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ABSTRACT

EFFECTS OF SURFACTANTS AND FENTON'S REAGENTS ON EXTRACTION AND DESTRUCTION OF PHENANTHRENE IN SPIKED SAND

by
Ming-Chin Chang

In this study, surfactants and Fenton's reagents (Fe(II) and H₂O₂) were proposed to solve contaminated site problems in situ on a lab scale. Phenanthrene is a simple PAHs (polynuclear aromatic hydrocarbons). The phenanthrene spiked ottawa sand simulated contaminated soil. HPLC was used for phenanthrene analysis because it provided excellent separation and no interference. Six surfactants (including nonionic and ionic) were tested. The operating conditions were optimized based on process and economic considerations such as reaction time, mixing speed, concentrations of surfactants and concentrations of Fenton's reagents. Surfactants could effectively dissolve phenanthrene from the spiked sand. In the absence of surfactants, Fenton's reactions could efficiently decompose the target compound on the sand surface. Running a sequence of Fenton's reactions was more effective than a single reaction. The combinations of a surfactant and Fenton's reaction were better than the effect of a surfactant only. A model was developed that can qualitatively predict the residual phenanthrene concentration on sand surface as a function of time, mixing speed and concentrations of surfactant and Fenton's reagents. The model was in excellent agreement with the experimental results.

**EFFECTS OF SURFACTANTS AND
FENTON'S REAGENTS ON EXTRACTION AND
DESTRUCTION OF PHENANTHRENE IN SPIKED SAND**

by
Ming-Chin Chang

**A Dissertation
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy**

**Department of Chemical Engineering,
Chemistry, and Environmental Science**

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APPROVAL PAGE

EFFECTS OF SURFACTANTS AND
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This Dissertation is dedicated to
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CHAPTER 1

INTRODUCTION

1.1 Objective

The PAHs (Polycyclic Aromatic Hydrocarbons) are getting more and more attention in the recent years as one of the problems in the cleanup of contaminated sites. Especially they do not easily decompose in the soil, they are becoming a serious environmental problem. The PAHs is a group of hydrocarbon compounds with multi-benzene rings (at least 2 rings) and double bonds. Because they are insoluble in water but soluble in some organic solvents, they are quite stable in environmental media. Some PAHs were proved as carcinogenic such as the most famous one: Benzo[a]pyrene ($C_{20}H_{12}$). The PAHs are found around petrochemical refineries and some other chemical manufacturing plants. Many researchers have tried to search for better techniques to deal with the PAHs problems. However, there is still much work to be done in this field. The effective solutions to solve the problem of PAH contaminated sites were studied in-situ rather than ex-situ, for economic reasons. In this study, some surfactants were employed to extract the PAHs and Fenton's reagents (Fe(II) with H_2O_2) were chemically reacted with PAHs. In addition, an attempt was made to determine some optimum operating conditions.

1.2 Proposed Methods

This study did not consider the traditional methods such as the "off-site treatment" for the problems. The major concern was in-situ remediation for the PAHs. The very first step in the laboratory would be the lab scale study of a single compound to check the behavior of the extractions by the surfactants and chemical reactions by the Fenton's reagents. In this study, Ottawa sand (mesh size 20-30) was used as a pure substrate and the phenanthrene ($C_{14}H_{10}$) was the target compound. The phenanthrene was spiked into the pure sand to simulate the contaminated soil. Six surfactants (four non-ionic: Brij 30, Triton X-100,

Tergitol NP-10, and Igepal CA-720; one anionic: Sodium Dodecyl Sulfate, SDS; and one cationic: Hexadecyl Trimethyl Ammonium Bromide, HTAB) were employed to compare the extraction effects. The surfactants could extract the phenanthrene from the sand under certain conditions. However, the dissolved phenanthrene in the surfactant solutions could result in further disposal problems.

Chemical treatment methods involve addition of some chemical reagents, heat or energy to chemically react with the target compounds to decompose or transfer them into harmless forms in the environmental media. Particularly, oxidation is used in such applications as the AOPs (Advanced Oxidation Processes). These are usually combinations of UV (Ultra-Violet) light with hydrogen peroxide (H_2O_2), ozone (O_3) with H_2O_2 , Titanium dioxide (TiO_2) with H_2O_2 or ferrous ion (Fe^{+2}) with H_2O_2 which can chemically oxidize the target compounds. Fenton's reaction is one of the oxidation processes which contains ferrous ions and hydrogen peroxide. The ferrous ions work as a catalyst to activate the production of free radicals from hydrogen peroxide. The radicals are known as the strongest oxidizing agents, and are capable of oxidizing organic compounds quickly and efficiently. In the past two decades, Fenton's reactions had been used more commonly in environmental applications since it successfully oxidizes many organic compounds which are difficult to be treated. Such organic compounds include dioxins, chlorophenols, PCB (polychlorobiphenyls). Also, it is more economical than other AOPs because there is no need for the use of energy, such as Ultra-Violet light or ozone generation. In this study, the Fenton's process was employed to deal with the phenanthrene on the spiked sand in certain conditions. In addition, some parameters were tested in the reactions to determine the optimum operating conditions.

The application of a series of the Fenton's reactions were studied to find the enhancement of the treatment efficiencies. Also, the combinations of the surfactant and the Fenton's reactions were applied to check if the effects were better than just the addition of surfactant only.

CHAPTER 2

LITERATURE REVIEW

The review of literature and previous studies is divided into three parts shown as follows: the properties of PAHs and target compound, the surfactant properties and enhancement for soil washing, and the soil remediation by Fenton's reactions.

2.1 The Properties of PAHs and Target Compound

The polynuclear aromatic hydrocarbons (PAHs) are a ubiquitous and persistent group of significantly toxic compounds in the environment. They appear on the EPA priority pollutant list. One of the PAHs, benzo[a]pyrene, is known as carcinogenic and mutagenic. Table 1 shows the name, formula and structure of some PAHs. Phenanthrene was chosen as the target compound. Pearlman, Yalkowsky and Banerjee (1984) summarized the water solubilities of PAHs, were found to be fairly low. The solubility of phenanthrene at 25°C was 6 µmole/L; and at 20°C about 15 µmole/L. These solubility studies were similar to that of other researchers. Verschueren (1983) summarized uses of phenanthrene properties such as for dyestuff, explosives, synthesis of drugs and biochemical research. It forms colorless leaflets, molecular weight 178.22, melting point 100°C, boiling point 340°C, with a solubility at 21°C of 0.816ppm, at 30°C 1.277ppm, at 15°C 1.6mg/L. The aqueous solubility of PAHs also investigated by May, Wasik and Freeman (1978, a and b). They found the phenanthrene solubility at 25°C was about 1.002 mg/Kg; at 29°C was about 1.220 mg/Kg. Sanders, Jones and Hamilton-Taylor (1993) investigated the photodegradable property of PAHs. They discussed a simple method to assess the susceptibility of 11 specific PAHs to photolytic decomposition under simulated natural light. The half-lives were determined to be < 2 hours for anthracene and 50 hours for fluoranthene. Magee, Lion and Lemley (1991) observed that in the presence of the dissolved organic matter (DOM) derived from soil, the phenanthrene—DOM “complex”

enhanced the transport of phenanthrene. The interactions of PAHs in three soils and montmorillonite clay for anthracene, phenanthrene and pyrene were studied by Karimi-Lotfabad, Pickard and Gray (1996). Up to 100% of anthracene and pyrene were not extractable from the soil, and up to 25% of the phenanthrene was not extractable.

Table 1 The name, formula, molecular weight and structure of some PAHs

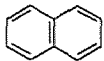
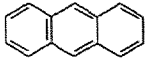
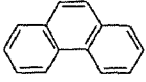
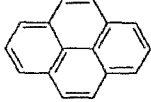
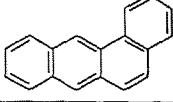
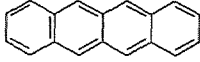
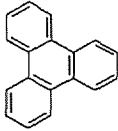
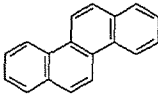
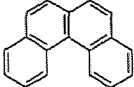
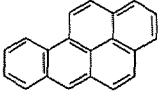
Name	Formula	MW	Structure
(1) Naphthalene	$C_{10}H_8$	128	
(2) Anthracene	$C_{14}H_{10}$	178	
(3) Phenanthrene	$C_{14}H_{10}$	178	
(4) Pyrene; Benzo[def]phenanthrene	$C_{16}H_{10}$	202	
(5) 1,2-Benzanthracene; Benz[a]anthracene; Tetraphene	$C_{18}H_{12}$	228	
(6) 2,3-Benzanthracene; Naphthacene; Tetracene	$C_{18}H_{12}$	228	
(7) 9,10-Benzophenanthrene; Triphenylene	$C_{18}H_{12}$	228	
(8) 1,2-Benzophenanthrene; Benzo[a]phenanthrene; Chrysene	$C_{18}H_{12}$	228	
(9) 3,4-Benzophenanthrene; Benzo(c)phenanthrene	$C_{18}H_{12}$	228	
(10) 3,4-Benzopyrene; Benzo[a]pyrene	$C_{20}H_{12}$	252	

Table 1 (continued)

