization detector (GC-FID).

A bench-scale micro-reactor system was developed to quantitate biodegradation rate of PAHs in sediment samples. A schematic of the micro-reactor system is shown in Figure 1. The length (L) was kept small (10 cm) to minimize axial profile along the length of the micro-reactor system. The diameter of the micro-reactor was 20 mm to minimize the effect of radial diffusion in the sediment. Preliminary experiments conducted with 10 cm diameter micro-reactors had shown that the PAH concentration profile exhibited less than 15% variation within a radial distance of 10 mm. Hence, the average PAH concentration was measured experimentally as a function of time, redox condition and addition of various biotreatment agents, such as air, argon, sulfate or nitrate containing water.
FIGURE 1. Schematic of the membrane micro-reactor system.

All micro-reactors were immersed in a constant temperature bath to maintain temperature during the experiment. 2 mm internal diameter polypropylene porous hollow fibers were used in the study. To minimize the impact of pore plugging due to microbial growth, two strategies were used: (1) the membrane hollow fibers were coated with a 1 to 3 micron thickness layer of palladium metal using electroless plating (Govind, et al., 1996), which prevented microbial attachment to the membrane surface; and (2) the pressure inside the hollow fiber was pulsed from 10 psia to 30 psia with a cycle time of 1 minute (membrane bubble pressure was 27 psia) to slough-off microbial growth from the pores and surface of the membrane hollow fibers. Application of these two strategies prevented membrane biofouling, a well-known problem with the application of membranes in biological environments.

The following biotreatment agents were studied: (1) air at 5 mL/minute flow rate to maintain aerobic conditions in the sediment; (2) argon gas at 5 mL/minute to maintain anaerobic conditions; (3) DI/DD water containing 15 mg/L sodium nitrate at a flow rate of 15 mL/minute; and (4) DI/DD water containing 12 mg/L of sodium sulfate at a flow rate of 15 mL/minute. The redox potential was measured by a platinum electrode calomel half cell connected to a meter.

Chemical binding of PAHs to organic matter has been studied in the literature (Govind and Ramani, 2001). Almost all of the biodegradation studies in the literature ignore the effect of chemical binding and measure disappearance of parent compound (not extractable) as indication of biodegradation. Mineralization studies which involve the measurement of radiolabelled carbon dioxide from spiked radiolabelled PAHs ignore the impact of aging, which results in chemical binding. Measurement of carbon dioxide evolution from aged contaminated sediments measures the combination of PAH mineralization and degradation of organic matter, and hence are not indicative of purely PAH mineralization. In our studies, chemical binding effects were measured by using sterilized sediments, by addition of sodium azide. Separate measurements of gas (carbon dioxide, methane, hydrogen sulfide, nitrogen) evolution (not presented here) demonstrated that addition of sodium azide did not result in any bioactivity for the
experimental time periods used in our studies. Using sterilized sediments, non-extractability of PAHs was used as quantitation of chemical binding to sediment organic matter.

% biotransformation in this paper is inclusive of chemical binding (also shown separately), since it is postulated that oxidative enzymes, produced by bacteria during the aging time period, rather than active bacteria are involved in initial hydrolysis of PAHs which results in chemical binding (Govind and Ramani, 2001).

Silica Gel Bead Studies

Application of alginate-silica gel beads has been studied for treatment of chlorinated contaminants, such as trichloroethylene (TCE), in ground water (Tian and Govind, 2001). Other experimental studies have confirmed the fact that gel beads can be used successfully to deliver nutrients, use entrapped acclimated organisms, and other agents for effecting biodegradation of organics (Stormo and Crawford, 1992). Use of gel beads can be combined with membranes to enhance biodegradation rates in contaminated sediments.

RESULTS AND DISCUSSION

Membrane Reactor Studies

Experimental studies conducted over a 90 day time period showed that all PAHs were biotransformed (only parent compounds were analyzed) under both low and high redox potentials, and the extent of biotransformation decreased under reducing conditions. The extent of biotransformation decreased with increasing ring size. Physical adsorption of PAH compounds on the surface of hollow fibers and glassware, measured by decrease in PAH concentration from aqueous solutions, was found to be negligible (less than 1%), compared to the extent of biotransformation.

Experiments with sterilized contaminated sediments revealed chemical binding to organic matter of sediments under only positive redox potential conditions (Govind and Ramani, 2001), as shown by hatched bars in Figure 2. The extent of chemical binding increased with increasing positive redox potential and with increasing ring size. Chemical binding was not observed under reducing conditions, indicating that chemical binding of PAHs to organic matter is an oxidative process.

Relatively rapid biotransformation of PAHs was observed experimentally, (Figure 3) when air was passed through the membrane fiber. The oxidation reduction potential exceeded +600. The extent of biotransformation decreased with increasing ring size. 2-ring PAHs were completely biotransformed in 60 days while about 57% of 6-ring PAHs were biotransformed.
FIGURE 2. Extent of PAH biotransformation under various redox potentials. Extent of chemical binding is shown by the hatched bars.
FIGURE 3. Extent of PAH biotransformation under aerobic conditions. Chemical binding of PAHs to organic matter is shown by hatched bars.

The extent of chemical binding under aerobic conditions increased with time, and with increasing ring size. The order of ring size, as shown for 5 days, is the same for all time periods. As mentioned earlier, % biotransformation is inclusive of chemical binding and in 90 days, almost half of the 6-ring PAHs are chemically bound to sediment organic matter.

When argon gas was passed through the hollow fiber membranes, anaerobic conditions prevailed in the sediment sample, with a redox potential below –240 mV.
PAH biodegradation was observed, although the rate of biodegradation was considerably slower than the aerobic case. Figure 4 shows the extent of PAH biodegradation under anaerobic conditions. The acclimation time for the onset of biodegradation was about 35 days, and this time period is not shown in the graph. No chemical binding was observed under anaerobic conditions.

![Image of Figure 4: Extent of PAH biodegradation under anaerobic conditions.](image)

**FIGURE 4.** Extent of PAH biodegradation under anaerobic conditions.

The order of ring size, as shown for 5, 10 and 15 days is the same for all remaining time periods.

Under denitrifying conditions, with nitrate water as the biotreatment agent, the extent of biodegradation was high, although lower than in the case of aerobic conditions. The acclimation time period for the onset of biodegradation was 30 days (not shown in the graph). PAH biodegradation under denitrifying conditions has also been studied (Mihelcic and Luthy, 1988), and degradation of acenaphthene and naphthalene occurred from an initial aqueous-phase concentration of 1 mg/L to nondetectable levels in less than 9 weeks. Figure 5 shows the extent of PAH biodegradation under denitrifying conditions. No chemical binding was observed under denitrifying conditions.

When sulfate water was used resulting in sulfate-reducing conditions in the micro-reactor, the extent of PAH biodegradation decreased considerably, and the acclimation time was 45 days (not shown in the graph). PAH degradation under sulfate reducing conditions has only been reported recently (Young, 1999). Figure 6 shows the extent of PAH biodegradation under sulfate–reducing conditions.
The above results showed that PAHs in contaminated sediments can be biodegraded successfully under various redox conditions using a membrane delivery system. Porous membranes can provide biotreatment agents to alter the intrinsic redox potentials in the contaminated zone, and the use of palladium coated hollow fibers with pressure back pulsing prevents biomass clogging effects usually observed with the use of membranes in environmental biosystems.
The effect of radial diffusion has shown that a single hollow fiber membrane can effect the intrinsic redox potential within a radial distance of about 10 times the fiber radius, and this is mainly due to the fact that the rate of biodegradation compared to aqueous diffusivity of the biotreatment agent is relatively slow. It is shown that chemical binding of PAHs to sediment organic matter is an important mechanism for PAHs, which previously has been largely ignored in biodegradation and bioavailability studies. Chemical binding of PAHs occurs only under positive redox conditions, increasing with increasing positive redox values and with increasing PAH ring size.

**Application of gel beads**

Gel beads can be used to alter conditions *in-situ* with the objective of enhancing the extent and rate of biodegradation of recalcitrant contaminants. Figure 7 shows a conceptual diagram for enhancing the biodegradation of PAHs in anaerobic sediments. Figure 8 illustrates application of gel beads for achieving biodegradation of polychlorinated biphenyls (PCBs) in aerobic sediments. Further experimental studies at the microcosm level are needed to implement and demonstrate the effectiveness of gel beads in these and other applications.

**CONCLUSIONS**

Experimental studies conducted with membrane hollow fibers has demonstrated that PAHs (2 to 6 ring sizes) can be successfully biotransformed in New York harbor sediments under various redox conditions. Control studies showed less than 1% adsorption losses to the membrane surface and reactor glassware. Generally the extent of biotransformation decreased with increasing PAH ring size. Biotransformation under aerobic conditions showed the highest rates, followed by denitrifying, anaerobic and sulfate reducing conditions. The hollow fiber was effective upto 10 times its diameter in terms of effecting the redox potential in the sediment. Experiments with sterilized sediments were used to determine the extent of chemical binding. Chemical binding only occurred under positive redox conditions, increasing with PAH ring size. It has been postulated that chemical binding of PAHs to organic matter is an oxidative process involving enzymatic hydrolysis as the first step (Govind and Ramani, 2001). Although experimental studies with gel beads using contaminated sediments have not yet been conducted, conceptual diagrams showing the potential application of gel beads for treating sediments contaminated with PAHs and PCBs were presented. Further microcosm level studies need to be conducted to explore potential application of gel beads for treating contaminated sediments. Combination of membrane and gel beads also offers great promise in developing *in-situ* contaminated sediment treatment technologies.
FIGURE 7. Application of gel beads for enhancing biodegradation of PAHs in anaerobic sediments.

FIGURE 8. Application of gel beads for enhancing biodegradation of PCBs in aerobic sediments.
REFERENCES


Appendix 2

Aerobic Simulation of 2 Ring PAHs

clear; %Flushing memory

format long;

%---------------------------------------initializing mesh parameter---------------------------------------

-----------------%

days=60; %observation time.

range=1; %domain of interest in cms.

N=(64*60*4)+1; %division in mesh for Observation-Time interval for process 50 days so deltat becomes 0.25.

I=9; %Domain is of 11 points that is 10 cm distance delta r is 1.

deltar=range/(I-1); %deltar is 1 cm.

deltat=days/(N-1); %deltat is 0.25 days.

if (deltat/(deltar*deltar)>=0.5)
    disp('quit - Not Stable i.e deltat/(deltar*deltar)>=0.5')
    exit;
end

%---------------------------------------initializing the derivatives and variables over the mesh---------------------------------------

---------%

---------%
% dcdt=zeros(N,I);
% dcbdt=zeros(N,I);
% dxdt=zeros(N,I);
% dedt=zeros(N,I);
% dchdt=zeros(N,I);
% dodt=zeros(N,I);
% oxygen=zeros(N,I);
% PAH=zeros(N,I);
% PAHdiol=zeros(N,I);
% PAHbound=zeros(N,I);
% biomass=zeros(N,I);
% enzym=zeros(N,I);
% integral=zeros(N,1);

% i=1;                           %Counter for space domain % conditions for 2 - ring
% for i=2:I-1

% oxygen(1,i)=8;             %8   ppm
% PAH(1,i)=3.2;              %42  ppm
% PAHdiol(1,i)=3.2;          %1   ppm
% PAHbound(1,i)=0;           %1   ppm
% biomass(1,i)=10;           %10  ppm
% enzym(1,i)=0;              %1   ppm

% end
% Enforcing Boundary Condition on the variables over the mesh---

% n=1; %Counter for time domain
% for n=1:N % forcing Boundary Condition
%    oxygen(n,1)=8; % 8 ppm
%    PAH(n,1)=0; % 0 ppm
%    PAHdiol(n,1)=0; % 0 ppm
%    PAHbound(n,1)=0; % 0 ppm
%    biomass(n,1)=0; % 0 ppm
%    enzym(n,1)=0; % 0 ppm
% end
%
%
% EXPERIMENTAL VALUES INPUT START--------------------------------------

days1 = 9;
input_PAH=zeros(days1,2);
input_PAH(1,1)=0;
input_PAH(1,2)=100-0;
input_PAH(2,1)=5;
input_PAH(2,2)=100-24; % PAH remaining has to be taken in from the data of percentage biodegraded ... so 100 - value

input_PAH(3,1)=10;
input_PAH(3,2)=100-36;
input_PAH(4,1)=15;
input_PAH(4,2)=100-50;
input_PAH(5,1)=20;
input_PAH(5,2)=100-68;
input_PAH(6,1)=30;
input_PAH(6,2)=100-79;
input_PAH(7,1)=40;
input_PAH(7,2)=100-88;
input_PAH(8,1)=50;
input_PAH(8,2)=100-96;
input_PAH(9,1)=60;
input_PAH(9,2)=100-99;
% input_PAH(10,1)=70;
% input_PAH(10,2)=100-99.3;
% input_PAH(11,1)=80;
% input_PAH(11,2)=100-99.6;
% input_PAH(12,1)=90;
% input_PAH(12,2)=100-99.9;
%----------------EXPERIMENTAL VALUES INPUT END------------------------------------------

----%  

%------------------------------------------------------------------------------------------

