

## ADVANCED OXIDATION PRETREATMENT TO ENHANCE BIOLOGICAL REMEDICATION OF PAH-CONTAMINATED SOILS.

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### INTRODUCTION:

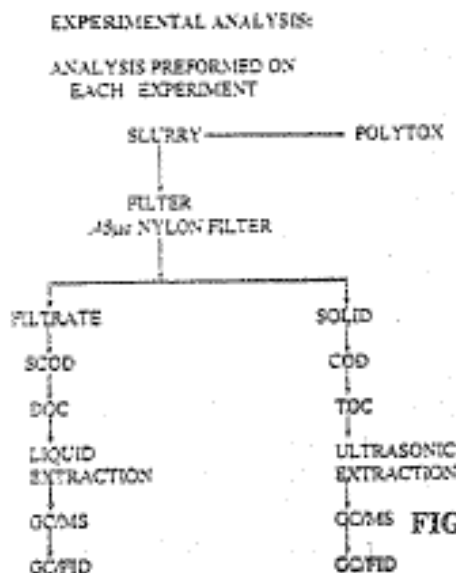
Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds containing two or more fused aromatic rings. They are present in fuel oils, crude oils, and creosote. Due to their low solubility and high carbon partitioning characteristics, PAHs accumulate in soils. The US EPA has listed 16 PAHs as priority<sup>1</sup> pollutants. Eight of them are known to be possible or probable carcinogens. Others are possible or probable mutagens. The generally accepted soil remediation goal is 0.1 mg/kg for individual carcinogenic PAHs<sup>2</sup>. Soil contamination can be in the 1000's mg/kg range for coal tar contaminated sites<sup>3</sup>, thus the importance of developing an economical soil remediation technology for PAH contaminated soils.

There has been extensive research in the last 5 to 10 years on biological remediation technologies. This research has varied from studying specific isolates and degradation pathways<sup>4,5</sup> to optimizing biological reactors with mixed cultures<sup>6,7</sup>. Aqueous phase biological treatment of 2- through 6-ring PAHs are well documented and are readily degradable even at pilot scale.<sup>11</sup> PAH removal from MGP soil biotreatments have shown remediation of 2 and 3-ring compounds within 6 to 8 weeks but little removal of the 4 to 6-ring compounds.<sup>12</sup> The commonly cited rate limiting step has been the desorption and solubilization of the compound into the bulk liquid. It is widely assumed that sorption of organic compounds reduces the bioavailability of the compound, but some isolates have been found to have the capacity to mineralize sorbed naphthalene<sup>13</sup>. The solubilization limiting step has been addressed by researchers by utilizing surfactants to increase solubility. Chemical solubilizing agents increased solubility but were not found to enhance biodegradation<sup>14</sup> while bioemulsifiers did tend to increase degradation of the higher ringed PAHs<sup>15</sup>. Surfactants have had limited success in enhancement of bioremediation thus another pretreatment process must be developed.

An emerging field in the treatment of PAH is the remediation of aqueous phase PAHs using Advance Oxidation Processes. AOPs are processes involving the generation of OH radical from ozone, hydrogen peroxide, and UV light<sup>16</sup>. Trapido<sup>17</sup> and Beltran<sup>18</sup> subjected aqueous phase PAHs to various AOP processes and obtained complete mineralization within eight minutes. These promising results have lead to the application of AOP processes to PAH contaminated soils. The work in this area is limited. Yao and Matsen<sup>19</sup> subjected soil, spiked with individual PAH placed in a column, to gaseous ozone for one hour to obtain 70% removal of phenanthrene and 10% removal of pyrene. Another study incorporates an oxidation pretreatment to enhance the bioremediation of Phenanthrene contaminated soils<sup>20</sup>, this research shows promising results for the desorption of the PAH into the aqueous phase and enhancement of biological degradation of the reaction products. In this study, we hypothesized that the AOP pretreatment processes will introduce hydroxylated and ring cleavage products which will be desorb and be more amenable to biodegradation. This paper will focus on using an integrated approach of physicochemical pretreatment processes (AOPs) to enhance subsequent biological degradation of PAH contaminated soils. The concentrations of the parent PAH compounds and the oxidation products were tracked in both the solid and the aqueous phase.