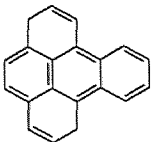
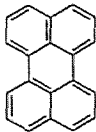
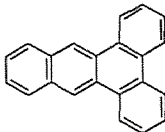
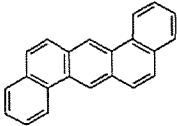
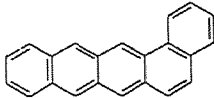
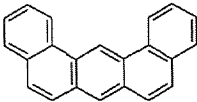
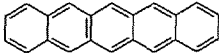
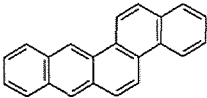
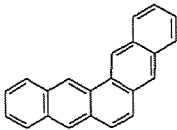
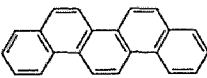
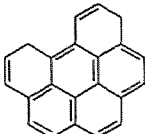
Name	Formula	MW	Structure
(11) 4,5-Benzopyrene; Benzo[e]pyrene; Teratogen	$C_{20}H_{12}$	252	
(12) Perylene; Dibenz[de,kl]anthracene	$C_{20}H_{12}$	252	
(13) 1,2,3,4-Dibenzanthracene; Dibenz[a,c]anthracene	$C_{22}H_{14}$	278	
(14) 1,2,5,6-Dibenzanthracene; Dibenz[a,h]anthracene	$C_{22}H_{14}$	278	
(15) 1,2,6,7-Dibenzanthracene; 1,2-Benzonaphthacene; Isopentaphene	$C_{22}H_{14}$	278	
(16) 1,2,7,8-Dibenzanthracene; Dinaphthantracene; Dibenz[a,j]anthracene	$C_{22}H_{14}$	278	
(17) 2,3,6,7-Dibenzanthracene; Benzo[b]naphthacene; Pentacne	$C_{22}H_{14}$	278	
(18) 1,2,6,7-Dibenzophenanthrene; 3,4-Benzotetraphene; Benzo[b]chryscene	$C_{22}H_{14}$	278	
(19) 2,3,6,7-Dibenzophenanthrene; Dibenzo[b,h]phenanthrene; Pentaphene	$C_{22}H_{14}$	278	

Table 1 (continued)

Name	Formula	MW	Structure
(20) 3,4-Benzochrysene; Dibenzo[a,i]phenanthracene; Picene	$C_{22}H_{14}$	278	
(21) Benzo[g,h,i]perylene; 1,12-Benzoperylene	$C_{22}H_{12}$	276	

PAHs are present in all soils as a result of atmospheric deposition or contamination by oil spills. PAHs are produced by the incomplete combustion of organic matter. PAHs contamination on industrial sites is commonly associated with spill and leaks from storage tanks (under or above ground) and with the conveyance, processing, use and disposal of these fuel/oil products. Luthy, et al. (1994) summarized that soil and groundwater contamination problems exist at many former manufactured gas plant (MGP) sites because of prior process operations and residuals management practices. The gas production process residuals were dominated by six primary classes of chemicals : polyaromatic hydrocarbons (PAHs), volatile aromatic compounds, phenolics, inorganic compounds of sulfur and nitrogen, and metals. Wild, et al. (1990) investigated the PAHs in an agricultural soil with a known history of sewage sludge amendments. They found the total number of PAHs increased over time in a controlled and long term sludge experiment. Generally, the higher molecular weight PAHs have been more persistent in biodegradation.

The analytical methods for determination of PAHs are important for obtaining the accurate amounts in the environmental media. Several researchers used different analysis techniques. Dale, et al. (1994) analyzed the PAHs in atmospheric particulate directly by laser desorption mass spectrometry. Krahn, et al. (1993) made the comparison of high performance liquid chromatography/Fluorescence screening and gas chromatography/mass spectrometry analysis for aromatic compounds in sediments sampled after the *Exxon*

Valdez oil spill. Analytical methods were developed by Chuang, Callahan, Menton and Gordon (1995) for PAHs and their distribution in house dust and track-in soil. By obtaining the PAHs concentration profile in house dust and track-in soil, they determined the concentration of PAHs in house dust of the track-in of outdoor soil. In general, the concentration trend was as follows: entryway soil > house dust > pathway soil > foundation soil. The analytical procedure for the PAHs and TPH (total petroleum hydrocarbons) was described in detail including extraction and clean-up by Huesemann (1995). Meanwhile, Bender (1968) obtained both the one dimensional and two dimensional thin-layer chromatographic and spectrophotofluorometric identification and estimation for Dibenzo(a,e)pyrene.

2.2 Surfactant Properties and Enhancement for Soil Washing

The aqueous surfactant solutions can enhance the solubilities of the hydrophobic compounds. There were some studies showed the effects as follows. Grimberg, Nagel and Aitken (1995) employed four commercially available non-ionic surfactants and two synthetic, non-ionic glycolipids to enhance the apparent liquid saturation concentration of phenanthrene and obtain the observed mass transfer coefficient in a completely mixed batch system. The phenanthrene was quantified as a function of surfactant concentrations. The mass transfer coefficients for phenanthrene dissolution into water were in the range of 0.01-0.025cm/min in the presence of surfactant micelles. Without surfactants, the coefficient was 0.1cm/min. Wang and Brusseau (1993) observed the effect of cyclopentanol on the solubilization of six PAHs by β -cyclodextrin (β -CD) and γ -cyclodextrin (γ -CD). The addition of 0.1% v/v cyclopentanol significantly enhanced the solubilization power of β -CD for pyrene, acenaphthene, phenanthrene and fluoranthene. The solubilization of PAHs was studied by Edwards, Luthy and Liu (1991, a, b) in micellar non-ionic surfactant solutions. Four commercial, nonionic surfactants : an alkyl polyoxyethylene (POE) type, two octylphenol POE types, and a nonylphenol POE type

could enhance apparently solubilities of naphthalene, phenanthrene and pyrene. Solubilization of each PAH compound was proportional to the concentrations of surfactants in micelle forms. Meanwhile, Kile, Chiou, and Helburn (1990) investigated the water solubility enhancements of 1,1-bis(p-chloro-phenyl)-2,2,2-trichloroethane (DDT) and 1,2,3-trichlorobenaene (TCB) by some commercial petroleum sulfonates. The petroleum sulfonate surfactants are mixtures of sulfonated hydrocarbons and free mineral oils, which form stable emulsions in water and thus behave much like a bulk organic phase in concentrating organic solutes. The enhancement was linearly proportional to the concentration of the petroleum sulfonate-oil (PSO) emulsion. Gannon et al. (1989) obtained the increased solubilization of some hydrophobic compounds such as : *p*-dichlorobenzene (DCB), naphthalene, and biphenyl in aqueous solutions of sodium dodecylsulfate (SDS). Meanwhile, Vigon and Rubin (1989) evaluated the practical considerations in the surfactant aided mobilization of contaminants (biphenyl and anthracene) in aquifers. The surfactant selections and dosage optimization parameters were considered.

The surfactants were also employed in the surface and subsurface soil and groundwater for the applications of the solubility enhancement studies of the hydrophobic compounds. The ability of aqueous surfactant solutions to recover tetrachloroethylene (PCE) entrapped in Ottawa sand was evaluated in four column experiments by Pennell, Jin, Abriola and Pope (1994). The solubilization and mineralization of ¹⁴C-phenanthrene in soil-water systems was examined with several surfactants by Laha and Luthy (1992). They found the non-ionic surfactant solubilization of sorbed hydrophobic organic compounds from soil may not be beneficial for the enhancement of soil bioremediation. The nonionic surfactant (polyoxyethylene sorbitan monooleate) enhanced solubilization of residual dodecane in soil columns was investigated by Penell, Abriola and Webber (1993). Meanwhile, Abriola, Dekker and Pennell (1993) developed a model which incorporated aqueous phase transport equations for organic and surfactant components as well as a

mass balance for the organic phase. It is important to understand the remediation of aquifers by subsurface injection of surfactants. Therefore, a review for the surfactants and the subsurface remediation was summarized by West and Harwell (1992). They concluded the efficiency of surfactant solubilization (soil washing); and the behavior and ultimate fate of these compounds in aquifer should be of concern. The viability of a surfactant based remediation process depends on selecting surfactants for optimum efficiency, environmental acceptability and balanced biological degradation. Most importantly, it must be ascertained that the use of surfactants in subsurface remediation will not add to the deterioration of groundwater. Rouse et al.(1996) evaluated the ethoxylated alkylsulfate surfactants for use in subsurface remediation. It was hypothesized that ethoxylated anionic surfactants will exhibit lower losses in the subsurface due to precipitation and sorption as a function of increasing ethoxylation while maintaining high hydrocarbon solubilization potentials. The ethoxylated anionic surfactants were less prone to sorption on soil than nonethoxylated anionic and nonionic surfactants.