-----------%  

%-------------------------------------------------MOB STARTS from here ------------------------

-----------------------%  

%-----------------------------------------------------------------initializing the starting Parameters for MOB------------------

-----------------------%  

for counter_MOB = 1:5

if counter_MOB==1
    K1_start = 13;
    K2_start = 0.021;
    Do_pivot_start = 0.0059; %(cm^2/hrs.)
    meu_pivot_start =0.03;
    Kc_pivot_start =30;
    Ko_pivot_start =33.1;
    Ye_pivot_start =0.42;
    Yh_pivot_start =0.42;
    Yo_pivot_start =0.08;

```
% K1_max = 13;
% K2_max = 0.1;
Do_max_start = 0.01;
% meu_max_start = 0.06;
meu_max_start = 0.3;
Kc_max_start = 50;
Ko_max_start = 50;
Ye_max_start = 1.62;
Yh_max_start = 1.62;
Yo_max_start = 1.5;

% K1_min = 13;
% K2_min = 0.001;
Do_min_start = 0.001;
meu_min_start = 0.09;
% Kc_min_start = 3;
Kc_min_start = 15;
% Ko_min_start = 3;
Ko_min_start = 15;
Ye_min_start = 0.4;
Yh_min_start = 0.4;
Yo_min_start = 0.04;
format long;

box = zeros(7,7);

box(1,4)=Do_pivot_start;
box(1,1)=Do_min_start;
box(1,7)=Do_max_start;
box(2,4)=meu_pivot_start;
box(2,1)=meu_min_start;
box(2,7)=meu_max_start;
box(3,4)=Kc_pivot_start;
box(3,1)=Kc_min_start;
box(3,7)=Kc_max_start;
box(4,4)=Ko_pivot_start;
box(4,1)=Ko_min_start;
box(4,7)=Ko_max_start;
box(5,4)=Ye_pivot_start;
box(5,1)=Ye_min_start;
box(5,7)=Ye_max_start;
box(6,4)=Yh_pivot_start;
box(6,1)=Yh_min_start;
box(6,7)=Yh_max_start;
box(7,4)=Yo_pivot_start;
box(7,1)=Yo_max_start;
box(7,7)=Yo_min_start;

%---------------------------------------------filling the box ------------------------------

%---------------------------------------------

% box rows i.e. parameter is travelled in columns while the row indexes are for
different params

for param_index=1:7
    for box_param_intializn_cntr = 2:6
        if box_param_intializn_cntr <= 4
            box(param_index, box_param_intializn_cntr)=box(param_index, 1) +
            (box_param_intializn_cntr-1)*(box(param_index, 4)-box(param_index, 1))/3;
        else
            box(param_index, box_param_intializn_cntr)=box(param_index, 4) +
            (box_param_intializn_cntr-4)*(box(param_index, 7)-box(param_index, 4))/3;
        end
    end
end

%---------------------------------------------filled "initial" box ------------------------------

---------------------------------------------%

K1=K1_start;  

%Reaction kinetics parameter for the degradation of Contaminant PAH in (mg/Kg.day)
K2=K2_start;  %Reaction kinetics parameter for the formation of bound contaminant in day^-1

Do=Do_pivot_start;  %Diffusivity of oxygen in centimeter^2/Day

meu=meu_pivot_start;  %Growth factor for the microorganisms in day^-1

Kc=Kc_pivot_start;  %Half saturation constant for substrate diol in ppm

Ko=Ko_pivot_start;  %Half saturation constant for oxygen in ppm

Ye=Ye_pivot_start;  %Yield parameter for enzym in ppm

Yh=Yh_pivot_start;  %Yield parameter for diol in ppm

Yo=Yo_pivot_start;  %Yield parameter for oxygen in ppm

disp(box);
end

% if rem(counter_MOB,20) == 0
% disp(box);
% end

% if counter_MOB <=20
% if rem(counter_MOB,5) == 0
% disp(box);
if counter_MOB <= 5
    disp(box);
    disp(counter_MOB);
end

%---------------------------------------------inside the box----------------------------------------

------------%

for param_index=1:7          % box rows --- i.e. parameter is travelled in columns
while the row indexes are for different params
    RRE_matrix = zeros(2,6);
    %---------------------------------------------filling the box while run-------------------------
end

%---------------------------------------------inside the box----------------------------------------

for param_index=1:7          % box rows --- i.e. parameter is travelled in columns
while the row indexes are for different params
    RRE_matrix = zeros(2,6);
    %---------------------------------------------filling the box while run-------------------------
end

if counter_MOB ~= 1
    for box_param_intializn_cntr = 2:6
        if box_param_intializn_cntr <= 4
            box(param_index, box_param_intializn_cntr)=box(param_index, 1) +
            (box_param_intializn_cntr-1)*(box(param_index, 4)-box(param_index, 1))/3;
        else
            
    else
box(param_index, box_param_initialization_cntr)=box(param_index, 4) +
(box_param_initialization_cntr-4)*(box(param_index, 7)-box(param_index, 4))/3;
end
end
end

% debugging print in matlab window---
if param_index == 7
    if counter_MOB<=5
        disp(box);
        disp(counter_MOB);
    end
end

end

% debugging print ---

for param_counter = 1:6

    %--------------------------------------------------------------
    %--------------------------------------------------------------
    %------------------------initializing the derivatives and variables over the mesh------
    %--------------------------------------------------------------
    %--------------------------------------------------------------
    %--------------------------------------------------------------
    %--------------------------------------------------------------

    dcdt=zeros(N,I);

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debdt=zeros(N,I);
dxdt=zeros(N,I);
dedt=zeros(N,I);
dchdt=zeros(N,I);
dodt=zeros(N,I);
oxygen=zeros(N,I);
PAH=zeros(N,I);
PAHdiol=zeros(N,I);
PAHbound=zeros(N,I);
biomass=zeros(N,I);
enzym=zeros(N,I);
integral=zeros(N,1);

i=1;                           %Counter for space domain % conditions for 2 - ring

for i=2:I-1
    oxygen(1,i)=8;              %8  ppm
    PAH(1,i)=3.2;                %42  ppm
    PAHdiol(1,i)=3.2;            %1   ppm
    PAHbound(1,i)=0;            %1   ppm
    biomass(1,i)=10;            %10  ppm
    enzym(1,i)=0;               %1   ppm
end
n=1;                        %Counter for time domain
for n=1:N                   %forcing Boundary Condition
oxygen(n,1)=8;              %8 ppm
% PAH(n,1)=0;                %0 ppm
% PAHdiol(n,1)=0;            %0 ppm
% PAHbound(n,1)=0;           %0 ppm
% biomass(n,1)=0;            %0 ppm
% enzym(n,1)=0;              %0 ppm
end

%---------------------------------------------------------------
%---------------------------------------------------------------

%-----------------------------------initializing the Parameter over the
mesh-----------------------------------%
% K1=13; %Reaction kinetics parameter for the degradation of Contaminant PAH in (mg/Kg.day)
% K2=0.021; %Reaction kinetics parameter for the formation of bound contaminant in day^-1

if param_index == 1
    Do=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2; % Do (box (i,j) + box (i,j+1))/ 2
end

if param_index == 2
    meu=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2; % meu=0.08 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 3
    Kc=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2; % Kc=45 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 4
    Ko=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2; % Ko=43.1 (box (i,j) + box (i,j+1))/ 2
end
if param_index == 5

Ye=(box(param_index,param_counter) +
box(param_index,(param_counter+1)))/2;  % Ye=0.62 \( \text{box} (i,j) + \text{box} (i,j+1)/ 2 \)
end

if param_index == 6

Yh=(box(param_index,param_counter) +
box(param_index,(param_counter+1)))/2;  % Yh=0.62 \( \text{box} (i,j) + \text{box} (i,j+1)/ 2 \)
end

if param_index == 7

Yo=(box(param_index,param_counter) +
box(param_index,(param_counter+1)))/2;  % Yo=0.08 \( \text{box} (i,j) + \text{box} (i,j+1)/ 2 \)
end

%------------------------------------------------------------------------------
--------------------------------------%
% input_PAH(m,1)=input('for the day number:');
% input_PAH(m,2)=input('% degraded');
% input_PAH(m,2)=100-input_PAH(m,2);
%end

%disp(' day number % remaining');
%disp(input_PAH);

% %------------EXPERIMENTAL VALUES INPUT START-enter %
% biodegraded here --------------------------------------------%

% days1 = 6;
% input_PAH=zeros(days1,2);
% input_PAH(1,1)=0;
% input_PAH(1,2)=100-0;
% input_PAH(2,1)=50;
% input_PAH(2,2)=100-64.4; % PAH remaining has to be taken in
% from the data of percentage biodegraded ... so 100 - value
% input_PAH(3,1)=100;
% input_PAH(3,2)=100-74.3;
% input_PAH(4,1)=150;
% input_PAH(4,2)=100-86.2;
% input_PAH(5,1)=200;
% input_PAH(5,2)=100-98.1;
% input_PAH(6,1)=250;
n=1; %Counter for time domain
i=1; %Counter for space domain
for n=1:N-1
    for i=2:I-1
        diffusion1=0;
        diffusion2=0;
        biomass_consumption=0;
        dcdt(n,i)=0-(K1*enzym(n,i)*PAH(n,i)); %rate of PAH decay *PAH(n,i)* enzym(n,i)
        PAH(n+1,i)=PAH(n,i)+deltat*dcdt(n,i);
        if PAH(n+1,i)<=0
            PAH(n+1,i)=0;
            dcdt(n,i)=-PAH(n,i)/deltat;
        end
        dcbdt(n,i)=K2*PAHdiol(n,i); %rate of bound contaminant formation
        PAHbound(n+1,i)=PAHbound(n,i)+deltat*dcbdt(n,i);
    end
end
dxdt(n,i)=(meu*biomass(n,i)*PAHdiol(n,i)*oxygen(n,i))/((Kc+PAHdiol(n,i))*(Ko+oxygen(n,i)))); %rate of biomass growth

biomass(n+1,i)=biomass(n,i)+deltat*dxdt(n,i);

if PAH(n,i)<=0
dedt(n,i)=(dxdt(n,i)/Ye);

%+enzym(n,i)*dcdt(n,i)/PAH(n,i) rate of enzym concn change
else
dedt(n,i)=(dxdt(n,i)/Ye)+enzym(n,i)*dcdt(n,i)/PAH(n,i);
end

enzym(n+1,i)=enzym(n,i)+deltat*dedt(n,i);
dchdt(n,i)=0-(dxdt(n,i)/Yh)-dcdt(n,i)-dcbdt(n,i);

%rate of diol concn change
PAHdiol(n+1,i)=PAHdiol(n,i)+deltat*dchdt(n,i);
diffusion1=((oxygen(n,i+1)-2*oxygen(n,i)+oxygen(n,i-1))/((deltar)*(deltar)));
diffusion2=((oxygen(n,i+1)-oxygen(n,i-1))/(2*deltar*((i-1)*deltar)));
biomass_consumption=(dxdt(n,i)/Yo);
dodt(n,i)=24*Do*(diffusion1+diffusion2)-biomass_consumption;

%rate of the oxygen concn change and we can calculate radius(n) as (n-1)*deltar = r(n)
oxygen(n+1,i)=oxygen(n,i)+deltat*dodt(n,i);
oxygen(n+1,I)=oxygen(n+1,I-1);

% comment from here to end
% if(rem((n-1),4)==0 & rem(i,2)==0)
% hold on;
% plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'r*');

% PAHdiol(n,i)+PAH(n,i)
% elseif(rem((n-1),4)==0 & rem(i,2)==0)
% hold on;
% plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'b*');
% end

end

end

% hold on;
% limit_ordinate= PAH(1,2)+PAHdiol(1,2)+5;
% axis([0 days 0 limit_ordinate]);
% title('Simulation of PAH FOR K= 13');
% grid on;
% xlabel('Time');
% ylabel('Concentration of PAH');

%-----------------------------------------------------------------------------------------------------------Plotiing Biomass and Oxygen-----------------------------------------------------------------------------------------------------------

% for i=1:I
% for n=1:N

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% hold on;
% plot((n-1)/4,biomass(n,i),'-k','LineWidth',3);
% hold on;
% plot((n-1)/4,oxygen(n,i),'-g','LineWidth',3);
% line((n-1)/4,PAH(n,i))
% end
% end

%----------------------------------------------Integration with RK-2-----
% for n=1:N
% for i=2:I-1
% k1=deltar*(deltar*i)*(PAH(n,i)+PAHdiol(n,i));
% k2=deltar*(deltar*(i+deltar))*(PAH(n,i+deltar)+PAHdiol(n,i+deltar));
% integral(n)=integral(n)+(k1+k2)/2;
% end
% integral(n)=2*integral(n)/(((I-1)*(I-1)-4)*deltar*deltar);

%finding the average of the integral value.
% end
%----------------------------------------------Integration with RK-4-----
%----------------------------------------------%
for n=1:N

    integral(n)=0;

    for i=2:2:I-1                               % keep the I odd as it has to be odd in order to
                                                % have increment 2 cover all.

        k1=2*deltar*(deltar*i)*(PAH(n,i)+PAHdiol(n,i));
        %         k1=2*deltar*(PAH(n,i)+PAHdiol(n,i));

        % if n <=3
        %     disp(n);disp(i);disp('times k1=');disp(k1);
        % end

        k2=2*deltar*(deltar*(i+1))*(PAH(n,i+1)+PAHdiol(n,i+1));
        %         k2=2*deltar*(PAH(n,i+1)+PAHdiol(n,i+1));

        % if n <=3
        %     disp(n);disp(i);disp('times k2=');disp(k2);
        % end
k3=2*deltar*(deltar*(i+1))*(PAH(n,i+1)+PAHdiol(n,i+1));

%    k3=2*deltar*(PAH(n,i+1)+PAHdiol(n,i+1));

%    if n <=3
%        disp(n);disp(i);disp('times k3=');disp(k3);
%    end

if i==(I-1)
    k4=k3;
else
    k4=2*deltar*(deltar*(i+2))*(PAH(n,i+2)+PAHdiol(n,i+2));
%    k4=2*deltar*(PAH(n,i+2)+PAHdiol(n,i+2));
end

%    if n <=3
%        disp(n);disp(i);disp('times k4=');disp(k4);
%    end

integral(n)=integral(n)+(k1+2*k2+2*k3+k4)/6;

%    if n <=3
% disp(n);disp(i);disp('integral r');disp(integral(n));
% end

end

integral(n)=2*integral(n)/(((I-1)*(I-1))*deltar*deltar);