## MATERIALS AND METHODS:

The employed Advanced Oxidation Processes (AOPs) were Ozone and Ozone/Hydrogen Peroxide. Each AOP process was tested at three pH conditions. Soils were spiked per Sims<sup>21</sup> using a concentration of 0.85g/kg Phenanthrene, Pyrene, and Benzo[a]pyrene dissolved in a methylene chloride solution. A soil slurry of 3% solids by weight was prepared and placed in a complete mix batch reactor. After a 30 minute reaction time the reactor was analyzed per the flow sheet shown in Figure 1.:



- Relative toxicity test analyzed per Polytox system developed by Polybac.
- SCOD and COD analyzed per the HACH closed reflux micro method using the HACH DR/2000 direct reading spectrophotometer.
- DOC and TOC analyzed by EPA Method 415.1 and performed by Mountain States Analytical of Salt Lake City Utah.
- Phase separation and DCM extraction
- GC/FID HP 6890 w/ nonpolar Restek column. Data HP Chemstation.
- GC/MS HP 6890 w/ HP 6890MSD w/ nonpolar DB-1 column.
- Ozone residual analyzed per Standard Methods 4500-O<sub>3</sub>B the indigo colorimetric method.
- Hydrogen peroxide residual analyzed using the photometric method developed by Bader<sup>22</sup>.

FIGURE 1: FLOW SHEET OF EXPERIMENTAL ANALYSIS

From the TOC, DOC, SCOD, and COD data the total Oxidation State and the dissolved Oxidation state for each sample shall be determined. The Oxidation state is defined as: Oxidation State = OX =  $[4(TOC-COD)]/TOC$ . COD/TOC-vs-Oxidation State and the SCOD/DOC-vs-dissolved Oxidation State was plotted to show relative ability for biological remediation as developed by W. Eckenfelder. The Oxidation State parameter shall be used to determine relative degree of biodegradability in lieu of BOD as suggested by W. Eckenfelder<sup>23</sup> in his book "Industrial Pollution Control" and in a joint paper with A. Bowers etc..