The sorption of non-ionic organic compounds : 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane (*p,p'*-DDT); 2,2',4,4',5,5'-hexachlorobiphenyl (2,2',4,4',5,5'-PCB) and 1,2,4-trichlorobenzene (1,2,4-TCB) in soil-water systems containing a micelle-forming surfactant (Triton X-100) was investigated by Sun, Inskeep and Boyd (1995). Below 200mg/L, surfactant monomers in the aqueous phase were relatively ineffective as a partitioning medium for nonionic organic compounds (NOCs), while the sorbed surfactant molecules increased the sorptive capacity of the solid phase. Above 200mg/L, however, surfactant micelles in the aqueous phase began to compete with the sorbed surfactant as an effective partitioning medium for the poorly water-soluble NOCs, resulting in a 10-fold decrease in K^* (soil-water distribution coefficients) at a C_{TX} (concentration of Triton X-100) of about 600 mg/L. Sun and Boyd (1993) investigated the effects of petroleum sulfonate -oil (PSO) surfactants on sorption of representative nonionic organic contaminants: naphthalene, phenanthrene and 2,2',4,4',5,5'-hexachlorobiphenyl

(2,2',4,4',5,5'-PCB) in an soil-water system. The results suggested the utility of petronate surfactants for substantially increasing the aqueous phase concentrations of poorly water soluble organic contaminants present in soils. Meanwhile, the sorption and transport kinetics studies for a nonionic surfactant, Triton X-100, through an aquifer sediment were developed by Adeel and Luthy (1995). Unusual two-step breakthrough curves were observed in the column tests, suggesting the existence of two sorption regimes dependent on the sorbed surfactant concentrations and molecular conformation. Edwards, Adeel and Luthy (1994) investigated the distribution of nonionic surfactant and phenanthrene in a sediment/aqueous system. The Triton X-100 can act either to enhance or to inhibit phenanthrene sorption from bulk solution onto Lincoln fine sand, depending on the bulk solution surfactant concentration. Triton X-100 micelles in the bulk solution can greatly enhance the solubilization of phenanthrene and its desorption from the sand. Crocker, Guerin and Boyd (1995) studied the bioavailability of naphthalene sorbed to cationic surfactant (hexadecyltrimethylammonium, HDTMA) modified smectite clay. The sorbed naphthalene was available only upon its desorption from the HDTMA modified smectite clay for the bacterium, *Alcaligenes* sp. Strain NP-Alk., Xu and Boyd (1995) found that the organoclays formed in soil from the addition of the cationic surfactant hexadecyltrimethylammonium (HDTMA) can effectively immobilize organic contaminants dissolved in water. The adsorption and desorption of HDTMA in a subsoil was studied to determine the stability of surfactant-soil clay complexes as affected by surfactant retention mechanism. Liu, Edwards and Luthy (1992) investigated the sorption of non-ionic surfactants onto soil in a batch soil/aqueous systems. They mentioned that the understanding of surfactant sorption onto soil was needed to assess surfactant mobility. Meanwhile, a model was developed by Di Toro, Dodge and Hand (1990) for the anionic surfactant sorption to soils, sediments and sludge.

The soil washing techniques were employed by some researchers. Park and Jaffe (1995) investigated the phenanthrene removal from soil slurries with surfactant treated

oxides. The technique was based on first transferring the sorbed phenanthrene from the soil to anionic surfactant-coated oxide particles, and then separating these anionic surfactant-coated oxide particles with the sorbed phenanthrene from the soil slurry via a magnetic separation technique. The washing technique was effective in removing a strongly sorbing nonionic organic contaminant from soil slurry. Laboratory studies of surfactant (alcohol ethoxylate) enhanced washing of polychlorinated biphenyls (PCBs) from sandy soil were investigated by Abdul and Gibson (1991). Their laboratory results indicated that by using surfactant solution, PCBs could be effectively washed from the sand. A review was summarized by Ouyang, Mansell and Rhue (1995) for the emulsion mediated transport of nonaqueous phase liquids (NAPLs) in porous media. The use of surfactants as a remediation technique to remove hazardous NAPLs from soil and groundwater has been explored in some detail. However, cost-effective and high-efficiency remediation approaches using surfactants have yet to be accomplished. Minimizing surfactant losses using twin-head anionic surfactants in subsurface remediation was investigated by Rouse, Sabatini and Harwell (1993). Twin head groups exhibited lower losses in the subsurface as compared to single head group surfactants while maintaining high solubilization. Clarke et al. (1993) obtained the soil clean-up by surfactant washing. The components of a pilot-scale system to recycle and reuse a surfactant solution containing contaminants from remediated soil were designed, fabricated and successfully tested. Underwood, Debelak and Wilson (1995) studied the soil cleanup by in-situ surfactant flushing. Solvent extraction with hexane has been studied for to reclaim contaminated surfactant solutions for the reuse in remediation of hazardous waste sites. The hexane flow rate, sodium dodecylsulfate (SDS) concentration and contaminant mixture were varied to determine their effects on the removal of multicomponent mixtures of phenanthrene, naphthalene and biphenyl.

Lee, Russell and White (1995) developed a model of the kinetics of biodegradation of anionic surfactants by biofilm bacteria from polluted riverine sites. A comparison of five

classes of surfactants at three sites was studied. The bioavailable property of surfactant solutions forming the micelle with the contaminants were studied, and the models to describe the phenomena were developed. The bioavailability of hydrophobic compounds partitioned into the micellar phase of non-ionic surfactants was investigated by Guha and Jaffe (1996). The apparent solubility of PAHs can be increased in the presence of surfactants. A model describing the biodegradation of the directly bioavailable micellar-phase substrate was presented. The model was based on the hypothesis by the following steps: (1) the contaminants were transported by filled micelles from the bulk solution to the proximity of the cells; (2) the exchange of the filled micelle with the hemimicellar layer around the cell delivers the contaminants to the cell; (3) the contaminant diffused into the cell and was biodegraded.

2.3 Soil Remediation by Fenton's Reactions

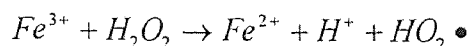
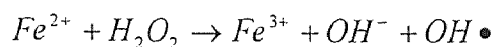
Anderson (1993) summarized the chemical treatment methods for converting the hazardous constituents into less environmentally objectionable forms. He divided chemical treatment into three processes including substitution, oxidation and precipitation. Meanwhile, chemical oxidation, UV photodegradation/photolysis and advanced oxidation processes (AOPs) were introduced in the oxidation processes. The iron (II) catalyzed H_2O_2 oxidation (Fenton's reagents) was classified as one of the emerging technologies. The most common source of ferrous ion used in the laboratory process is ferrous sulfate, typically obtained as its heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). Hydrogen peroxide is commercially available in a range of concentrations from 30 to 70% by weight in water. Typically, hydrogen peroxide is most easily and safely handled at concentrations of 10 to 30% by weight in water. The destruction of organic contaminants was achieved by combining the chemical oxidizing agent with a source of ultraviolet radiation to generate a hydroxyl radical ($\text{OH}\cdot$). The process was called Advanced Oxidation Processes (AOPs) which generally applies ultraviolet (UV) radiation with ozone (O_3) or hydrogen peroxide (H_2O_2).

Shu (1993) summarized the use of AOPs to degrade the range of treatable organics in water such as nitrosamines in groundwater and industrial wastewater; Total Organic Carbon (TOC) in distilled water and tap water; various halogenated aliphatics; aromatic organics (benzene, toluene, chlorobenzene, phenol, chlorophenols, dimethyl phthalate and diethyl phthalate, etc.); 2,4-Dinitrotoluene (explosive from military munition facilities); groundwater contaminated with TCE (Trichloroethylene), 1,1-DCA (1,1-Dichloroethane), and 1,1,1-TCA (1,1,1-Trichloroethane); bleaching water in paper industry, etc..

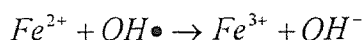
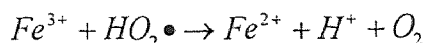
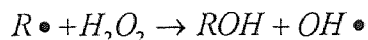
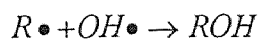
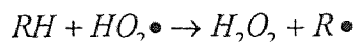
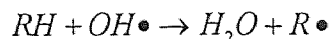
H_2O_2 is a colorless, rather stable and weak acid that is completely miscible in water. Abbot and Brown (1990) investigated the kinetics of hydrogen peroxide solutions under alkaline condition at 20°C in the presence of both supported iron catalysts and in systems with iron initially in solution. They found that the decomposition reaction was the first order with respect to total peroxide concentration with an iron-alumina supported catalyst. Wastewater contained toxic organics must be pretreated before being introduced to conventional biological waste treatment system. Chemical oxidation of aromatic compounds: comparison of hydrogen peroxide (H_2O_2), ozone (O_3) and potassium permanganate (KMnO_4) for toxicity reduction and improvements in biodegradability was done by Bowers, Cho and Singh (1992). The oxidation resulted in 17 to 79% ultimate conversion of the organic carbon to CO_2 while ozone resulted in 0 to 74% ultimate conversion and 22 to 68% conversion by KMnO_4 . The toxicity of the reactive compounds was typically greatly reduced, however several compounds exhibited an increase in toxicity after oxidation. The $\text{H}_2\text{O}_2/\text{UV}$ reaction generated hydroxyl radicals (the strong oxidants like $\text{OH}\cdot$ and $\text{HO}_2\cdot$) and other reactive species by photochemical reaction of UV light on hydrogen peroxide to degrade the organics such as formic, acetic, and propionic acids. Besides, the destruction of aromatic pollutants such as benzene, toluene, chlorobenzene, phenol, chlorophenols, dimethyl phthalate, and diethyl phthalate by $\text{H}_2\text{O}_2/\text{UV}$ process were also investigated. Moreover, the application of $\text{H}_2\text{O}_2/\text{UV}$ was also studied for the decomposition of 2,4-dinitrotoluene (DNT) in aqueous solution, for

remediation of explosive nitro-compounds from military munition facilities. The H_2O_2/UV process could also be used to treat TCE (trichloroethylene), 1,1-DCA (1,1-dichloroethane), and 1,1,1-TCA (1,1,1-trichloroethane) in contaminated groundwater (Lewis et al. 1990). The removal efficiencies obtained for TCE and total VOCs (Volatile Organic Compounds) were as high as 99% and 90%, respectively; for 1,1-DCA, and 1,1,1-TCA about 65% and 85%, respectively. For the applications of photolytic ozonation, the UV/O_3 process had very significant effects on the decomposition of THM (Trihalomethanes), TCE (Trichloroethylene) and PCE (Tetrachloroethylene) in groundwater; the degradation of polysaccharide alginic acid, pentachlorophenol in groundwater; the destruction of 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and humic acids.