%finding the average of the integral value.
integral(n)=2*integral(n)/(((I-1)*(I-1)-1)*deltar*deltar);

% ---Error Suppression --
% if integral(n) > PAH(1,2)+PAHdiol(1,2)
% integral(n)=PAH(1,2)+PAHdiol(1,2);
% end

% if n <=3
% disp(n);disp(i);disp('avg integral=');disp(integral(n));
% end
end

%----------------------------------------------Integration with RK-4 for oxygen--------------------------------------%
% for n=1:N
% for i=2:2:I-1 % keep the I odd as it has to be odd in order to have increment 2 cover all.

  % k1=2*deltar*(deltar*i)*(oxygen(n,i));
  % k2=2*deltar*(deltar*(i+deltar))*(oxygen(n,i+deltar));
  % k3=2*deltar*(deltar*(i+deltar))*(oxygen(n,i+deltar));
  % if i==(I-1)
  %  k4=k4;
  % else
  %
  
k4=2*deltar*(deltar*(i+2*deltar))*(PAH(n,i+2*deltar)+PAHdiol(n,i+2*deltar));
  % end
  %

integral_oxygen(n)=integral_oxygen(n)+(k1+2*k2+2*k3+k4)/6;
  % end
  % integral(n)=2*integral_oxygen(n)/(((I-1)*(I-1)-4)*deltar*deltar); %finding the average of the integral value.
  % end

%------------------------------------------------------------------------integrated plot---------------------

% for n=1:N

% hold on;

% plot((n-1)/4,integral(n),'k+','LineWidth',1);
% end

% %----------------------------------- experimental plot----------------
%-----------------------------------%
% for n=1:days1
% hold on;
% dummy = input_PAH(n,2)*(PAH(1,2)+PAHdiol(1,2))/100;
% plot(input_PAH(n,1),dummy,'R*','LineWidth',4);
% end

% %----------------------------------- Verification---------------------
%-----------------------------------%  

TRRE=0;

Trre1=0;

for l=1:days1

j=input_PAH(l,1);

k=(j/deltat)+1;

dummy1 = input_PAH(l,2)*(PAH(1,2)+PAHdiol(1,2))/100;

% error watch

% disp(input_PAH(l,1));

% disp(k);

% disp(integral(k));
% disp(dummy1);
% disp((integral(k)-dummy1)/(dummy1));

% disp((integral(k)-dummy1)/(dummy1))

\[ Trr1 = Trr1 + \text{abs}((\text{integral}(k)-\text{dummy1})/(\text{dummy1})) \]

% ---
% \[ Trr1 = Trr1 + ((\text{integral}(k)-\text{dummy1})\times(\text{integral}(k)-\text{dummy1})) \]

% TRRE=TRRE+((integral(k)/(PAH(1,2)+PAHdiol(1,2))*100)-input_PAH(1,2)/input_PAH(1,2))*((integral(k)/(PAH(1,2)+PAHdiol(1,2))*100)-input_PAH(1,2)/input_PAH(1,2));

end

RRE1=\text{abs}(\text{sqrt}(Trr1))/\text{days1};
% RRE = \text{sqrt}(TRRE)/\text{days1};

%-----------------------------filling the RRE matrix index and value-----------------------------

%-------------------------------% 
RRE\_matrix(1,param\_counter)=param\_counter;
RRE\_matrix(2,param\_counter)=RRE1;

end

%-------------------------------------E of loop for param count------------------------------------

%-------------------------------%
%----------------------------------finding the minimum in RRE matrix index and value--
-----------------------------------%

temp_RRE = RRE_matrix(2,1);
temp_index = 1;

for count = 1:6
    if temp_RRE <= RRE_matrix(2,count)
        temp_index = temp_index;
        temp_RRE = temp_RRE;
    else
        temp_RRE = RRE_matrix(2,count);
        temp_index = RRE_matrix(1,count);
    end
end

%-----------------------------------found the minimum and now assign the pivot min and max
for the new box--------------%
    box(param_index,1) = box(param_index,temp_index);
    box(param_index,4) = (box(param_index,temp_index) +
                          box(param_index,(temp_index+1)))/2;
    box(param_index,7) = box(param_index,(temp_index+1));
% modified value after the iteration is kept here in this
if param_index == 1
    Do=box(param_index,4); % Assigning the new value for the next iteration
end

if param_index == 2
    meu=box(param_index,4); % Assigning the new value for the next iteration
end

if param_index == 3
    Kc=box(param_index,4); % Assigning the new value for the next iteration
end

if param_index == 4
    Ko=box(param_index,4); % Assigning the new value for the next iteration
end

if param_index == 5
    Ye=box(param_index,4); % Assigning the new value for the next iteration
end

if param_index == 6
    Yh=box(param_index,4);  % Assigning the new value for the
    next iteration
end

if param_index == 7
    Yo=box(param_index,4);  % Assigning the new value for the
    next iteration
end

end

%--------------------------------------------------------E of loop for param index-------------------------

%--------------------------------------------------------

final_RRE = temp_RRE;
end

%--------------------------------------------------------MOB at end ---------------------------------------------

hold on;

limit_ordinate= PAH(1,2)+PAHdiol(1,2)+2;
%axis([0 100 0 15]);
axis([0 days 0 limit_ordinate]);
title('Simulation of PAH Biodegradation FOR K= 13 and K2 = 0.021');
grid on;
xlabel('Time (Days )');
ylabel('Concentration of PAH ( ppm - mg/Kg )');
hold on;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%------integrated plot--------------------------------------
---------------------------------------------------

for n=1:N
    hold on;
    plot((n-1)*deltat,integral(n),'k*','LineWidth',2);
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%------experimental plot--------------------------------------
---------------------------------------------------

for n=1:days1
    hold on;
    dummy = input_PAH(n,2)*(PAH(1,2)+PAHdiol(1,2))/100;
    plot(input_PAH(n,1),dummy,'R*','LineWidth',4);
disp(final_RRE);

for i=2:I-1
    for n=1:N-1
        hold on;
        if (rem(i,2)~=0)
            plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'r--');
        else
            plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'b--');
        end
        if(rem((n-1),4)==0 & rem(i,2)~=0)
            hold on;
            plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'r--');
        elseif(rem((n-1),4)==0 & rem(i,2)==0)
            hold on;
            plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'b*');
        end
    end
end
\% end

\% % plot((n-1)/4,biomass(n,i),'-k','LineWidth',3);

\% % hold on;

\% % plot((n-1)/4,oxygen(n,i),'-g','LineWidth',3);

\% % line((n-1)/4,PAH(n,i))

end

end
Appendix 3

Denitrifying Simulation of 2 Ring PAHs

clear;  %Flushing memory

format long;

%-----------------------------------------------------initializing mesh parameter-----------------------------------------------------

-----------------------

days=90;                      %observation time.
range=1;                      %domain of interest in cms.
N=(64*90*4)+1;                   %division in mesh for Observation-Time interval for process 50 days so deltat becomes 0.25.
I=9;                           %Domain is of 11 points that is 10 cm distance delta r is 1.
deltar=range/(I-1);           %deltar is 1 cm.
deltat=days/(N-1);            %deltat is 0.25 days.

if (deltat/(deltar*deltar)>=0.5)
    disp('quit - Not Stable i.e deltat/(deltar*deltar)>=0.5')
    exit;
end

%----------------------------------------------------initializing the derivatives and variables over the mesh---------------------

-----------%
% dcdt=zeros(N,I);
% dcbdt=zeros(N,I);
% dxdt=zeros(N,I);
% dedt=zeros(N,I);
% dchdt=zeros(N,I);
% dodt=zeros(N,I);
% oxygen=zeros(N,I);
% PAH=zeros(N,I);
% PAHdiol=zeros(N,I);
% PAHbound=zeros(N,I);
% biomass=zeros(N,I);
% enzym=zeros(N,I);
% integral=zeros(N,1);

% i=1;                           %Counter for space domain % conditions for 2 - ring %
% for i=2:I-1

%   oxygen(1,i)=8;              %8   ppm
%   PAH(1,i)=3.2;                %42  ppm
%   PAHdiol(1,i)=3.2;            %1   ppm
%   PAHbound(1,i)=0;             %1   ppm
%   biomass(1,i)=10;             %10  ppm
%   enzym(1,i)=0;                %1   ppm
% end
% %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%------------------------Enforcing Boundary Condition on the variables over the mesh---
% n=1;                        %Counter for time domain
% for n=1:N                   %forcing Boundary Condition
%   oxygen(n,1)=8;              %8   ppm
% %   PAH(n,1)=0;                %0   ppm
% %   PAHdiol(n,1)=0;            %0   ppm
% %   PAHbound(n,1)=0;           %0   ppm
% %   biomass(n,1)=0;            %0   ppm
% %   enzym(n,1)=0;              %0   ppm
% end
%
%
%------------EXPERIMENTAL VALUES INPUT START---------------------------------------------%
days1 = 12;
input_PAH=zeros(days1,2);
input_PAH(1,1)=0;
input_PAH(1,2)=100-0;
input_PAH(2,1)=5;
input_PAH(2,2)=100-15; % PAH remaining has to be taken in from the data of percentage biodegraded ... so 100 - value
input_PAH(3,1)=10;
input_PAH(3,2)=100-21;
input_PAH(4,1)=15;
input_PAH(4,2)=100-23;
input_PAH(5,1)=20;
input_PAH(5,2)=100-35;
input_PAH(6,1)=30;
input_PAH(6,2)=100-45;
input_PAH(7,1)=40;
input_PAH(7,2)=100-55;
input_PAH(8,1)=50;
input_PAH(8,2)=100-65;
input_PAH(9,1)=60;
input_PAH(9,2)=100-72;
input_PAH(10,1)=70;
input_PAH(10,2)=100-85;
input_PAH(11,1)=80;
input_PAH(11,2)=100-90;
input_PAH(12,1)=90;
input_PAH(12,2)=100-95;
SOD = 0.02; % g m-2 day-1 divide by the total depth then
%---------------EXPERIMENTAL VALUES INPUT END-----------------------------------------

----%

%-----------------------------------------------------------------------

%----------------------------------MOB STARTS from here ------------------------

%----------------------------------initializing the starting Parameters for MOB---------------------

for counter_MOB = 1:5

    if counter_MOB==1
        K1_start = 13;
        K2_start = 0.001;
        Do_pivot_start = 0.00059; %(cm^2/hrs.)
        meu_pivot_start =0.03;
        Kc_pivot_start =15;
        Ko_pivot_start =30;
        Ye_pivot_start =1.42;
        Yh_pivot_start =1.42;
        Yo_pivot_start =1.08;

    end

end
% K1_max = 13;
% K2_max = 0.1;

Do_max_start = 0.001;
% meu_max_start =0.06;
meu_max_start =0.3;
Kc_max_start =30;
Ko_max_start =60;
Ye_max_start =2.62;
Yh_max_start =2.62;
Yo_max_start =2.5;

% K1_min = 13;
% K2_min = 0.001;

Do_min_start = 0.0001;
meu_min_start =0.09;
% Kc_min_start =3;
Kc_min_start =1;
% Ko_min_start =3;
Ko_min_start =1;
Ye_min_start =0.004;
Yh_min_start =0.004;
Yo_min_start =0.004;
format long;
box = zeros(7,7);

box(1,4)=Do_pivot_start;
box(1,1)=Do_min_start;
box(1,7)=Do_max_start;
box(2,4)=meu_pivot_start;
box(2,1)=meu_min_start;
box(2,7)=meu_max_start;
box(3,4)=Kc_pivot_start;
box(3,1)=Kc_min_start;
box(3,7)=Kc_max_start;
box(4,4)=Ko_pivot_start;
box(4,1)=Ko_min_start;
box(4,7)=Ko_max_start;
box(5,4)=Ye_pivot_start;
box(5,1)=Ye_min_start;
box(5,7)=Ye_max_start;
box(6,4)=Yh_pivot_start;
box(6,1)=Yh_min_start;
box(6,7)=Yh_max_start;
box(7,4)=Yo_pivot_start;
box(7,1)=Yo_max_start;
box(7,7)=Yo_min_start;
%
---------------------------------------------filling the box ---------------------------------------------

% box rows i.e. parameter is travelled in columns while the row indexes are for different params

    for param_index=1:7
        for box_param_intializn_cntr = 2:6
            if box_param_intializn_cntr <= 4
                box(param_index, box_param_intializn_cntr)=box(param_index, 1) +
                (box_param_intializn_cntr-1)*(box(param_index, 4)-box(param_index, 1))/3;
            else
                box(param_index, box_param_intializn_cntr)=box(param_index, 4) +
                (box_param_intializn_cntr-4)*(box(param_index, 7)-box(param_index, 4))/3;
            end
        end
    end

%---------------------------------------------filled "initial" box -----------------------------

--------------------------------%     %Reaction kinetics parameter for the degradation of Contaminant PAH in (mg/Kg.day)

    K1=K1_start;
K2=K2_start; % Reaction kinetics parameter for the formation of bound contaminant in day^-1
Do=Do_pivot_start; % Diffusivity of oxygen in centimeter^2/Day
meu=meu_pivot_start; % Growth factor for the microorganisms in day^-1
Kc=Kc_pivot_start; % Half saturation constant for substrate diol in ppm
Ko=Ko_pivot_start; % Half saturation constant for oxygen in ppm
Ye=Ye_pivot_start; % Yield parameter for enzym in ppm
Yh=Yh_pivot_start; % Yield parameter for diol in ppm
Yo=Yo_pivot_start; % Yield parameter for oxygen in ppm

disp(box);
end

% if rem(counter_MOB,20) == 0
% disp(box);
% end

% if counter_MOB <=20
% if rem(counter_MOB,5) == 0
% disp(box);
% end
% end

if counter_MOB<=5
    disp(box);
    disp(counter_MOB);
end

---------------------------------------------inside the box----------------------------------------
%---------------------------------------------filling the box while run-------------------------
---------------------------%  