## RESULTS:

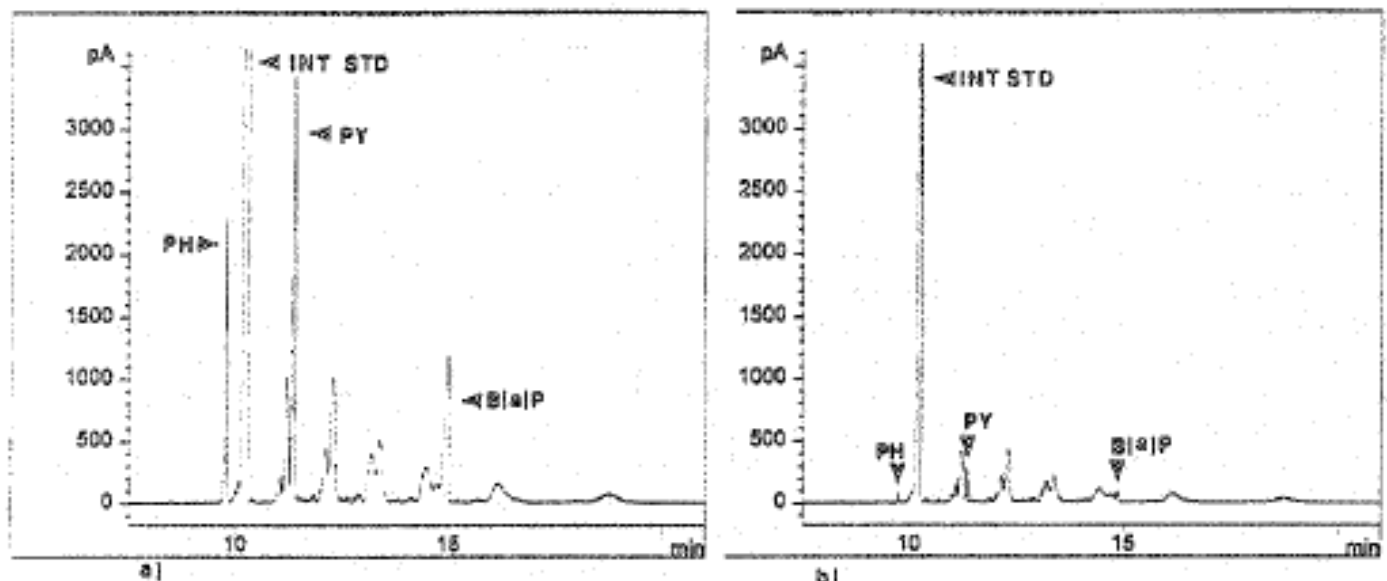
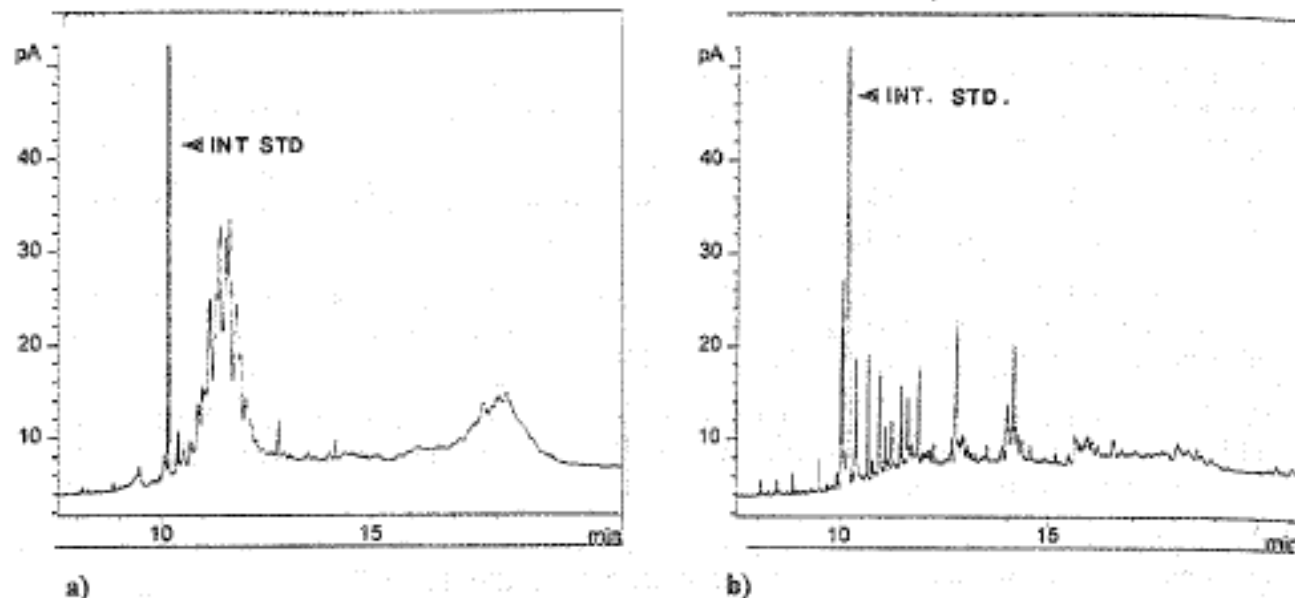


FIGURE 2: GC/FID ANALYSIS OF 30 MIN PRETREATMENT W/ O<sub>3</sub> @ pH 3.5 (PH-phenanthrene, INT STD-Internal Standard, PY-pyrene, B(a)P-Benzo(a)pyrene)  
 a) Soil Phase Time=0; b) Soil Phase Time=30min



**FIGURE 3: GC/FID ANALYSIS OF 30 MIN PRETREATMENT W/ O<sub>3</sub> @ pH 3.5**  
 (PH-phenanthrene, INT STD-Internal Standard, PY-pyrene, B(a)P-Benzo(a)pyrene)  
 a) Aqueous Phase Time=0; b) Aqueous Phase Time=30 min

#### CONCLUSIONS:

Ozone is an effective oxidant for absorbed as well as soluble PAHs. A 30 minute reaction time resulted in a two order of magnitude decrease in the solid phase PAH concentrations. There were no parent PAH compounds found in the aqueous phase after pretreatment. The most abundant reaction products were hydroxylated 1,2-Benzenedicarboxylic acids per GC/MS analysis. The COD decreased from 564mg/L to 138 mg/L while the SCOD increased from 1mg/L to 226mg/L during treatment. There was no detectible inhibition after ozone treatment per the polytox test. Thus AOP pretreatment of slurry-phase PAH contaminated soils is a promising remediation technology. In its final form, this paper will present GC/MS data elucidating intermediates and products of AOP pretreatment as well as biodegradability enhancement data at different stages of pretreatment.

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