About 100 years ago (1894), H.J.H. Fenton reported that ferrous ion strongly promoted the oxidation of malic acid by hydrogen peroxide. The combination of H_2O_2 and Fe(II) salt was then named as the “Fenton’s reagents” which are effective oxidants of a wide variety of organic substrates. The Fenton’s reactions have been employed increasingly in the environmental applications in the past two decades. The mechanism of this process is very similar to that of AOPs. The hydroxyl radicals were enhanced to decompose the target compounds. However, it is more economical and energy saving than the traditional AOPs. The stoichiometry of Fenton’s reactions included the radical oxidations and reductions were introduced by Walling (1975). He also reported the hydroxyl radicals reacted very rapidly with the aromatics. The Fenton’s reagents consist of Fe(II) and H_2O_2 . The Fe(II) can potentially be used as a catalyst to improve the performance of H_2O_2 as an oxidizing agent. The generation of free radicals by Fenton's reagents involves the following steps:

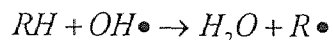
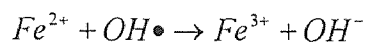
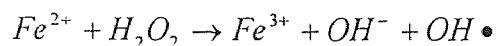


Both hydroxyl radical $\text{OH}\bullet$ and perhydroxyl radical $\text{HO}_2\bullet$ are high in oxidation potential and are capable of oxidizing most organic compounds. Fenton's reagent also involves numerous competing reactions:



Where RH represents an organic contaminant and $\text{R}\bullet$ is an organic radical.

Sawyer, Kang, Liobet and Redman (1993) discussed the mechanism of the Fenton's reactions. Most regard with Fenton chemistry as synonymous with the in situ production of free hydroxyl radical ($\text{HO}\bullet$) from the one-to-one combination of iron (II) and hydrogen peroxide. With this assumption, subsequent reactions have been based on the primary chemistry of $\text{HO}\bullet$ which reacts with iron (II) and hydrocarbons (RH). The kinetics for substrate reactivities with Fenton-generated " $\text{HO}\bullet$ " usually are determined via the relative rate of disappearance of iron (II) to that of the substrate.



Several studies using the Fenton's reagents for decomposition of the hazardous substances have proved promising. Arnold, Hickey and Harris (1995) investigated the degradation of atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine) which

contains the double bonds: N=N in water. The chemical degradation of chlorophenols in aqueous solutions was investigated by Barbeni, Minero and Pelizzetti (1987). The chlorophenols: 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 3,4-dichlorophenol and 2,4,5-trichlorophenol were effectively removed by the Fenton's reactions. The mineralization of these chlorinated aromatic substrates to CO₂ and free Cl⁻ has been studied as a function of [Fe²⁺] and [HClO₄]. Increasing the concentration of Fe²⁺ enhance the decomposition process, while an increasing in the concentration of HClO₄, inhibits the reaction. The oxidation of chlorinated phenols using Fenton's reagents was investigated by Potter and Roth (1993). The kinetics of the Fenton's oxidation of the three monochlorophenol isomers and five of the six dichlorophenol isomers were examined under batch and semibatch conditions. The monochlorinated phenols oxidized about as rapidly as phenol itself. The dichlorinated phenols demonstrated a wide range of oxidation rates under the same test conditions. The reaction products of benzene, toluene, phenylacetic acid and phenyl substituted alcohols with Fenton's reagents were examined by Walling and Johnson (1975). The hydroxyl radicals added to the aromatic system and the resulting hydroxycyclohexadienyl radicals may dimerize, be oxidized to phenols, or undergo a reversible acid-catalyzed collapse to radical cations. These, in turn may be reduced to starting material by Fe²⁺ or, when possible, may undergo side-chain cleavage (with toluene and phenylacetic acid to benzyl radicals) followed by dimerization or further oxidation. Sedlak and Andren (1991) investigated the oxidation of chlorobenzene with Fenton's reagents. They found in the absence of oxygen, chlorophenols, dichlorobiphenyls (DCBs) and phenolic polymers were the predominant initial products. In the presence of oxygen, DCB yield decreased markedly and chlorobenzoquinone was also formed. The highest yield of product formed per mole of H₂O₂ consumed was observed in the pH range of 2-3. Lipczynska-Kochany, Sprah and Harms (1995) investigated the degradation of 4-chlorophenol in aqueous solutions containing various anions by the Fenton's reactions. The reaction rate was found to decrease in the following order for anions (at the same

concentrations): $\text{ClO}_4^- \sim \text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- \gg \text{HPO}_4^{2-} > \text{HCO}_3^-$. Mohanty and Wei (1993) investigated the oxidation of explosive 2,4-dinitrotoluene (2,4-DNT) using the Fenton's reagents. They studied the reaction mechanisms and their practical applications. They found the 2,4-DNT to be effectively oxidized in aqueous solutions and to be completely removed in 5 hours by the Fenton's reagents. The degradation of chlorinated aromatics by Fenton oxidation and methanogenic digester sludge was investigated by Koyama, Kamagata and Nakamura (1992). The breakdown products were readily converted to methane by methanogenic digester sludge without any acclimation with the products. The process was quite effective for decomposition of chlorobenzoates, chlorophenols, dichlorophenols and *p*-chlorobiphenyl.

Some studies suggested that the addition of ultraviolet light with the Fenton's reactions could enhance the treatment efficiency. Zepp, Faust and Holgne (1992) observed the hydroxyl radicals formation in aqueous reactions (pH 3-8) in photo-Fenton reactions. The kinetics studies of the indirect photooxidation of trace hydroxyl radical ($\text{OH}\cdot$) probes in aqueous solutions were used to evaluate the nature and formation efficiency of the transient oxidants that are generated when hydrogen peroxide reacts with Fe(II) that is produced from photo-reduction of Fe(III). Ruppert, Bauer, Heisler and Novaliv (1993) investigated the mineralization of cyclic organic water contaminants by the photo-Fenton reactions. They discussed the influence of structure and substituents. The mineralization of phenol, hydroquinone, 4-chlorophenol and 4-chloroaniline reached between 92% and 98% after 5 hours of illumination with a 250W tungsten lamp. In addition, the measurement of TOC (Total Organic Carbon) reduction of 3-nitroaniline and 4-nitroaniline was 76% and 74%, respectively. Meanwhile, Spacek, Bauer and Heisler (1995) compared the oxidative destruction of phenol, cyclohexanol (CyOH) and 4-nitroaniline (4-NA) in aqueous solution by the photo-Fenton reactions and $\text{TiO}_2/\text{UV-A}$. The degradation rates with the photo-Fenton reaction had the following order: phenol > 4-NA >> CyOH, in contrast to the order CyOH > phenol > 4-NA obtained with $\text{TiO}_2/\text{UV-A}$.

The Fenton's like process was employed as the Fe(III) with hydrogen peroxide or photoassisted Fe(III) with H₂O₂. The mechanism of the ferric ion (Fe³⁺) catalyzed decomposition of hydrogen peroxide in HClO₄ solution by a number of organic substrates was investigated by Walling and Goosen (1973). Results with acetone, acetic acid and tert-butyl alcohol are consistent with the redox chain mechanism on the assumption that the substrates trap hydroxyl radicals which otherwise react with H₂O₂. The degradation of polychlorinated dibenzo-p-dioxin (PCDD) and dibenzofuran (PCDF) contaminants in the herbicide 2,4,5-trichlorophenoxyacetic acid by photoassisted iron (III) catalyzed hydrogen peroxide was investigated by Pignatello and Huang (1993). Treatment with Fe³⁺/H₂O₂/hν (mole ratio 2,4,5-T: Fe³⁺: H₂O₂: 1:10:200) in aerated solution at pH 2.8 resulted in 89-100% removal of all PCDD/F peaks. The degradation of PCBs by ferric ion (Fe³⁺), hydrogen peroxide and UV light (300-400 nm) was investigated by Pignatello and Chapa (1994). Up to 88% PCB (commercial oil Aroclor 1242) removal and 85% dechlorination were obtained. The order of reactivity was di- > tri- > tetra- ~ higher chlorinated biphenyls. Pignatello and Sun (1995) obtained the Metolachlor [2-chloro-*N*-(2-methyl-6-ethylphenyl)-*N*-(2-methylethyl)acetamide] or methyl parathion [*O,O*-dimethyl-4-nitrophenyl phosphorothioate] in water was rapidly decomposed by the photoassisted Fenton's reactions (Fe³⁺/H₂O₂/UV). At 10⁻²M H₂O₂ and blacklight UV (300-400 nm), metolachlor reacted in 8 minutes and was completely mineralized to HCl in 40 minutes and CO₂ in 6 hours. The aromatic ring was mineralized in 2.5 hours. Agrawal and Tratnyek (1996) investigated the reduction of nitro aromatic (NACs) compounds by zero-valent iron metal. Nitrobenzene was reduced by iron under anaerobic conditions to aniline. First-order reduction rates were similar for nitrobenzene and nitrosobenzene.