for param_index=1:7 % box rows --- i.e. parameter is travelled in columns
while the row indexes are for different params
    RRE_matrix = zeros(2,6);
    %---------------------------------------------filling the box while run-------------------------
---------------------------------------------%

if counter_MOB ~= 1
    for box_param_intializn_cntr = 2:6
        if box_param_intializn_cntr <= 4
            box(param_index, box_param_intializn_cntr)=box(param_index, 1) + (box_param_intializn_cntr-1)*(box(param_index, 4)-box(param_index, 1))/3;
        else
            
end
box(param_index, box_param_intializn_cntr)=box(param_index, 4) +
  (box_param_intializn_cntr-4)*(box(param_index, 7)-box(param_index, 4))/3;
  end
  end
  end

% debugging print in matlab window---
  if param_index == 7
    if counter_MOB<=5
      disp(box);
      disp(counter_MOB);
    end
  end
  end

% debugging print ---
  for param_counter = 1:6


%--------------------------------------------------------------
%--------------------------------------------------------------
%------------------------initializing the derivatives and variables over the mesh------
%--------------------------------------------------------------
%--------------------------------------------------------------
%--------------------------------------------------------------

%--------------------------------------------------------------%

dcdt=zeros(N,I);
dcbdt=zeros(N,I);
dxdt=zeros(N,I);
dedt=zeros(N,I);

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dchdt=zeros(N,I);
dodt=zeros(N,I);
oxygen=zeros(N,I);
PAH=zeros(N,I);
PAHdiol=zeros(N,I);
PAHbound=zeros(N,I);
biomass=zeros(N,I);
enzym=zeros(N,I);
integral=zeros(N,1);
i=1;                           %Counter for space domain % conditions for

2 - ring

for i=2:I-1
    oxygen(1,i)=15;              %8   ppm HERE oxygen CORRESPONDS TO
    %UNEVA
    PAH(1,i)=3.2;                %42  ppm NITRATE :)% conditions for
    PAHdiol(1,i)=3.2;            %1   ppm
    PAHbound(1,i)=0;            %1   ppm
    biomass(1,i)=10;            %10  ppm
    enzym(1,i)=0;               %1   ppm
    end

%-----------------------------------------------------------------------------------

-----------------------------------------------------------------------------------%
%-------------------------------------------------------------
% Enforcing Boundary Condition on the variables over the mesh----------------------------------%

n=1;                        %Counter for time domain

for n=1:N                   %forcing Boundary Condition

    oxygen(n,1)=15;              %8 ppm HERE oxygen CORRESPONDS TO NITRATE :) 

    PAH(n,1)=0;                  %0 ppm
    PAHdiol(n,1)=0;               %0 ppm
    PAHbound(n,1)=0;              %0 ppm
    biomass(n,1)=0;               %0 ppm
    enzym(n,1)=0;                 %0 ppm

end

%-------------------------------------------------------------
%-------------------------------------------------------------
%-------------------------------------------------------------

%-------------------------------------------------------------
%initializing the Parameter over the mesh------------------------%

K1=13;                      %Reaction kinetics parameter for the degradation of Contaminant PAH in (mg/Kg.day)
% K2=0.021; % Reaction kinetics parameter for the formation of bound contaminant in day^-1

if param_index == 1
    Do=(box(param_index,param_counter) +
        box(param_index,(param_counter+1)))/2; % Do (box (i,j) + box (i,j+1))/ 2
end

if param_index == 2
    meu=(box(param_index,param_counter) +
        box(param_index,(param_counter+1)))/2; % meu=0.08 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 3
    Kc=(box(param_index,param_counter) +
        box(param_index,(param_counter+1)))/2; % Kc=45 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 4
    Ko=(box(param_index,param_counter) +
        box(param_index,(param_counter+1)))/2; % Ko=43.1 (box (i,j) + box (i,j+1))/ 2
end
if param_index == 5
    Ye=(box(param_index,param_counter) +
    box(param_index,(param_counter+1)))/2;  \% Ye=0.62 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 6
    Yh=(box(param_index,param_counter) +
    box(param_index,(param_counter+1)))/2;  \% Yh=0.62 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 7
    Yo=(box(param_index,param_counter) +
    box(param_index,(param_counter+1)))/2;  \% Yo=0.08 (box (i,j) + box (i,j+1))/ 2
end

%------------------------------------------------------------------------------
--------------------------------------%

%days=input('please input the number of days required');
%input_PAH=zeros(days,2);
%for m=1:days
%    input_PAH(m,1)=input('for the day number:');
%    input_PAH(m,2)=input('% degraded');

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input_PAH(m,2)=100-input_PAH(m,2);

end

disp(' day number   % remaining');
disp(input_PAH);

%-----------------EXPERIMENTAL VALUES INPUT START-enter %
biodegraded here --------------------------------------------%

days1 = 6;

input_PAH=zeros(days1,2);

input_PAH(1,1)=0;

input_PAH(1,2)=100-0;

input_PAH(2,1)=50;

input_PAH(2,2)=100-64.4;   % PAH remaining has to be taken in
from the data of percentage biodegraded ... so 100 - value

input_PAH(3,1)=100;

input_PAH(3,2)=100-74.3;

input_PAH(4,1)=150;

input_PAH(4,2)=100-86.2;

input_PAH(5,1)=200;

input_PAH(5,2)=100-98.1;

input_PAH(6,1)=250;

input_PAH(6,2)=100-99.24;
n=1; %Counter for time domain
i=1; %Counter for space domain
for n=1:N-1
    for i=2:I-1
        diffusion1=0;
        diffusion2=0;
        biomass_consumption=0;
        dcdt(n,i)=0-(K1*enzym(n,i)*PAH(n,i));
        %rate of PAH decay *PAH(n,i)* enzym(n,i)
        PAH(n+1,i)=PAH(n,i)+deltat*dcdt(n,i);
        if PAH(n+1,i)<=0
            PAH(n+1,i)=0;
            dcdt(n,i)=-PAH(n,i)/deltat;
        end
        dcbdt(n,i)=K2*PAHdiol(n,i); %rate of bound contaminant formation
        dxdt(n,i)=(meu*biomass(n,i)*PAHdiol(n,i)*oxygen(n,i))/{(Kc+PAHdiol(n,i))*(Ko+oxygen(n,i))}; %rate of biomass growth
        PAHbound(n+1,i)=PAHbound(n,i)+deltat*dcbdt(n,i);
        dcdt(n,i)=0-(K1*enzym(n,i)*PAH(n,i));
    end
end
biomass(n+1,i)=biomass(n,i)+deltat*dxdt(n,i);

if PAH(n,i)<=0
    dedt(n,i)=(dxdt(n,i)/Ye);
else
    dedt(n,i)=(dxdt(n,i)/Ye)+enzym(n,i)*dcdt(n,i)/PAH(n,i);
end

enzym(n+1,i)=enzym(n,i)+deltat*dedt(n,i);
dchdt(n,i)=0-(dxdt(n,i)/Yh)-dcdt(n,i)-dcbdt(n,i);

% rate of diol concn change
PAHdiol(n+1,i)=PAHdiol(n,i)+deltat*dchdt(n,i);
diffusion1=((oxygen(n,i+1)-2*oxygen(n,i)+oxygen(n,i-1))/((deltar)*(deltar)));
diffusion2=((oxygen(n,i+1)-oxygen(n,i-1))/(2*deltar*(((i-1)*deltar))));
biomass_consumption=(dxdt(n,i)/Yo);
dodt(n,i)=24*Do*(diffusion1+diffusion2)-biomass_consumption;

% rate of the oxygen concn change and we can calculate radius(n) as (n-1)*deltar = r(n)
oxygen(n+1,i)=oxygen(n,i)+deltat*dodt(n,i);
oxygen(n+1,I)=oxygen(n+1,I-1);

% comment from here to end

% if(rem((n-1),4)==0 & rem(i,2)==0)
% hold on;
% plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'r*');

% PAHdiol(n,i)+PAH(n,i)
% elseif(rem((n-1),4)==0 & rem(i,2)==0)
% hold on;
% plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'b*');
% end

e n d

% hold on;
% limit_ordinate= PAH(1,2)+PAHdiol(1,2)+5;
% axis([0 days 0 limit_ordinate]);
% title('Simulation of PAH FOR K= 13');
% grid on;
% xlabel('Time');
% ylabel('Concentration of PAH');

%----------------------------------------------Plotiing Biomass and Oxygen-----------------------------------------%
%  for i=1:I
%         for n=1:N
%             hold on;
%             plot((n-1)/4,biomass(n,i),'-k','LineWidth',3);  

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% hold on;
% plot((n-1)/4,oxygen(n,i),'-g','LineWidth',3);
% line((n-1)/4,PAH(n,i))
% end
% end

%----------------------------------------------Integration with RK-2-----
----------------------------------------%
% for n=1:N
% for i=2:I-1
%     k1=deltar*(deltar*i)*(PAH(n,i)+PAHdiol(n,i));
%     k2=deltar*(deltar*(i+deltar))*(PAH(n,i+deltar)+PAHdiol(n,i+deltar));
%     integral(n)=integral(n)+(k1+k2)/2;
% end
% integral(n)=2*integral(n)/(((I-1)*(I-1)-4)*deltar*deltar);
%finding the average of the integral value.
% end
%----------------------------------------------Integration with RK-4-----
----------------------------------------%
format long;
for n=1:N
    integral(n)=0;
end

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for i=2:2:I-1 % keep the I odd as it has to be odd in order to have increment 2 cover all.

k1=2*deltar*(deltar*i)*(PAH(n,i)+PAHdiol(n,i));
% k1=2*deltar*(PAH(n,i)+PAHdiol(n,i));

% if n <=3
% disp(n);disp(i);disp('times k1=');disp(k1);
% end

k2=2*deltar*(deltar*(i+1))*(PAH(n,i+1)+PAHdiol(n,i+1));
% k2=2*deltar*(PAH(n,i+1)+PAHdiol(n,i+1));

% if n <=3
% disp(n);disp(i);disp('times k2=');disp(k2);
% end

k3=2*deltar*(deltar*(i+1))*(PAH(n,i+1)+PAHdiol(n,i+1));
k3 = 2*deltar*(PAH(n,i+1)+PAHdiol(n,i+1));

if n <= 3
    disp(n); disp(i); disp('times k3 ='); disp(k3);
end

if i == (I-1)
    k4 = k3;
else
    k4 = 2*deltar*(deltar*(i+2))*(PAH(n,i+2)+PAHdiol(n,i+2));
end

integral(n) = integral(n) + (k1 + 2*k2 + 2*k3 + k4) / 6;

if n <= 3
    disp(n); disp(i); disp('integral r ='); disp(integral(n));
end
end

integral(n)=2*integral(n)/(((I-1)*(I-1))*deltar*deltar);
%finding the average of the integral value.

integral(n)=2*integral(n)/(((I-1)*(I-1)-1)*deltar*deltar);

% ---Error Suppression --
% if integral(n) > PAH(1,2)+PAHdiol(1,2)
% integral(n)=PAH(1,2)+PAHdiol(1,2);
% end

% if n <=3
% disp(n);disp(i);disp('avg integral=');disp(integral(n));
% end

end

%---------------------------------------------------------Integration with RK-4 for oxygen-------------------------------------------------------%

% for n=1:N
% for i=2:2:I-1 % keep the I odd as it has to be odd in order to have increment 2 cover all.
% k1=2*deltar*(deltar*i)*(oxygen(n,i));
% k2 = 2 * deltar * (deltar * (i + deltar)) * (oxygen(n, i + deltar));
% k3 = 2 * deltar * (deltar * (i + deltar)) * (oxygen(n, i + deltar));
% if i == (I - 1)
% k4 = k4;
% else
%
% k4 = 2 * deltar * (deltar * (i + 2 * deltar)) * (PAH(n, i + 2 * deltar) + PAHdiol(n, i + 2 * deltar));
% end
%
integral_oxygen(n) = integral_oxygen(n) + (k1 + 2 * k2 + 2 * k3 + k4) / 6;
% end
%
% integral(n) = 2 * integral_oxygen(n) / (((I - 1) * (I - 1) - 4) * deltar * deltar);
% finding the average of the integral value.
% end
%
%-----------------------------------------------------------------------------------------------integrated plot---

%--------------- -------------------------------integrated plot---------------

% for n = 1:N
% hold on;
% plot((n - 1) / 4, integral(n), 'k+', 'LineWidth', 1);
% end
% %----------------------------------------------------------experimental plot---------
---------------------------------------------%  

% for n=1:days1
%    hold on;
%    dummy = input_PAH(n,2)*(PAH(1,2)+PAHdiol(1,2))/100;
%    plot(input_PAH(n,1),dummy,'R*','LineWidth',4);
%    end

%----------------------------------------------------------Verification------------------------

TRRE=0;
    Trre1=0;
    for l=1:days1
        j=input_PAH(l,1);
        k=(j/deltat)+1;
        dummy1 = input_PAH(l,2)*(PAH(1,2)+PAHdiol(1,2))/100;
% error watch
%    disp(input_PAH(l,1));
%    disp(k);
%    disp(integral(k));
%    disp(dummy1);
%    disp((integral(k)-dummy1)/(dummy1));
\[
\text{Trre}_1 = \text{Trre}_1 + \text{abs}(\text{integral}(k) - \text{dummy}_1) / \text{dummy}_1); \\
\text{RRE}_1 = \text{abs}(\sqrt{\text{Trre}_1}) / \text{days}_1; \\
\text{RRE}_\text{matrix}(1, \text{param}_\text{counter}) = \text{param}_\text{counter}; \\
\text{RRE}_\text{matrix}(2, \text{param}_\text{counter}) = \text{RRE}_1; \\
\text{E of loop for param count} \\
\text{finding the minimum in RRE matrix index and value} \\
\]
temp_RRE = RRE_matrix(2,1);
temp_index = 1;

for count = 1:6
    if temp_RRE <= RRE_matrix(2,count)
        temp_index = temp_index;
        temp_RRE = temp_RRE;
    else
        temp_RRE = RRE_matrix(2,count);
        temp_index = RRE_matrix(1,count);
    end
end

%------------------------------found the minimum and now assign the pivot min and max for the new box--------------%

for param_index = 1
    box(param_index,1) = box(param_index,temp_index);
    box(param_index,4) = (box(param_index,temp_index) + box(param_index,(temp_index+1)))/2;
    box(param_index,7) = box(param_index,(temp_index+1));
end

% modified value after the iteration is kept here in this
    if param_index == 1