The decoloring of dye wastewater with Fenton's reagents was investigated by Kuo (1992). The simulated dye wastewater could be treated to achieve an average percent removal of chemical oxygen demand (COD) of about 90% and the average percent decolorization was about 97%.

Kelly, Gauger and Srivastava (1990) investigated the PAHs and PAH-contaminated soils by Fenton's treatment in the Institute of Gas Technology (IGT). Fenton's processes were very reactive with PAHs, causing rapid modification of the parent compounds to oxidized products and complete degradation to CO₂. The manufactured gas plant (MGP) soils were contaminated primarily with PAHs. The MGP soil remediation in a slurry-phase system with a pilot scale test was investigated by Liu, et al (1993). The test matrix consisted of eight semi-continuous runs designed to evaluate the effects of PAHs concentration, total solids concentration, residence time, and a number of chemical reagent additions. Besides, the IGT has developed and demonstrated an integrated chemical/biological (CBT) process to efficiently remediate soils contaminated with PAHs, BTEX and PCBs. A field scale process for MGP sites was investigated by Srivastava, Kelly, Paterek, Hayes, Nelson, Golchin (1993). The field tests results showed the chemically enhanced bioremediation using CBT process results in up to 90% improvement over conventional bioremediation for total PAHs degradation. The degradation of PAHs by *Sphingomonas paucimobilis* was investigated by Ye, et al.(1996). After 16 hours of incubation with 10 ppm of a PAH, a resting cell suspension (1mg wet cells/mL) of *S. paucimobilis* grown on fluoranthrene degraded 80, 72.9, 31.5, 33.3, 12.5, and 7.8% of pyrene, benz[a]anthracene (B[a]A), chrysene, benzo[a]pyrene (B[a]P), benzo[b]fluoranthene (B[b]F), and dibenz[a,h]anthracene (DB[a,h]A), respectively. No degradation of dibenzo[a,l]pyrene was detected under these conditions. The SITE demonstration of slurry-phase biodegradation of PAHs contaminated soil in a pilot scale bioreactors was investigated by Lewis (1993). Total PAHs degradation average of about 93% in the 12 weeks. The review of bioremediation of soil contaminated with PAHs was summarized by Wilson and Jones (1993). Current in-situ remediation techniques are considered ineffective for the removal of most PAHs from contaminated sites. On-site "landfarming" methods have been used successfully in a reasonable period of time to degrade only those PAHs with three or fewer aromatic rings. Bioreactors have proved

most effective. However, bioreactors are still at the development stage, and further research is required to optimize their efficiency and economy for routine use. Cerniglia (1993) also reviewed the biodegradation of PAHs. The biochemical principles, pathway of catabolism for PAHs were examined. Meanwhile, the relationship between the chemical structure and the rate of biodegradation in aqueous and terrestrial ecosystem was discussed.

The feasibility of using hydrogen peroxide as a chemical oxidant for in-situ treatment of contaminated surface soils was investigated by Ravikumar and Gurol (1994). The process has been tested in the presence and absence of ferrous sulfate on sand-packed columns, which contained pentachlorophenol (PCP) and trichloroethylene (TCE) as model compounds. PCP and TCE adsorbed on the sand surface were oxidized effectively and a stoichiometric release of organic bound chlorine as chloride ion was found. The laboratory studies were conducted to determine the feasibility of injecting and mixing hydrogen peroxide solutions into clay soils contaminated with trichloroethylene (TCE) to achieve in-situ chemical oxidation by Gates and Siegrist (1995). TCE reductions as high as 95% of the initial concentration were achieved with a H_2O_2 dose of 28g H_2O_2 /kg soil. The petroleum contaminated soils were studied in the pilot field by Watts (1992). The TPH (total petroleum hydrocarbons) could be destroyed through on-site and in situ process applications. The treatment of silica sand contaminated with pentachlorophenol (PCP) using the standard Fenton's reagent procedure was investigated by Watts, Udell and Monsen (1990). The treatment of PCP was investigated as a basis for the on site and in situ treatment of contaminated surface soils by Watts, Udell, Rauch and Leung (1990). Mineralization of PCP was demonstrated in a silica sand system by the removal of the parent compound and total organic carbon with corresponding stoichiometric recovery of chloride. Pentachlorophenol (PCP) was used as a model contaminant in the Fenton's reagent treatment of soils of varying complexity was investigated by Watts, Udell and Leung (1992). Mineralization of PCP was demonstrated by the removal of the parent

compound (PCP) and the total organic carbon (TOC) associated with the PCP. In addition, stoichiometric quantities of chloride were recovered. The treatment of soils contaminated with octachlorodibenzo-*p*-dioxin (OCDD) using a Fenton-like reaction was investigated by Watts and Smith (1991).

In-situ bioremediation for the toxic organic substances in contaminated sites was employed by some researchers. Zacharias, Lang and Hanert (1995) investigated the biodegradation of chlorinated aromatic hydrocarbons in slow sand filters simulating conditions in contaminated soil. The pilot study was employed for *in situ* cleaning of an industrial site. The gas saturated water was continuously recycled through the fixed bed columns. The gases supplied were either pure oxygen, air or nitrogen. After 110 days, in all aerated plants more than 99% of the chlorobenzenes (CB), 96% of the chlorophenols (CP) and 94% of the adsorbable organic halogens (AOX) were removed. In comparison, only 82% of CB, 78% of CP and 49% of AOX of these compounds were removed in the nitrogen-supplied plant.

CHAPTER 3

THEORY

In this chapter, a mathematical model was developed on effects by surfactants and Fenton's reagents on the reaction and the destruction of phenanthrene in spiked sand. The model was to be used to predict the relations between the residual phenanthrene concentration on the sand surface and the system variables such as time, mixing speed and concentrations of surfactants, Fe(II) and H₂O₂. There are three parts in the model: (1) dissolving of phenanthrene from sand surface by surfactant, (2) Fenton's reaction with phenanthrene on sand surface, and (3) combination effects of the surfactant and Fenton's reaction on the removal of phenanthrene on sand surface. The model is based on the assumption that the surfactant is not oxidized by Fenton's reagents (see appendix 1).

3.1 Dissolving of Phenanthrene from Sand Surface by Surfactants

When an aqueous solution of a surfactant is mixed with sand spiked with phenanthrene, the surfactant may be in the following forms:

- (1) single molecules in the aqueous phase.
- (2) micelles of surfactant in the aqueous phase.
- (3) a surfactant-phenanthrene complex on the sand surface and,
- (4) a surfactant covered phenanthrene emulsion in the aqueous phase.

Single molecules of surfactant will form micelles of surfactants in the aqueous phase when the concentration of single molecules reaches to a critical values.

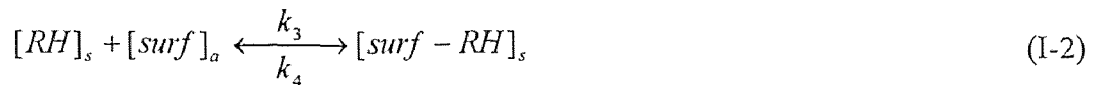


where $[surf]_a$ is the concentration of single molecules of surfactant and $[surf]_{micelles}$ represents the concentration of micelles of surfactant. k_1 and k_2 are forward and backward rate constants.

k_2 is a function of the mixing speed which may cause the breakdown of micelles into single molecules beyond a certain speed. Thus, when the mixing speed is increased, the $[surf]_a$ increases.

The dissociation of phenanthrene from sand surface by surfactant is modeled as reactions with two steps:

- (1) The interfacial reaction of phenanthrene on sand surface and single molecules in the aqueous phase to form a complex.
- (2) The dissociation of the phenanthrene-surfactant complex on sand surface to the aqueous phase.



where $[RH]_s$ is the concentration of phenanthrene on sand surface. $[surf-RH]_s$ is the concentration of the complex in the aqueous phase. k_3 and k_4 are rate constants.

The rate expressions for $[RH]_s$ and $[surf-RH]_s$ can be written as :

$$\frac{d[RH]_s}{dt} = -k_3[RH]_s[surf]_a + k_4[surf - RH]_s \quad (I-4)$$

$$\frac{d[surf - RH]_s}{dt} = k_3[RH]_s[surf]_a - k_4[surf - RH]_s - k_5[surf - RH]_s \quad (I-5)$$

The rate expression of phenanthrene leaving the sand surface is :

$$\frac{d[surf - RH]_a}{dt} = k_5[surf - RH]_s \quad (I-6)$$

At the beginning of the reaction, the forward reaction of Equation (I-2) is the predominant reaction. From Equation (I-4), the concentration of phenanthrene should have an exponential decay with respect to time. After a certain time, the whole system reaches its equilibrium. At equilibrium, Equation (I-3) becomes :

$$[surf - RH]_s \xrightleftharpoons[k_6]{k_5} [surf - RH]_a \quad (I-7)$$

Therefore,

$$[surf - RH]_a = \frac{k_5}{k_6} [surf - RH]_s \quad (I-8)$$

Equation (I-4) becomes :

$$k_3[RH]_s[surf]_a = k_4[surf-RH]_s \quad (I-9)$$

Combining Equation (I-8) and (I-9) yields :

$$[surf - RH]_a = \frac{k_3 k_5}{k_4 k_6} [RH]_s [surf]_a \quad (I-10)$$

Equation (I-10) may be incorporated into the equilibrium value of residual phenanthrene concentration percentage in sand (RPCPIS) as follows :

$$RPCPIS = \frac{[RH]_{s0} - m[surf - RH]_a}{[RH]_{s0}} = 1 - m \frac{k_3 k_5 [RH]_s}{k_4 k_6 [RH]_{s0}} [surf]_a \quad (I-11)$$

where $[RH]_{s0}$ is the initial phenanthrene concentration in sand and m is the ratio of volume of the aqueous phase and the total area of sand surface.