Do=box(param_index,4); % Assigning the new value for the next iteration
end

if param_index == 2
meu=box(param_index,4); % Assigning the new value for the next iteration
end

if param_index == 3
Kc=box(param_index,4); % Assigning the new value for the next iteration
end

if param_index == 4
Ko=box(param_index,4); % Assigning the new value for the next iteration
end

if param_index == 5
Ye=box(param_index,4); % Assigning the new value for the next iteration
end
if param_index == 6
    Yh=box(param_index,4); % Assigning the new value for the next iteration
end

if param_index == 7
    Yo=box(param_index,4); % Assigning the new value for the next iteration
end

%---------------------------------------------E of loop for param index--------------------------

%---------------------------------------------MOB at end ---------------------------------------------

hold on;
limit_ordinate= PAH(1,2)+PAHdiol(1,2)+2;

%axis([0 100 0 15]);
axis([0 days 0 limit_ordinate]);

title('Simulation of PAH Biodegradation FOR K= 13 and K2 = 0.021');

grid on;

xlabel('Time (Days) ');

ylabel('Concentration of PAH ( ppm - mg/Kg )');

hold on;

%----------------------------------------------integrated plot------------------------------------------

%----------------------------------------------experimental plot--------------------------------------

for n=1:N
    hold on;
    plot((n-1)*deltat,integral(n),'k*','LineWidth',2);
end

for n=1:days1
    hold on;
    dummy = input_PAH(n,2)*(PAH(1,2)+PAHdiol(1,2))/100;
    plot(input_PAH(n,1),dummy,'R*','LineWidth',4);
end
disp(final_RRE);
%
disp(perc_RRE);

for i=2:I-1
  for n=1:N-1
    hold on;
    if (rem(i,2)~=0)
      plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'r--');
    else
      plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'b--');
    end
    if(rem((n-1),4)==0 & rem(i,2)~=0)
      hold on;
      % plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'r--');
      %PAHdiol(n,i)+PAH(n,i)
      elseif(rem((n-1),4)==0 & rem(i,2)==0)
      hold on;
      % plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'b*');
    end
  end
end
plot((n-1)/4,biomass(n,i),'-k','LineWidth',3);

hold on;

plot((n-1)/4,oxygen(n,i),'-g','LineWidth',3);

line((n-1)/4,PAH(n,i))

end
end
clear;                      %Flushing memory
format long;

%---------------------------------------initializing mesh parameter---------------------------------------

--------------------

days=90;                    %observation time.
range=1;                    %domain of interest in cms.
N=(64*90*4)+1;                    %division in mesh for Observation-Time interval for
process 50 days so deltat becomes 0.25.
I=9;                       %Domain is of 11 points that is 10 cm distance delta r is 1.
deltar=range/(I-1);         %deltar is 1 cm.
deltat=days/(N-1);          %deltat is 0.25 days.

if (deltat/(deltar*deltar)>=0.5)
   disp('quit - Not Stable i.e deltat/(deltar*deltar)>=0.5')
   exit;
end

%%%%%%%%%%%%%%%%%%%%%%%%%%%%% initializing the derivatives and variables over the mesh%%%%%%%%%%%%%%%%


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% dcdt=zeros(N,I);
% dcdbdt=zeros(N,I);
% dxdt=zeros(N,I);
% dedt=zeros(N,I);
% dcldt=zeros(N,I);
% dodd=zeros(N,I);
% oxygen=zeros(N,I);
% PAH=zeros(N,I);
% PAHdiol=zeros(N,I);
% PAHbound=zeros(N,I);
% biomass=zeros(N,I);
% enzym=zeros(N,I);
% integral=zeros(N,1);

% i=1;                           %Counter for space domain % conditions for 2 - ring
% for i=2:I-1
    % oxygen(1,i)=8;              %8   ppm
    % PAH(1,i)=3.2;                %42  ppm
    % PAHdiol(1,i)=3.2;            %1   ppm
    % PAHbound(1,i)=0;             %1   ppm
    % biomass(1,i)=10;             %10  ppm
    % enzym(1,i)=0;                %1   ppm
% end
% %Enforcing Boundary Condition on the variables over the mesh---

% n=1;                        %Counter for time domain
% for n=1:N                   %forcing Boundary Condition
%     oxygen(n,1)=8;              %8 ppm
% %    PAH(n,1)=0;                %0 ppm
% %    PAHdiol(n,1)=0;            %0 ppm
% %    PAHbound(n,1)=0;           %0 ppm
% %    biomass(n,1)=0;            %0 ppm
% %    enzym(n,1)=0;              %0 ppm
% end
%

%------------EXPERIMENTAL VALUES INPUT START--------------------------------------

days1 = 12;
input_PAH=zeros(days1,2);

input_PAH(1,1)=0;
input_PAH(1,2)=100-0;
input_PAH(2,1)=5;
input_PAH(2,2)=100-2;  % PAH remaining has to be taken in from the data of percentage biodegraded ... so 100 - value
input_PAH(3,1)=10;
input_PAH(3,2)=100-4;
input_PAH(4,1)=15;
input_PAH(4,2)=100-5;
input_PAH(5,1)=20;
input_PAH(5,2)=100-7;
input_PAH(6,1)=30;
input_PAH(6,2)=100-8;
input_PAH(7,1)=40;
input_PAH(7,2)=100-9;
input_PAH(8,1)=50;
input_PAH(8,2)=100-9.5;
input_PAH(9,1)=60;
input_PAH(9,2)=100-11;
input_PAH(10,1)=70;
input_PAH(10,2)=100-17;
input_PAH(11,1)=80;
input_PAH(11,2)=100-21;
input_PAH(12,1)=90;
input_PAH(12,2)=100-32;
for counter_MOB = 1:5

    if counter_MOB==1
        K1_start = 13;
        K2_start = 0.01;
        Do_pivot_start = 0.0003;%(cm^2/hrs.)
        meu_pivot_start =0.0009;
        Kc_pivot_start =30;
        Ko_pivot_start =33.1;
        Ye_pivot_start =0.42;
        Yh_pivot_start =0.42;
        Yo_pivot_start =0.8;
% K1_max = 13;
% K2_max = 0.1;

Do_max_start = 0.0005;

% meu_max_start = 0.06;
meu_max_start = 0.003;

Kc_max_start = 50;
Ko_max_start = 50;

Ye_max_start = 1.62;
Yh_max_start = 1.62;
Yo_max_start = 1.5;

% K1_min = 13;
% K2_min = 0.001;

Do_min_start = 0.0001;

% meu_min_start = 0.0001;
meu_min_start = 0.0001;

% Kc_min_start = 3;
Kc_min_start = 15;

% Ko_min_start = 3;
Ko_min_start = 15;

Ye_min_start = 0.4;
Yh_min_start = 0.4;
Yo_min_start = 0.04;
format long;
box = zeros(7,7);

box(1,4)=Do_pivot_start;
box(1,1)=Do_min_start;
box(1,7)=Do_max_start;
box(2,4)=meu_pivot_start;
box(2,1)=meu_min_start;
box(2,7)=meu_max_start;
box(3,4)=Kc_pivot_start;
box(3,1)=Kc_min_start;
box(3,7)=Kc_max_start;
box(4,4)=Ko_pivot_start;
box(4,1)=Ko_min_start;
box(4,7)=Ko_max_start;
box(5,4)=Ye_pivot_start;
box(5,1)=Ye_min_start;
box(5,7)=Ye_max_start;
box(6,4)=Yh_pivot_start;
box(6,1)=Yh_min_start;
box(6,7)=Yh_max_start;
box(7,4)=Yo_pivot_start;
box(7,1)=Yo_max_start;
box(7,7)=Yo_min_start;

%---------------------------------------------filling the box ---------------------------------

-------------------% 
% box rows i.e. parameter is travelled in columns while the row indexes are for
different params

    for param_index=1:7

    for box_param_intializn_cntr = 2:6

        if box_param_intializn_cntr <= 4
            box(param_index, box_param_intializn_cntr)=box(param_index, 1) +
            (box_param_intializn_cntr-1)*(box(param_index, 4)-box(param_index, 1))/3;
        elseif box_param_intializn_cntr <= 4
            box(param_index, box_param_intializn_cntr)=box(param_index, 4) +
            (box_param_intializn_cntr-4)*(box(param_index, 7)-box(param_index, 4))/3;
        end

    end

end

%---------------------------------------------filled "initial" box ------------------------

%---------------------------------------------%

K1=K1_start;             %Reaction kinetics parameter for the
degradation of Contaminant PAH in (mg/Kg.day)
K2 = K2_start; % Reaction kinetics parameter for the formation of bound contaminant in day^-1
Do = Do_pivot_start; % Diffusivity of oxygen in centimeter^2/Day
meu = meu_pivot_start; % Growth factor for the microorganisms in day^-1
Kc = Kc_pivot_start; % Half saturation constant for substrate diol in ppm
Ko = Ko_pivot_start; % Half saturation constant for oxygen in ppm
Ye = Ye_pivot_start; % Yield parameter for enzym in ppm
Yh = Yh_pivot_start; % Yield parameter for diol in ppm
Yo = Yo_pivot_start; % Yield parameter for oxygen in ppm

disp(box);
end

% if rem(counter_MOB,20) == 0
% disp(box);
% end

% if counter_MOB <= 20
% if rem(counter_MOB,5) == 0
% disp(box);
%   if counter_MOB<=5
%       disp(box);
%       disp(counter_MOB);
%   end

%---------------------------------------------inside the box----------------------------------------

------------% for param_index=1:7  % box rows --- i.e. parameter is travelled in columns while the row indexes are for different params

RRE_matrix = zeros(2,6);

%---------------------------------------------filling the box while run-------------------------

---------------------------%

-----%

if counter_MOB ~= 1

for box_param_intializn_cntr = 2:6

    if box_param_intializn_cntr <= 4

        box(param_index, box_param_intializn_cntr)=box(param_index, 1) + 
(box_param_intializn_cntr-1)*(box(param_index, 4)-box(param_index, 1))/3;

    else

        %

    end

end

else

    %

end
box(param_index, box_param_initializn_cntr)=box(param_index, 4) +
(box_param_initializn_cntr-4)*(box(param_index, 7)-box(param_index, 4))/3;
end
end
end

% debugging print in matlab window---
if param_index == 7
    if counter_MOB<=5
        disp(box);
disp(counter_MOB);
    end
end
end

% debugging print ---
for param_counter = 1:6

%-----------------------------------------------------------------
%-----------------------------------------------------------------
%------------------------initializing the derivatives and variables over the mesh------
%-----------------------------------------------------------------
%-----------------------------------------------------------------

dcdt=zeros(N,I);
dcbdt=zeros(N,I);
dxdt=zeros(N,I);
dedt=zeros(N,I);
dchdt=zeros(N,I);
dodt=zeros(N,I);
oxygen=zeros(N,I);
PAH=zeros(N,I);
PAHdiol=zeros(N,I);
PAHbound=zeros(N,I);
biomass=zeros(N,I);
enzym=zeros(N,I);
integral=zeros(N,1);
i=1;                           %Counter for space domain % conditions for

2 - ring

for i=2:I-1
    oxygen(1,i)=12;              %8 ppm HERE oxygen CORRESPONDS TO
    PAH(1,i)=3.2;                %42 ppm
    PAHdiol(1,i)=3.2;            %1 ppm
    PAHbound(1,i)=0;            %1 ppm
    biomass(1,i)=10;            %10 ppm
    enzym(1,i)=0;               %1 ppm
end

%-------------------------------------------------------------------------------------------------------------

%----------------------------------------------------------------------------------------------------------------

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Enforcing Boundary Condition on the variables over the mesh:

%------------------- Enforcing Boundary Condition on the
variables over the mesh-------------------------%

n=1;                        %Counter for time domain
for n=1:N                   %forcing Boundary Condition
    oxygen(n,1)=12;              %8 ppm HERE oxygen CORRESPONDS TO
                                 % NITRATE :)                  
                                 %  PAH(n,1)=0;                 %0 ppm
                                 %  PAHdiol(n,1)=0;             %0 ppm
                                 %  PAHbound(n,1)=0;            %0 ppm
                                 %  biomass(n,1)=0;             %0 ppm
                                 %  enzym(n,1)=0;               %0 ppm
end

%--------------------------------------------------------
%--------------------------------------------------------

%------------ initializing the Parameter over the
mesh---------------------------------------------------%

%  K1=13;                                                %Reaction kinetics parameter for the
degradation of Contaminant PAH in (mg/Kg.day)
% K2=0.021;                %Reaction kinetics parameter for the formation of bound contaminant in day^-1

if param_index == 1
    Do=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2;  % Do (box (i,j) + box (i,j+1))/ 2
end

if param_index == 2
    meu=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2;  % meu=0.08 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 3
    Kc=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2;  % Kc=45 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 4
    Ko=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2;  % Ko=43.1 (box (i,j) + box (i,j+1))/ 2
end
if param_index == 5

Ye=(box(param_index,param_counter) +
box(param_index,(param_counter+1)))/2;  % Ye=0.62 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 6

Yh=(box(param_index,param_counter) +
box(param_index,(param_counter+1)))/2;  % Yh=0.62 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 7

Yo=(box(param_index,param_counter) +
box(param_index,(param_counter+1)))/2;  % Yo=0.08 (box (i,j) + box (i,j+1))/ 2
end

%------------------------------------------------------------------------------