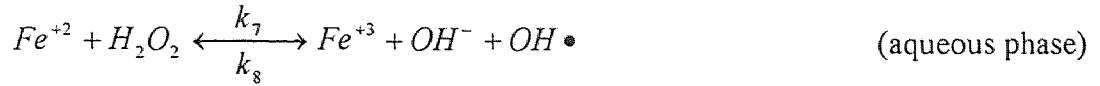
Equation (I-11) may be used to interpret the effects of surfactant concentration and mixing speed on the equilibrium value of residual phenanthrene concentration in sand.

Under equilibrium conditions, $[surf]_a$ should increase with respect to initial surfactant concentration $[surf]_{a0}$ at low $[surf]_{a0}$. When $[surf]_{a0}$ is larger than a certain critical value, micelles will form and $[surf]_a$ becomes independent of $[surf]_{a0}$. The effect of $[surf]_a$ on RPCPIS is shown in Equation (I-11). Our model predicts a linear drop on RPCPIS in the region of low surfactant concentration. After the critical concentration of micelle formation, RPCPIS will remain at a constant value.

Under equilibrium conditions, the mixing speed will cause the backward reaction of Equation (I-1). Thus, higher mixing speed will increase the value of k_2 and thus a larger value of equilibrium $[surf]_a$. Equation (I-11) predicts that a lower value of RPCPIS will be obtained in comparison the case of no mixing.

3.2 Fenton's Reaction with Phenanthrene on Sand Surface

The free radical oxidation of phenanthrene on sand surface by Fenton's reagents involves the following steps: (1) the generation of hydroxyl radicals in the aqueous phase, (2) the oxidation of phenanthrene at the interface of the aqueous phase and the sand surface, and (3) the termination reaction of free radicals.



During the early time of the reaction, the backward reaction at the interface maybe neglected, then

$$K_p = \frac{k_7}{k_8} = \frac{[Fe^{+3}][OH^-][OH\bullet]}{[Fe^{+2}][H_2O_2]} \quad (\text{II-1})$$

$$-\frac{d[RH]_s}{dt} = k_9[RH]_s[OH\bullet] = k_9[RH]_s \frac{K_p[Fe^{+2}][H_2O_2]}{[OH^-][Fe^{+3}]} \quad (\text{II-2})$$

By material balance :

$$[Fe^{+2}]_0 = [Fe^{+2}] + [Fe^{+3}] \quad (\text{II-3})$$

where $[Fe^{+2}]_0$ is the ferrous ion concentration at $t=0$

By combining (II-1), (II-2) and (II-3) yields:

$$-\frac{d[RH]_s}{dt} = k_9[RH]_s \frac{K_p \{ [Fe^{+2}]_0 - [Fe^{+3}] \} [H_2O_2]}{[OH^-][Fe^{+3}]} \quad (\text{II-4})$$

At the beginning of the reaction; $t \rightarrow 0$, $[Fe^{+3}]$ is small :

$$-\left. \frac{d[RH]_s}{dt} \right|_{t=0} = k_9[RH]_s \frac{K_p[Fe^{+2}]_0[H_2O_2]}{[OH^-][Fe^{+3}]} \quad (II-5)$$

Equation (II-4) predicts that the initial rate of phenanthrene reduction in sand follows an exponential decay. Equation (II-5) shows that initial rate of phenanthrene reduction will increase with respect to the initial concentration of ferrous ion, $[Fe^{+2}]_0$.

As time moved on, $-\frac{d[RH]_s}{dt} = 0$, as the interphase reactions also reaches equilibrium,

$$k_9[RH]_s[OH\bullet] = k_{10}[R\bullet] \quad (II-6)$$

$$k_{11}[OH\bullet][R\bullet] = k_{12}[ROH] \quad (II-7)$$

Combining Equation (II-1) with (II-6) and (II-7), yields :

$$[RH]_s = \frac{k_{10}k_{12}[ROH][OH^-]^2[Fe^{+3}]^2}{k_9k_{11}K_p^2[Fe^{+2}]^2[H_2O_2]^2} \quad (II-8)$$

Equation (II-8) shows that the residual phenanthrene on sand surface will be reduced when a larger dose of $[Fe^{+2}]_0$ is used. Meanwhile, Equation (II-8) also shows the same effect with a larger dose of $[H_2O_2]$ being used.

3.3 Combination Effects of the Surfactant and Fenton's Reaction on the Removal of Phenanthrene on Sand Surface

Two assumptions were made in this part of the modeling. Firstly, we assumed that the effects of surfactant extraction and Fenton's reagent oxidation on phenanthrene removal

from sand surface are independent of each other. Secondly, the surfactant and the surfactant-phenanthrene emulsion in the aqueous phase are immune to the oxidation of Fenton's reagents. When equilibrium reaches, the material balance of phenanthrene becomes :

$$[RH]_{s0} = [RH]_s + [surf-RH]_s + m[surf-RH]_a + [RH]_{s,rxn} \quad (III-1)$$

where $[RH]_{s0}$ is the initial phenanthrene concentration in spiked sand. $[RH]_s$ and $[surf-RH]_s$ are the concentration which remained on the sand surface. m is the ratio of volume of the aqueous phase and the total area of sand surface. $m[surf-RH]_a$ is the concentration which goes to the aqueous phase by surfactant.. $[RH]_{s,rxn}$ is the concentration which disappeared by reaction.

The RPCPIS represents the residual phenanthrene concentration percentage in sand. Thus, RPCPIS is equal to the residual phenanthrene concentration on sand surface over the initial phenanthrene concentration as follows:

$$RPCPIS = \frac{[RH]_s + [surf - RH]_s}{[RH]_{s0}} \quad (III-2)$$

From Equation (III-1), $[RH]_s + [surf-RH]_s = [RH]_{s0} - m[surf-RH]_a - [RH]_{s,rxn}$. Substituting $[RH]_s + [surf-RH]_s$ into Equation (III-2) yields Equation (III-3) :

$$RPCPIS = 1 - \frac{m[surf - RH]_a}{[RH]_{s0}} - \frac{[RH]_{s,rxn}}{[RH]_{s0}} \quad (III-3)$$

The reacted concentration, $[RH]_{s,rxn}$, is equal to the initial concentration minus the equilibrium concentration : $[RH]_{s,rxn} = [RH]_{s,t=0} - [RH]_{s,equil}$. of Section 3.2.

From Equation (II-8) : $[RH]_s = \frac{k_{10}k_{12}[ROH][OH^-]^2[Fe^{+3}]^2}{k_9k_{11}K_p^2[Fe^{+2}]^2[H_2O_2]^2}$,

Thus,

$$[RH]_{s,rxn} = [RH]_{s0} - \frac{k_{10}k_{12}[ROH][Fe^{+3}]^2[OH^-]^2}{k_9k_{10}k_p^2[Fe^{+2}]^2[H_2O_2]^2} \quad (III-4)$$

Combining (III-3) and (III-4), gives:

$$RPCPIS = 1 - \frac{m[surf - RH]_a}{[RH]_{s0}} - \left(1 - \frac{k_{10}k_{12}[ROH][Fe^{+3}]^2[OH^-]^2}{[RH]_{s0}k_9k_{11}k_p^2[Fe^{+2}]^2[H_2O_2]^2}\right) \quad (III-5)$$

Substituting Equation (I-11) to Equation (III-5) yields :

$$RPCPIS = -\frac{k_3k_5m[RH]_s[surf]_a}{k_4k_6[RH]_{s0}} + \frac{k_{10}k_{12}[ROH][Fe^{+3}]^2[OH^-]^2}{[RH]_{s0}k_9k_{11}k_p^2[Fe^{+2}]^2[H_2O_2]^2} \quad (III-6)$$

$$=-A+B \quad (\text{note: } B>A)$$

where A is $\frac{k_3k_5m[RH]_s[surf]_a}{k_4k_6[RH]_{s0}}$, and B is $\frac{k_{10}k_{12}[ROH][Fe^{+3}]^2[OH^-]^2}{[RH]_{s0}k_9k_{11}k_p^2[Fe^{+2}]^2[H_2O_2]^2}$

Equation (III-6) summarizes the relationship between residual phenanthrene concentration and operational variables. It predicts that, in order to further reduction of phenanthrene, we should increase the initial concentration of Fe^{+2} and H_2O_2 , but not the surfactant. Also the decrease of pH in the aqueous phase showed enhance the removal of phenanthrene on sand surface.

CHAPTER 4

EQUIPMENT AND EXPERIMENTS

4.1 Materials and Chemicals

Ottawa sand (mesh size 20-30) was used as the uncontaminated sand; the EPA 40 mL amber vials with screw caps were used as the reacting vessels in the lab scale; and the 2 mL HPLC autosampling vials with septa were bought from Fisher Scientific Co. (Springfield, NJ). $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was the reacting chemical which was bought from Fluka (Ronkonkoma, NY). The phenanthrene ($\text{C}_{14}\text{H}_{10}$, 95%) was the target compound which was obtained from Aldrich (Milwaukee, WI). Na_2SO_4 was the drying agent from Fisher Scientific Co.. The reagents such as H_2O_2 (about 35%) was obtained from Fluka; acetone was used as the spiking solvent from Fisher Scientific Co.; Hexane and Dichloromethane were used in the mobile phase of the HPLC from Fisher Scientific Co.. The surfactants used were Brij 30 (BR), Triton X-100 (TR), and Tergitol NP-10 (TE) from Sigma (St. Louis, MO); Igepal CA-720 (IG) from Aldrich; Sodium Dodecyl Sulfate (SDS, 95%) from Sigma; and the Hexadecyl Trimethyl Ammonium Bromide (HTAB, 95%) from Pfaltz & Bauer (Waterburg, CT). Table 2 shows the six different surfactants used in this study including the names, formulas, molecular weights, and densities (for the liquid state). All materials and chemicals obtained from the commercial companies were used without further purification.

In order to make the different concentrations, the surfactants were diluted with distilled water. The non-ionic original commercial products were diluted by volume. However, the anionic and cationic ones in powder form were made by dissolution in the distilled water by weight/volume. Therefore, the non-ionic surfactants (BR, TR, TE, and IG) were diluted by vol./vol. in distilled water to make the concentrations as 0.1%, 1%, 4%, 6%, and 10%. The SDS (anionic) and HTAB (anionic)

Table 2 The surfactants used in this study

Surfactant		Formula		MW	Density
Brij30, (BR)	nonionic	$C_{12}H_{25}O(CH_2CH_2O)_4H$	$C_{12}E_4$	362	0.950
Triton X-100, (TR)	nonionic	$C_9H_{17}C_6H_4O(CH_2CH_2O)_{9.5}H$	$C_8PE_{9.5}$	628	1.070
Tergitol NP-10, (TE)	nonionic	$C_9H_{19}C_6H_4O(CH_2CH_2O)_{10.5}H$	$C_9PE_{10.5}$	682	1.062
Igepal CA-720, (IG)	nonionic	$C_8H_{17}C_6H_4O(CH_2CH_2O)_{12}H$	C_8PE_{12}	735	1.104
Sodium Dodecyl Sulfate, (SDS)	anionic	$CH_3(CH_2)_{11}OSO_3Na$	---	288	---
Hexadecyl Trimethyl Ammonium Brimide, (HTAB)	cationic	$CH_3(CH_2)_{15}HN(CH_3)_3Br$	---	365	---

*Brij 30 (BR): polyoxyethylene 4 lauryl ether; polyoxyethylenated straight chain alcohol

*Tergitol NP-10 (TE) : polyglycol ether

* Sodium Dodecyl Sulfate (SDS) : lauryl sulfate sodium salt

were made by weight/volume in distilled water. The Fe(II) solutions were made by weighing the $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ and dissolving in the distilled water to make 0.4g/L, 2g/L, 4g/L, 6g/L, and 8 g/L. H_2O_2 was prepared in five different dilution from the original reagent : 0.035%, 0.07%, 0.14%, 0.7%, and 1.4% by volume/volume dilution in the distilled water.

4.2 Apparatus and Equipments

The balance model GT2100 (OHAUS) was employed for measuring accurate weights of reagents such as the phenanthrene, non-ionic surfactants, Na_2SO_4 and sand samples. The G24 environmental incubator shaker by New Brunswick Scientific Co.(Edison, NJ) was used to mix the surfactant solutions and Fenton's reagents with the spiked sand samples. The ultrasonic bath was manufactured by Fisher Scientific Co. (with timer, 225Kw) which provided the ultrasonic energy to extract the phenanthrene from the sand samples into the hexane for the HPLC analysis. The HPLC (High Performance Liquid Chromatography) was used to obtain the final extracted concentrations of phenanthrene in hexane. The HPLC includes a system controller, Waters 600E, a chromatography server; an autosampler from Hewlett Packard series 1050 and two detectors (Ultra-Violet and Fluorescence), Waters. The column was from Phenomenex (150x3.2mm with silica, 3 μ in diameter). The computer software used for the data acquisition and processing was the "Minichrom" (VG Data System, Ltd.)

4.3 Analytical Methods

In order to find out the best analytical methods including the sample preparations, extraction methods and the instrumental analysis, the first consideration would be how to spike the pure sand by phenanthrene to simulate the contaminated soil. Acetone was the good solvent for spiking the phenanthrene into sand. Using hexane as solvent for extraction, recovery efficiencies reached above 90% to the acceptable level. The

extraction for samples before HPLC analysis was considered by the EPA method which suggested sonication by using the ultrasonic energy to extract the organic compounds in the soil. The chromatographic analysis by HPLC could provide the better separations and less interference for analyzing the target compound in the mixture samples. However, it would be a major concern for the instrumental analysis to keep the good operation techniques including instrumental conditions, set-up, and maintenance. The samples were made in duplicate for the extraction's by the surfactants and the Fenton's reactions.

4.3.1 Spike and Extraction

The "spike" was to make the phenanthrene mix with the sand to simulate contaminated soil. The phenanthrene was dissolved in acetone, then the acetone solution was mixed with sand. While the acetone was evaporating, the phenanthrene was distributed on the sand surface homogeneously. To prepare the spiked sand, 1.0 kg pure sand was put in a 1000 mL beaker. The target compound, phenanthrene, 100 mg, was dissolved completely in acetone. Then, the phenanthrene-acetone solution was mixed with the sand in the 1000 mL beaker. The beaker wall was wrapped with aluminum foil to prevent decomposition from light. The wrapped beaker was kept in the hood and the acetone allowed to evaporate. The phenanthrene then was crystallized and distributed on the sand surface. The initial concentration was made as 100 mg phenanthrene/kg soil. During the drying in the hood, the sand and acetone solution in the beaker was frequently agitated with a the mixing rod frequently to obtain a homogeneous distribution of the phenanthrene. Then, the dried spiked sand was stored in amber bottles with caps for the experiments.

Once the spike was finished, the first step before any further test was proceeded was to check the recovery efficiencies and that the distribution of phenanthrene on the sand surface was homogeneous. The 1.0 kg spiked sand samples were divided into 5 parts. From each part, 2.0 g was measured in duplicates. The samples then were extracted by the sonication and analyzed by the HPLC to obtain the recovery efficiencies. Every batch of

the spiked sand was checked for the recovery efficiencies before any further tests. Only if the recovery efficiencies of the phenanthrene was above 90%, was the batch used in the experiments.

In both the extraction's by the surfactants and chemical reactions with the Fenton's reagents, some solutions were added to the sand samples. The mixture solutions could result in the interference with the phenanthrene measurements. Therefore, distilled water was employed to determine the interference effects. The spiked sand samples in the vials were mixed with 1 mL distilled water to replace the added reagents (surfactants and Fenton's reagents). Then, the supernatant was pipetted out and transferred into the 6 mL vials. 5.0 mL hexane was added. The vials were shaken in 1 minute by hand vigorously for extracting the phenanthrene into hexane. The wet sand samples then were air dried in the venting hood for 1 hour to remove excess the moisture which was also one of the interference sources. After 1 hour, the Na_2SO_4 (drying agent) was added and mixed well with the wet sand samples to absorb the residual moisture in the sand samples. Then, 5.0 mL hexane were added into the sand samples which were sonicated for 30 minutes. This step was repeated once to increase extraction efficiencies. After extracting, the phenanthrene-hexane solutions were transferred into the 2 mL HPLC vials for analysis. Therefore, the concentrations of phenanthrene in hexane from both in the solutions (supernatant) and in the residual wet sand samples were analyzed by the HPLC. Besides, the sums of these two parts were the total recovery efficiencies which were expected to reach the acceptable level above 90%. Once the distilled water tests could accomplish the acceptable level, the procedure could be employed for the surfactants and the Fenton's reactions. Therefore, the surfactants were added into the sand samples and the same procedure as the distilled water tests was followed: extracted by hand for solutions; the wet sand samples held in the venting hood to reduce the moisture and the drying agent added, extracted by sonication. Then, both parts (the solutions and wet sand samples) were analyzed by HPLC. The sums of recovery efficiencies of the solutions and wet sand

samples should obey the mass balance rule to approach almost 100% for the distilled water and surfactant tests. However, the Fenton's reagents could decompose some of the phenanthrene, so the mass balance rule cannot be followed. The sums of recovery efficiencies of both parts shows the decomposition efficiencies.

In order to check the recovery efficiencies of the spike, 2.0g dried sand samples was measured into the amber vials and 4.0g Na_2SO_4 were added. The drying agent was mixed with the sand samples in order to prevent interference from the moisture. Then, 5.0 mL hexane was added to the sample vials and they were sonicated for 30 minutes to extract the phenanthrene on the sand. The hexane solutions (phenanthrene in hexane) were transferred into the collection vials. Then, the extraction was repeated by adding another 5.0 mL hexane into the original wet sand vials, sonicating for 30 minutes again. The second hexane solutions (phenanthrene in hexane) were collected in the collection vials. At this point, there were about 10 mL hexane solutions (phenanthrene in hexane) in the collection vials. Then, about 2 mL phenanthrene-hexane solutions were pipetted into the HPLC vials for analysis.

4.3.2 HPLC Analysis

The extracted phenanthrene (in hexane) was analyzed by HPLC. The HPLC was chosen and tested for the phenanthrene analysis from the mixture solutions because that it provided good separations and reduced interference. In this study, the operation conditions of HPLC were as follows: The mobile phase was isocratic 90% hexane with 10% dichloromethane (CH_2Cl_2). The column was packed with 3μ silica particles. Retention time of phenanthrene was about 3 minutes and the pressure was about 1500 psi. Fluorescence and Ultra-violet were used for monitoring the chromatographs.