--------------------------------------%

days=input('please input the number of days required');

%input_PAH=zeros(days,2);

%for m=1:days
%  input_PAH(m,1)=input('for the day number:');
%  input_PAH(m,2)=input('% degraded');
% input_PAH(m,2)=100-input_PAH(m,2);
%
% end
%
% disp(' day number % remaining');
%
% disp(input_PAH);

% %------------EXPERIMENTAL VALUES INPUT START-enter %

biodegraded here --------------------------------------------%
%
% days1 = 6;
%
% input_PAH=zeros(days1,2);
%
% input_PAH(1,1)=0;
%
% input_PAH(1,2)=100-0;
%
% input_PAH(2,1)=50;
%
% input_PAH(2,2)=100-64.4; % PAH remaining has to be taken in
% from the data of percentage biodegraded ... so 100 - value
%
% input_PAH(3,1)=100;
%
% input_PAH(3,2)=100-74.3;
%
% input_PAH(4,1)=150;
%
% input_PAH(4,2)=100-86.2;
%
% input_PAH(5,1)=200;
%
% input_PAH(5,2)=100-98.1;
%
% input_PAH(6,1)=250;
%
% input_PAH(6,2)=100-99.24;
n=1; %Counter for time domain
i=1; %Counter for space domain

for n=1:N-1
    for i=2:I-1
        diffusion1=0;
        diffusion2=0;
        biomass_consumption=0;
        dcdt(n,i)=0-(K1*enzym(n,i)*PAH(n,i)); %rate of PAH decay *PAH(n,i)* enzym(n,i)
        if PAH(n+1,i)<=0
            PAH(n+1,i)=0;
            dcdt(n,i)=-PAH(n,i)/deltat;
        end
        dcbdt(n,i)=K2*PAHdiol(n,i); %rate of bound contaminant formation
        end
        dcbdt(n,i)=K2*PAHdiol(n,i);
        end
        PAHbound(n+1,i)=PAHbound(n,i)+deltat*dcbdt(n,i);
        dxdt(n,i)=(meu*biomass(n,i)*PAHdiol(n,i)*oxygen(n,i))/((Kc+PAHdiol(n,i))*(Ko+oxygen(n,i)))); %rate of biomass growth
biomass(n+1,i)=biomass(n,i)+deltat*dxdt(n,i);

if PAH(n,i)<=0
dedt(n,i)=(dxdt(n,i)/Ye);

%+enzym(n,i)*dcdt(n,i)/PAH(n,i) rate of enzym concn change
else
dedt(n,i)=(dxdt(n,i)/Ye)+enzym(n,i)*dcdt(n,i)/PAH(n,i);
end

enzym(n+1,i)=enzym(n,i)+deltat*dedt(n,i);
dchdt(n,i)=0-(dxdt(n,i)/Yh)-dcdt(n,i)-dcbdt(n,i);

%rate of diol concn change
PAHdiol(n+1,i)=PAHdiol(n,i)+deltat*dchdt(n,i);
diffusion1=((oxygen(n,i+1)-2*oxygen(n,i)+oxygen(n,i-1))/((deltar)*(deltar)));
diffusion2=((oxygen(n,i+1)-oxygen(n,i-1))/(2*deltar*((i-1)*deltar)));
biomassconsumption=(dxdt(n,i)/Yo);
dodt(n,i)=24*Do*(diffusion1+diffusion2)-biomassconsumption;

%rate of the oxygen concn change and we can calculate radius(n) as (n-1)*deltar = r(n)

oxygen(n+1,i)=oxygen(n,i)+deltat*dodt(n,i);
oxygen(n+1,1)=oxygen(n+1,1-1);

comment from here to end

if(rem((n-1),4)==0 & rem(i,2)==0)
hold on;
plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'r*');

PAHdiol(n,i)+PAH(n,i)

elseif(rem((n-1),4)==0 & rem(i,2)==0)

hold on;

plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'b*');

end

end

hold on;

limit_ordinate= PAH(1,2)+PAHdiol(1,2)+5;

axis([0 days 0 limit_ordinate]);

title('Simulation of PAH FOR K= 13');

grid on;

xlabel('Time');

ylabel('Concentration of PAH');

%----------------------------------------------Plotiing Biomass and Oxygen-----------------------------------------%

for i=1:I

for n=1:N

hold on;

plot((n-1)/4,biomass(n,i),'-k','LineWidth',3);

end

end

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% hold on;

% plot((n-1)/4,oxygen(n,i),'-g','LineWidth',3);

% line((n-1)/4,PAH(n,i))

% end

% end

%----------------------------------------------Integration with RK-2-----
%----------------------------------------% 

% for n=1:N
% for i=2:I-1
%     k1=deltar*(deltar*i)*(PAH(n,i)+PAHdiol(n,i));
%
%
k2=deltar*(deltar*(i+deltar))*(PAH(n,i+deltar)+PAHdiol(n,i+deltar));
% integral(n)=integral(n)+(k1+k2)/2;
% end
% integral(n)=2*integral(n)/(((I-1)*(I-1)-4)*deltar*deltar);

%finding the average of the integral value.
% end

%----------------------------------------------Integration with RK-4-----
%----------------------------------------%

format long;

for n=1:N
    integral(n)=0;
end
for i=2:2:I-1               % keep the I odd as it has to be odd in order to
have increment 2 cover all.

k1=2*deltar*(deltar*i)*(PAH(n,i)+PAHdiol(n,i));
%                    k1=2*deltar*(PAH(n,i)+PAHdiol(n,i));

% if n <=3
% disp(n);disp(i);disp('times k1=');disp(k1);
% end

k2=2*deltar*(deltar*(i+1))*(PAH(n,i+1)+PAHdiol(n,i+1));
%                    k2=2*deltar*(PAH(n,i+1)+PAHdiol(n,i+1));

% if n <=3
% disp(n);disp(i);disp('times k2=');disp(k2);
% end

k3=2*deltar*(deltar*(i+1))*(PAH(n,i+1)+PAHdiol(n,i+1));
% k3 = 2*deltar*(PAH(n,i+1)+PAHdiol(n,i+1));

% if n <= 3
% disp(n); disp(i); disp('times k3 ='); disp(k3);
% end

if i == (I-1)
    k4 = k3;
else
    k4 = 2*deltar*(deltar*(i+2))*(PAH(n,i+2)+PAHdiol(n,i+2));
% k4 = 2*deltar*(PAH(n,i+2)+PAHdiol(n,i+2));
end

% if n <= 3
% disp(n); disp(i); disp('times k4 ='); disp(k4);
% end

integral(n) = integral(n) + (k1 + 2*k2 + 2*k3 + k4)/6;

% if n <= 3
% disp(n); disp(i); disp('integral r'); disp(integral(n));
% end
end

integral(n)=2*integral(n)/(((I-1)*(I-1))*deltar*deltar);

%finding the average of the integral value.

integral(n)=2*integral(n)/(((I-1)*(I-1)-1)*deltar*deltar);

% ---Error Suppression --

% if integral(n) > PAH(1,2)+PAHdiol(1,2)

integral(n)=PAH(1,2)+PAHdiol(1,2);

% end

% if n <=3

disp(n);disp(i);disp('avg integral=');disp(integral(n));

% end

end

%-----------------------------------------------------------Integration with RK-4 for oxygen-----------------------------------------------------------%

% for n=1:N

% for i=2:2:I-1 % keep the I odd as it has to be odd in order to have increment 2 cover all.

% k1=2*deltar*(deltar*i)*(oxygen(n,i));
k2=2*deltar*(deltar*(i+deltar))*(oxygen(n,i+deltar));

k3=2*deltar*(deltar*(i+deltar))*(oxygen(n,i+deltar));

if i==(I-1)
    k4=k4;
else

    k4=2*deltar*(deltar*(i+2*deltar))*(PAH(n,i+2*deltar)+PAHdiol(n,i+2*deltar));

end

integral_oxygen(n)=integral_oxygen(n)+(k1+2*k2+2*k3+k4)/6;

end

integral(n)=2*integral_oxygen(n)/(((I-1)*(I-1)-4)*deltar*deltar); %finding the average of the integral value.

end

%-------------------------------------------------------------------------------integrated plot--------------------------

for n=1:N
    hold on;

    plot((n-1)/4,integral(n),'k+','LineWidth',1);

end
%.experimental plot-

for n=1:days1
  hold on;
  dummy = input_PAH(n,2)*(PAH(1,2)+PAHdiol(1,2))/100;
  plot(input_PAH(n,1),dummy,'R*','LineWidth',4);
end

%Verification-

TRRE=0;

Trre1=0;

for l=1:days1
  j=input_PAH(l,1);
  k=(j/deltat)+1;
  dummy1 = input_PAH(l,2)*(PAH(1,2)+PAHdiol(1,2))/100;
  %error watch
  disp(input_PAH(l,1));
  disp(k);
  disp(integral(k));
  disp(dummy1);
  disp((integral(k)-dummy1)/(dummy1));
% disp((integral(k)-dummy1)/(dummy1)*(integral(k)-
dummy1)/(dummy1));

    Trre1=Trre1+abs(((integral(k)-dummy1)/dummy1)*((integral(k)-
dummy1)/dummy1));

% ---        Trre1=Trre1+((integral(k)-dummy1)/dummy1)*(integral(k)-

%       TRRE=TRRE+((integral(k)/(PAH(1,2)+PAHdiol(1,2))*100)-

input_PAH(1,2)/input_PAH(1,2)*((integral(k)/(PAH(1,2)+PAHdiol(1,2))*100)-

input_PAH(1,2)/input_PAH(1,2);

    end

RRE1=abs(sqrt(Trre1))/days1;

% RRE = sqrt(TRRE)/days1;

%%%%%%%%%%%%%%%%%%%%%%%%%filling the RRE matrix index and value%%%%%%%%%%%%%%%%%%%%%%%%

                    %

                    %

RRE_matrix(1,param_counter)=param_counter;

    RRE_matrix(2,param_counter)=RRE1;

    end

%----------------------------------------------------------E of loop for param count----------------------------------------------------------

%----------------------------------------------------------

%----------------------------------------------------------finding the minimum in RRE matrix index and value--

%----------------------------------------------------------%
temp_RRE = RRE_matrix(2,1);

temp_index = 1;

for count = 1:6
    if temp_RRE <= RRE_matrix(2,count)
        temp_index = temp_index;
        temp_RRE = temp_RRE;
    else
        temp_RRE = RRE_matrix(2,count);
        temp_index = RRE_matrix(1,count);
    end
end

%-------------------------------found the minimum and now assign the pivot min and max

for the new box-------------%
    box(param_index,1) = box(param_index,temp_index);
    box(param_index,4) = (box(param_index,temp_index) +
    box(param_index,(temp_index+1)))/2;
    box(param_index,7) = box(param_index,(temp_index+1));

% modified value after the iteration is kept here in this
    if param_index == 1
Do=box(param_index,4);  % Assigning the new value for the
next iteration
end

if param_index == 2
meu=box(param_index,4);  % Assigning the new value for the
next iteration
end

if param_index == 3
Kc=box(param_index,4);  % Assigning the new value for the
next iteration
end

if param_index == 4
Ko=box(param_index,4);  % Assigning the new value for the
next iteration
end

if param_index == 5
Ye=box(param_index,4);  % Assigning the new value for the
next iteration
end
if param_index == 6
    Yh=box(param_index,4);  \% Assigning the new value for the next iteration
end

if param_index == 7
    Yo=box(param_index,4);  \% Assigning the new value for the next iteration
end

end

\%---------------------------------------------E of loop for param index--------------------------

\%---------------------------------------------MOB at end ---------------------------------------------

hold on;

limit_ordinate= PAH(1,2)+PAHdiol(1,2)+2;

axis([0 100 0 15]);
% axis([0 days 0 limit_ordinate]);
% title('Simulation of PAH Biodegradation FOR K= 13 and K2 = 0.01');
% grid on;
% xlabel('Time (Days )');
% ylabel('Concentration of PAH ( ppm - mg/Kg )');
% hold on;
%
%----------------------------------------------integrated plot------------------------------------------
%--------%
%
for n=1:N
    hold on;
    plot((n-1)*deltat,integral(n),'k*','LineWidth',2);
end
%
%----------------------------------------------experimental plot--------------------------------------
%----------%
%
for n=1:days1
    hold on;
    dummy = input_PAH(n,2)*(PAH(1,2)+PAHdiol(1,2))/100;
    plot(input_PAH(n,1),dummy,'R*','LineWidth',4);
end
disp(final_RRE);

for i=2:I-1
  for n=1:N-1
    hold on;
    if (rem(i,2)~=0)
      plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'r--');
    else
      plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'b--');
    end
    if(rem((n-1),4)==0 & rem(i,2)~=0)
      hold on;
      plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'r--');
    elseif(rem((n-1),4)==0 & rem(i,2)==0)
      hold on;
      plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'b*');
    end
end

310
%% plot((n-1)/4,biomass(n,i),'-k','LineWidth',3);
%
hold on;
%
plot((n-1)/4,oxygen(n,i),'-g','LineWidth',3);
%
line((n-1)/4,PAH(n,i))

end

end
Appendix 5

Anaerobic Simulation of 2 Ring PAHs

clear;                      %Flushing memory

format long;

%-------------------------------------------------initializing mesh parameter-----------------------------

------------------% 

days=90;                    %observation time.

range=1;                    %domain of interest in cms.

N=(64*90*4)+1;                    %division in mesh for Observation-Time interval for

process 50 days so deltat becomes 0.25.

I=9;                       %Domain is of 11 points that is 10 cm distance delta r is 1.

deltar=range/(I-1);         %deltar is 1 cm.

deltat=days/(N-1);          %deltat is 0.25 days.

if (deltat/(deltar*deltar)>=0.5)

    disp('quit - Not Stable i.e deltat/(deltar*deltar)>=0.5')

    exit;

end

%--------------------------------------------------------------------------------------------------------------------

% %----------------------------------------------------initializing the derivatives and variables over the mesh--------

%--------------------------------------------------------------------------------------------------------------------

312
%--------EXPERIMENTAL VALUES INPUT START--------------------------------------

--------%
days1 = 12;

input_PAH=zeros(days1,2);

input_PAH(1,1)=0;
input_PAH(1,2)=100-0;

input_PAH(2,1)=5;
input_PAH(2,2)=100-4;  % PAH remaining has to be taken in from the data of 
percentage biodegraded ... so 100 - value

input_PAH(3,1)=10;
input_PAH(3,2)=100-8;

input_PAH(4,1)=15;
input_PAH(4,2)=100-12;

input_PAH(5,1)=20;
input_PAH(5,2)=100-14;

input_PAH(6,1)=30;
input_PAH(6,2)=100-16;

input_PAH(7,1)=40;
input_PAH(7,2)=100-19;

input_PAH(8,1)=50;
input_PAH(8,2)=100-22;

input_PAH(9,1)=60;
input_PAH(9,2)=100-27;
input_PAH(10,1)=70;
input_PAH(10,2)=100-29;
input_PAH(11,1)=80;
input_PAH(11,2)=100-33;
input_PAH(12,1)=90;
input_PAH(12,2)=100-35;

%---------------EXPERIMENTAL VALUES INPUT END-----------------------------------------

----%

%---------------------------------------------------------------------------------------------------------
-----------%
%-------------------------------------------------MOB STARTS from here ------------------------
----------------------%
%-------------------------------initializing the starting Parameters for MOB---------------------
------------------------%

for counter_MOB = 1:5

    if counter_MOB==1
        K1_start = 13;
        K2_start = 0.001;
        Do_pivot_start = 0.003; %cm^2/hrs.)
    end

end
meu_pivot_start = 0.0009;
Kc_pivot_start = 50;
Ko_pivot_start = 33.1;
Ye_pivot_start = 1.42;
Yh_pivot_start = 1.42;
Yo_pivot_start = 1.8;

% K1_max = 13;
% K2_max = 0.1;
Do_max_start = 0.005;
% meu_max_start = 0.06;
meu_max_start = 0.003;
Kc_max_start = 100;
Ko_max_start = 50;
Ye_max_start = 2.62;
Yh_max_start = 2.62;
Yo_max_start = 2.5;

% K1_min = 13;
% K2_min = 0.001;
Do_min_start = 0.001;
meu_min_start = 0.0001;
% Kc_min_start = 3;
Kc_min_start =15;
% Ko_min_start =3;
Ko_min_start =15;
Ye_min_start =0.004;
Yh_min_start =0.004;
Yo_min_start =0.004;

format long;
box = zeros(7,7);
box(1,4)=Do_pivot_start;
box(1,1)=Do_min_start;
box(1,7)=Do_max_start;
box(2,4)=meu_pivot_start;
box(2,1)=meu_min_start;
box(2,7)=meu_max_start;
box(3,4)=Kc_pivot_start;
box(3,1)=Kc_min_start;
box(3,7)=Kc_max_start;
box(4,4)=Ko_pivot_start;
box(4,1)=Ko_min_start;
box(4,7)=Ko_max_start;
box(5,4)=Ye_pivot_start;
box(5,1)=Ye_min_start;
box(5,7)=Ye_max_start;
box(6,4)=Yh_pivot_start;
box(6,1)=Yh_min_start;
box(6,7)=Yh_max_start;
box(7,4)=Yo_pivot_start;
box(7,1)=Yo_max_start;
box(7,7)=Yo_min_start;

%---------------------------------------------filling the box ---------------------------------
% box rows i.e. parameter is travelled in columns while the row indexes are for
different params
for param_index=1:7
    for box_param_intializn_cntr = 2:6
        if box_param_intializn_cntr <= 4
            box(param_index, box_param_intializn_cntr)=box(param_index, 1) +
            (box_param_intializn_cntr-1)*(box(param_index, 4)-box(param_index, 1))/3;
        else
            box(param_index, box_param_intializn_cntr)=box(param_index, 4) +
            (box_param_intializn_cntr-4)*(box(param_index, 7)-box(param_index, 4))/3;
        end
    end
end

K1=K1_start; %Reaction kinetics parameter for the degradation of Contaminant PAH in (mg/Kg.day)
K2=K2_start; %Reaction kinetics parameter for the formation of bound contaminant in day^-1
Do=Do_pivot_start; %Diffusivity of oxygen in centimeter^2/Day
meu=meu_pivot_start; %Growth factor for the microorganisms in day^-1
Kc=Kc_pivot_start; %Half saturation constant for substrate diol in ppm
Ko=Ko_pivot_start; %Half saturation constant for oxygen in ppm
Ye=Ye_pivot_start; %Yield parameter for enzym in ppm
Yh=Yh_pivot_start; %Yield parameter for diol in ppm
Yo=Yo_pivot_start; %Yield parameter for oxygen in ppm

disp(box);
end

%    if rem(counter_MOB,20) == 0
%        disp(box);
% end

% if counter_MOB <= 20
%   if rem(counter_MOB,5) == 0
%     disp(box);
% end
% end

% if counter_MOB <= 5
% disp(box);
% disp(counter_MOB);
% end

%---------------------------------------------inside the box----------------------------------------

for param_index=1:7    % box rows --- i.e. parameter is travelled in columns
while the row indexes are for different params
    RRE_matrix = zeros(2,6);

    %---------------------------------------------filling the box while run---------------------------------

for box_param_intializn_cntr = 2:6

    if counter_MOB ~= 1
        for box_param_intializn_cntr = 2:6

319
if box_param_intializn_cntr <= 4
    box(param_index, box_param_intializn_cntr)=box(param_index, 1) +
    (box_param_intializn_cntr-1)*(box(param_index, 4)-box(param_index, 1))/3;
else
    box(param_index, box_param_intializn_cntr)=box(param_index, 4) +
    (box_param_intializn_cntr-4)*(box(param_index, 7)-box(param_index, 4))/3;
end
end
end

% debugging print in matlab window---
if param_index == 7
    if counter_MOB<=5
        disp(box);
        disp(counter_MOB);
    end
end

% debugging print ---
for param_counter = 1:6
    
    %---------------------------------------------
    %---------------------------------------------
    %----------------------------initializing the derivatives and variables over the mesh------
---------------------------------------------
---------------------------------------------

%---------------------------------------------%
dcddt=zeros(N,I);
dcbbdt=zeros(N,I);
dxdt=zeros(N,I);
dedt=zeros(N,I);
dchdt=zeros(N,I);
dodt=zeros(N,I);
oxygen=zeros(N,I);
PAH=zeros(N,I);
PAHdiol=zeros(N,I);
PAHbound=zeros(N,I);
biomass=zeros(N,I);
enzym=zeros(N,I);
integral=zeros(N,1);
i=1;                           %Counter for space domain % conditions for
2 - ring

for i=2:I-1

    oxygen(1,i)=15;              %8   ppm HERE oxygen CORRESPONDS TO
                                  % NITRATE :)
    PAH(1,i)=3.2;                %42  ppm
    PAHdiol(1,i)=3.2;            %1   ppm
    PAHbound(1,i)=0;            %1   ppm
    biomass(1,i)=10;            %10  ppm
    enzym(1,i)=0;               %1   ppm

321
end

%---------------------------------------------------------------

%-------------------initializing the Parameter over the mesh-------------------

n=1;                   %Counter for time domain
for n=1:N              %forcing Boundary Condition
    oxygen(n,1)=15;   %8 ppm HERE oxygen CORRESPONDS TO NITRATE :)
    PAH(n,1)=0;      %0 ppm
    PAHdiol(n,1)=0;   %0 ppm
    PAHbound(n,1)=0;  %0 ppm
    biomass(n,1)=0;   %0 ppm
    enzym(n,1)=0;    %0 ppm
end

%---------------------------------------------------------------

%---------------------------------------------------------------
% K1=13; %Reaction kinetics parameter for the degradation of Contaminant PAH in (mg/Kg.day)
%
K2=0.021; %Reaction kinetics parameter for the formation of bound contaminant in day^-1

if param_index == 1
    Do=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2; % Do (box (i,j) + box (i,j+1))/ 2
end

if param_index == 2
    meu=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2; % meu=0.08 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 3
    Kc=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2; % Kc=45 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 4

323
Ko=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2; % Ko=43.1 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 5
Ye=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2; % Ye=0.62 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 6
Yh=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2; % Yh=0.62 (box (i,j) + box (i,j+1))/ 2
end

if param_index == 7
Yo=(box(param_index,param_counter) + box(param_index,(param_counter+1)))/2; % Yo=0.08 (box (i,j) + box (i,j+1))/ 2
end

%------------------------------------------------------------------------------
%------------------------------------------------------------------------------
%------------------------------------------------------------------------------
%------------------------------------------------------------------------------
%------------------------------------------------------------------------------
%------------------------------------------------------------------------------
%------------------------------------------------------------------------------
%------------------------------------------------------------------------------
%------------------------------------------------------------------------------

%days=input('please input the number of days required');

324
%input_PAH=zeros(days,2);

%for m=1:days
  %input_PAH(m,1)=input('for the day number:');
  %input_PAH(m,2)=input('% degraded');
  %input_PAH(m,2)=100-input_PAH(m,2);
%end

%disp(' day number   % remaining');
%disp(input_PAH);

%-----------------EXPERIMENTAL VALUES INPUT START-enter %
biodegraded here ----------------------------------------------%
% days1 = 6;
% input_PAH=zeros(days1,2);
% input_PAH(1,1)=0;
% input_PAH(1,2)=100-0;
% input_PAH(2,1)=50;
% input_PAH(2,2)=100-64.4;     % PAH remaining has to be taken in
% from the data of percentage biodegraded ... so 100 - value
% input_PAH(3,1)=100;
% input_PAH(3,2)=100-74.3;
% input_PAH(4,1)=150;
% input_PAH(4,2)=100-86.2;
% input_PAH(5,1)=200;
input_PAH(5,2)=100-98.1;

input_PAH(6,1)=250;

input_PAH(6,2)=100-99.24;

% ---------------EXPERIMENTAL VALUES INPUT END--------------

%-----------------------------%

n=1; %Counter for time domain
i=1; %Counter for space domain

for n=1:N-1
    for i=2:I-1
        % diffusion1=0;
        % diffusion2=0;
        % biomass_consumption=0;
        if enzym(n,i)<=PAH(n,i)
            % dcdt(n,i)=0-(K1*enzym(n,i)*PAH(n,i));
            %rate of PAH decay *PAH(n,i)* enzym(n,i)
            dcdt(n,i)=0-(K1*enzym(n,i)*enzym(n,i)); %rate of PAH decay
            %PAH(n,i)* enzym(n,i)
        else
            dcdt(n,i)=0-(K1*PAH(n,i)*PAH(n,i));
            %rate of PAH decay *PAH(n,i)* enzym(n,i)
        end
        PAH(n+1,i)=PAH(n,i)+deltat*dcdt(n,i);
    end
end
if PAH(n+1,i) <= 0
    PAH(n+1,i) = 0;
    dcdt(n,i) = -PAH(n,i)/deltat;
end

dcbdt(n,i) = K2 * PAHdiol(n,i);  % rate of bound contaminant formation

PAHbound(n+1,i) = PAHbound(n,i) + deltat * dcbdt(n,i);

dxdt(n,i) = (meu * biomass(n,i) * PAHdiol(n,i)) / (Kc + PAHdiol(n,i)); % rate of biomass growth

biomass(n+1,i) = biomass(n,i) + deltat * dxdt(n,i);

if PAH(n,i) <= 0
    dedt(n,i) = (dxdt(n,i) / Ye);
% + enzym(n,i) * dcdt(n,i) / PAH(n,i) rate of enzym concn change
else
    dedt(n,i) = (dxdt(n,i) / Ye) + enzym(n,i) * dcdt(n,i) / PAH(n,i);
end

enzym(n+1,i) = enzym(n,i) + deltat * dedt(n,i);

dchdt(n,i) = 0 - (dxdt(n,i) / Yh) - dcdt(n,i) - dcbdt(n,i);
% rate of diol concn change

PAHdiol(n+1,i) = PAHdiol(n,i) + deltat * dchdt(n,i);

% diffusion1 = ((oxygen(n,i+1) - 2 * oxygen(n,i) + oxygen(n,i-1)) / ((deltar) * (deltar)));
% diffusion2 = ((oxygen(n,i+1) - oxygen(n,i-1)) / (2 * deltar * ((i - 1) * deltar)));

biomass_consumption=(dxdt(n,i)/Yo);

dodt(n,i)=24*Do*(diffusion1+diffusion2)-biomass_consumption;

% rate of the oxygen concn change and we can calculate radius(n) as (n-1)*deltar = r(n)

% oxygen(n+1,i)=oxygen(n,i)+deltat*dodt(n,i);

% oxygen(n+1,I)=oxygen(n+1,I-1);

% comment from here to end

% if(rem((n-1),4)==0 & rem(i,2)==0)
% hold on;
% plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'r*');

%PAHdiol(n,i)+PAH(n,i)

% elseif(rem((n-1),4)==0 & rem(i,2)==0)
% hold on;
% plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'b*');

% end

end

% hold on;
% limit_ordinate= PAH(1,2)+PAHdiol(1,2)+5;
% axis([0 days 0 limit_ordinate]);
% title('Simulation of PAH FOR K= 13');
% grid on;
% xlabel('Time');
% ylabel('Concentration of PAH');

%---------------------------------------------------------------Plotting Biomass and Oxygen---------------------------------------------------------------%
% for i=1:I
% for n=1:N
% hold on;
% plot((n-1)/4,biomass(n,i),'-k','LineWidth',3);
% hold on;
% plot((n-1)/4,oxygen(n,i),'-g','LineWidth',3);
% line((n-1)/4,PAH(n,i))
% end
% end

%---------------------------------------------------------------Integration with RK-2-----
% for n=1:N
% for i=2:I-1
% k1=deltar*(deltar*i)*(PAH(n,i)+PAHdiol(n,i));
% k2=deltar*(deltar*(i+deltar))*(PAH(n,i+deltar)+PAHdiol(n,i+deltar));
% integral(n)=integral(n)+(k1+k2)/2;
% end
\% integral(n)=2*integral(n)/(((I-1)*(I-1)-4)*deltar*deltar);

\%finding the average of the integral value.
\% end
\%----------------------------------------------------------Integration with RK-4-----
\%----------------------------------------------------------%

format long;

for n=1:N

    integral(n)=0;

    for i=2:2:I-1 % keep the I odd as it has to be odd in order to have increment 2 cover all.

        k1=2*deltar*(deltar*i)*(PAH(n,i)+PAHdiol(n,i));

        \% k1=2*deltar*(PAH(n,i)+PAHdiol(n,i));

        \% if n <=3
        \% disp(n);disp(i);disp('times k1=');disp(k1);
        \% end

        k2=2*deltar*(deltar*(i+1))*(PAH(n,i+1)+PAHdiol(n,i+1));

        \% k2=2*deltar*(PAH(n,i+1)+PAHdiol(n,i+1));
% if n <= 3
% disp(n);disp(i);disp('times k2=');disp(k2);
% end

k3=2*deltar*(deltar*(i+1))*(PAH(n,i+1)+PAHdiol(n,i+1));

% k3=2*deltar*(PAH(n,i+1)+PAHdiol(n,i+1));

% if n <= 3
% disp(n);disp(i);disp('times k3=');disp(k3);
% end

if i==(I-1)
    k4=k3;
else
    k4=2*deltar*(deltar*(i+2))*(PAH(n,i+2)+PAHdiol(n,i+2));
end

% if n <= 3
```
 integral(n)=integral(n)+(k1+2*k2+2*k3+k4)/6;

 if n <=3
    disp(n);disp(i);disp('integral r');disp(integral(n));
 end

 integral(n)=2*integral(n)/(((I-1)*(I-1))*deltar*deltar);

 if n <=3
    disp(n);disp(i);disp('avg integral=');disp(integral(n));
 end
```

---Integration with RK-4 for oxygen---

The code snippet above calculates the integral and finds its average using a numerical integration method, likely the Runge-Kutta method of order 4 (RK-4), for a process possibly related to oxygen. The integral is updated iteratively and the average is calculated to provide a more accurate result.
%-----------------------------------------------Verification-------------------

%-----------------------------------------------%

TRRE=0;

Trre1=0;

for l=1:days1

j=input_PAH(l,1);

k=(j/deltat)+1;

dummy1 = input_PAH(l,2)*(PAH(1,2)+PAHdiol(1,2))/100;

% error watch

% disp(input_PAH(l,1));
% disp(k);
% disp(integral(k));
% disp(dummy1);
% disp((integral(k)-dummy1)/(dummy1));
% disp(((integral(k)-dummy1)/dummy1)/(dummy1));

Trre1=Trre1+abs(((integral(k)-dummy1)/dummy1)*((integral(k)-dummy1)/dummy1));

% ---- Trre1=Trre1+((integral(k)-dummy1)*(integral(k)-dummy1));
% TRRE = TRRE + ((integral(k)/(PAH(1,2)+PAHdiol(1,2))*100) - input_PAH(1,2))/input_PAH(1,2) - ((integral(k)/(PAH(1,2)+PAHdiol(1,2))*100) - input_PAH(1,2))/input_PAH(1,2);

end

RRE1 = abs(sqrt(Trre1))/days1;

% RRE = sqrt(TRRE)/days1;

%------------------------------------filling the RRE matrix index and value---------------------

%---------------------------%  

RRE_matrix(1,param_counter)=param_counter;

RRE_matrix(2,param_counter)=RRE1;

end

%----------------------------------------E of loop for param count-----------------------------

%------------------------------------finding the minimum in RRE matrix index and value----

%---------------------------%  

temp_RRE = RRE_matrix(2,1);

temp_index = 1;

for count = 1:6


if temp_RRE \leq RRE_{\text{matrix}}(2,\text{count})
    \begin{align*}
    \text{temp\_index} &= \text{temp\_index}; \\
    \text{temp\_RRE} &= \text{temp\_RRE}; \\
    \end{align*}
else
    \begin{align*}
    \text{temp\_RRE} &= RRE_{\text{matrix}}(2,\text{count}); \\
    \text{temp\_index} &= RRE_{\text{matrix}}(1,\text{count}); \\
    \end{align*}
end

\%-----------------------------found the minimum and now assign the pivot min and max
for the new box---------\%
box(\text{param\_index},1) = box(\text{param\_index},\text{temp\_index});
box(\text{param\_index},4) = (box(\text{param\_index},\text{temp\_index}) + 
box(\text{param\_index},(\text{temp\_index}+1)))/2;
box(\text{param\_index},7) = box(\text{param\_index},(\text{temp\_index}+1));
\% modified value after the iteration is kept here in this
\begin{align*}
\text{if param\_index} &= 1 \\
    \text{Do} &= \text{box}(\text{param\_index},4); \quad \% \text{Assigning the new value for the} \\
\text{next iteration} \\
\end{align*}
end

\begin{align*}
\text{if param\_index} &= 2
\end{align*}
mur=box(param_index,4); % Assigning the new value for the
next iteration
end

if param_index == 3
Kc=box(param_index,4); % Assigning the new value for the
next iteration
end

if param_index == 4
Ko=box(param_index,4); % Assigning the new value for the
next iteration
end

if param_index == 5
Ye=box(param_index,4); % Assigning the new value for the
next iteration
end

if param_index == 6
Yh=box(param_index,4); % Assigning the new value for the
next iteration
end
if param_index == 7
    Yo=box(param_index,4);  % Assigning the new value for the next iteration
end

end

%-------------------------------------------------------------E of loop for param index--------------------------

%---------------------------------------------MOB at end ---------------------------------------------

hold on;
limit_ordinate= PAH(1,2)+PAHdiol(1,2)+2;
%axis([0 100 0 15]);
axis([0 days 0 limit_ordinate]);
title('Biodegradation of 2 Ring PAHs in Anaerobic Conditions');
grid on;
xlabel('Time (Days )');
ylabel('Concentration of PAH ( mg/Kg )');
hold on;

%----------------------------------------------------------integrated plot----------------------------------------------------------

--------%

for n=1:N
    hold on;
    plot((n-1)*deltat,integral(n),'k*','LineWidth',2);
end

%----------------------------------------------------------experimental plot----------------------------------------------------------

--------%

for n=1:days1
    hold on;
    dummy = input_PAH(n,2)*(PAH(1,2)+PAHdiol(1,2))/100;
    plot(input_PAH(n,1),dummy,'R*','LineWidth',4);
end

%----------------------------------------------------------displaying Final RRE----------------------------------------------------------

--------%

disp(final_RRE);
% disp(perc_RRE);

% for i=2:I-1
%    for n=1:N-1
%        hold on;
%        if (rem(i,2)~=0)
%            plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'r--');
%        else
%            plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'b--');
%        end
%    if(rem((n-1),4)==0 & rem(i,2)~=0)
%        hold on;
%        plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'r--');
%    PAHdiol(n,i)+PAH(n,i)
%    elseif(rem((n-1),4)==0 & rem(i,2)==0)
%        hold on;
%        plot((n-1)*deltat,PAHdiol(n,i)+PAH(n,i),'b*');
%    end
%    plot((n-1)/4,biomass(n,i),'-k','LineWidth',3);
%    hold on;
%    plot((n-1)/4,oxygen(n,i),'-g','LineWidth',3);
%    %line((n-1)/4,PAH(n,i))
% end