While the HPLC conditions were set-up for getting good chromatographs, the first step for routine analysis was to develop a multipoint calibration curve. Standards were made by dissolving the phenanthrene in hexane. In order to obtain a good linear relation, 6

points of standards were chosen. The concentrations were made such as 0.5, 1.0, 5.0, 10.0, 15.0, and 20.0 mg phenanthrene/L hexane. The coefficients of linearity was at least 0.99. The working standards were made fresh daily, so as were the calibration curves.

The chromatographic method was employed here because of the good separations and low interference in the mixture solutions. The daily fresh calibration curves were run and stored before analyzing the samples. By comparing with the calibration curves, the data processor could compute the phenanthrene concentrations of the unknown samples from extraction by the surfactants and chemical reactions by the Fenton's reagents.

4.4 Experiment

The experimental design contained two parts: extraction with the surfactants and chemical reaction by the Fenton's reactions. The surfactants were employed to extract the phenanthrene from the sands. Since the surfactants have been studied as the effective extractants, this work tried to find out the optimum operating parameters such as time, mixing, surfactant concentrations, and W/S (water/solid) ratio. The second part was the Fenton's reactions. The parameters which were optimized included time, mixing speeds, Fe(II) concentrations, and H₂O₂ concentrations.

4.4.1 Extractions by the Surfactants

The surfactant tests were to measure 2.0g phenanthrene spiked dried sand samples in the amber vials and added 1.0 mL surfactant solutions. The parameters such as the time, mixing speeds, surfactant concentrations and quantities were adjusted in order to determine the optimum values. After the surfactants extracting the phenanthrene, the samples were handled as in section 4.3.1. The supernatant solutions (about 0.5-0.6 mL) were decanted into the 6.0 mL vials and added 5.0 mL hexane was added. The vials were shaken vigorously by hand for 1 minute. The wet sand samples were dried in a hood for 1 hour and then 4.0 g Na₂SO₄ was added for drying the moisture. Then, 5.0 mL hexane was

added, and samples were sonicated for 30 minutes, twice. Both the solution and wet sand parts were analyzed by the HPLC. The sums of the recoveries of the phenanthrene concentrations should match the mass balance rule up to 100%.

4.4.1.1 Four Non-ionic Surfactants: The four non-ionic surfactants were employed in this study including Brij 30 (BR), Triton X-100 (TR), Tergitol NP-10 (TE), and Igepal CA-720 (IG). These surfactants were tested for time, mixing speeds, surfactant concentrations and the W/S ratios as follows:

The surfactant solutions were made the concentrations in 4% (vol./vol.) and mixed with the sand samples by the shaker. The sample vials were located in the shaker which was adjusted to 200 rpm for 10, 20, 30 and 60 minutes to find the optimum time for the following reactions.

The surfactants at 4% concentration were mixed with the sand samples and shaken for 30 minutes at 0rpm, 50rpm, 125rpm, 150rpm and 200rpm to obtain the optimum mixing speed.

The optimum surfactant concentration could be tested by testing the different concentrations. Under 125 rpm and 30 minute shaking time, the sand samples were mixed with five different concentrations of the surfactants such as 0.1%, 1%, 4%, 6% and 10% (vol./vol.).

The W/S (water to sand) ratio was employed by fixing the sand weights (2.0g). More surfactant volumes were added into the sand samples from 1mL to 2mL and 3 mL to compare the extraction effects of the surfactants.

4.4.1.2 Non-ionic and Ionic Surfactants: The better non-ionic surfactant (TE) was employed to compare with the anionic (SDS) and cationic (HTAB) surfactants. The parameters tested were the same as the above, including the time, mixing speeds, surfactant concentrations, and W/S ratios.

4.4.2 Fenton's Reactions

The chemical reactions by the Fenton's reagents were applied using five different concentrations of the Fe(II) solutions and five different concentrations of the H₂O₂ solutions. The related operating parameters such as the time, mixing speeds, Fe(II) concentrations and H₂O₂ concentrations were considered. All the tests were employed to have the same initial concentrations of phenanthrene in the sand samples. Therefore, 2.0g sand samples were measured in the amber vials and 1.0 mL reagent was added (0.5 mL Fe(II) solutions and 0.5 mL H₂O₂ solutions). The sample analysis included the extraction by hexane, sonication, and the HPLC analysis. However, the sums of phenanthrene concentrations from the solution parts and the residual parts in the sand samples could not obey the mass balance rule because the phenanthrene was decomposed by the Fenton's reactions. The residual phenanthrene concentration percentages could be the major indicators for the treatment effects.

In order to find out the optimum reaction time, the concentrations of the Fenton's reagents were made in [Fe(II)]= 4g/L and [H₂O₂]= 0.7%. The sand samples were added to the Fenton's reagents and shaken at 150 rpm. The reaction time was measured in 5, 10, 20, 30, 40, 50, and 60 minutes.

The relation between the mixing speeds, H₂O₂ and Fe(II) concentrations were observed. Two parameters were fixed and one was adjusted in each experiment. For example, the mixing speeds and the H₂O₂ concentrations were fixed, and the Fe(II) concentrations were adjusted. The mixing speeds of 50 rpm, 100 rpm, 150 rpm, and 200 rpm were applied for 30 minutes. The H₂O₂ concentrations were made by dilution in distilled water in 0.035%, 0.07%, 0.14%, 0.7% and 1.4% (vol./vol.). Firstly, the shaker was set to 50 rpm. The 2.0 g sand samples were prepared in 5 sets to which were added 0.5 mL H₂O₂ solutions at 0.035%, 0.07%, 0.14%, 0.7% and 1.4% for each set, respectively. Then, 0.5mL Fe(II) solutions were added in 0.4g/L to each vial to keep the total volume of added reagents 1.0 mL. In 50 rpm, the second and following tests were to

add Fe(II) solutions in 2g/L, 4g/L, 6g/L and 8g/L, respectively. Besides, in 0g/L, 0.5mL distilled water was used to replace the Fe(II) solutions. Therefore, there were six different Fe(II) solution concentrations (including 0g/L) in the 50 rpm tests. The next step was to adjust the mixing speed to 100 rpm, and the experiment repeated with the six different concentrations of the Fe(II) solutions. Again it was repeated at 150rpm and 200rpm.

4.4.3 Combined Effects

The Fenton's reactions were applied in three stages. Three sets of the sand samples were prepared in the vials in duplicate. The first stage was the $[\text{Fe(II)}]=4\text{g/L}$ and $[\text{H}_2\text{O}_2]=0.7\%$. The Fenton's reagents were added to the sand samples and shaken at 150rpm for 30 minutes. The residual phenanthrene concentrations in the first set of wet sand samples were measured. The second stage was to add the same amount of the Fenton's reagents to the second set of wet sand samples which were reacted after the first stage. They were shaken at 150 rpm for 30 minutes again. The residual phenanthrene concentrations in the wet sand samples were measured again. The third stage was continuous for the third set of wet sand samples from the second sets of samples by the same means as above. The residual phenanthrene concentration were measured to obtain the enhancement effects of three stages.

Except the three stages of Fenton's reactions, the combinations of the surfactant and Fenton's reagents were considered. One of the non-ionic surfactant, TE, in 4%, was chosen. The concentration conditions of the Fenton's reagents was $[\text{Fe(II)}]=4\text{g/L}$ and $[\text{H}_2\text{O}_2]=0.7\%$. The samples were shaken at 150rpm for 30 minutes. Two different combinations were performed. The first one was to add the TE and Fenton's reagents at the same time to the sand samples. The second try was to add the TE and shake at 150rpm for 30 minutes. Then the Fenton's reagents were added to the wet sand samples at 150rpm for 30 minutes again.

CHAPTER 5

RESULTS AND DISCUSSIONS

The residual phenanthrene concentration percentage (R%) values can be obtained from the ratios of the final residual phenanthrene concentrations in the sand samples divided by the initial phenanthrene concentrations (20 mg/L) in the spiked sand. The lower R% value expressed the lower residual phenanthrene concentrations in sand after extraction's of the surfactants or chemical reactions of the Fenton's reagents. Therefore, the more phenanthrene concentration was removed. The higher treatment efficiencies could be obtained.

5.1 Extractions by the Surfactants

The first part in the experimental design was extractions by surfactants from the phenanthrene-spiked sand. The extraction was used to wash out the target compound by the surfactants from sand. Then the phenanthrene was dissolved into surfactant solutions. In the extraction mechanism, no chemical reactions took place. There were six different surfactants employed in this study. Four of them were non-ionic and the other two were ionic: anionic and cationic. The phenanthrene was extracted by surfactants and dissolved into the surfactant solutions. Therefore, the sum of phenanthrene concentration recovery efficiencies should contain both the dissolved parts in the surfactant solutions and the residual parts in sand. By the mass balance rule, the sum of this two parts should approach to 100% except for minor experimental errors. Figure 1 and 2 show two different examples of the phenanthrene concentration recovery efficiencies at different conditions. The initial concentrations of phenanthrene-spiked sand samples were made at 20 mg phenanthrene/L hexane. In Figure 1, 8 tests including : blank (2.0 g dried spiked sand), blank with 1.0 mL distilled water, and blank with 6 different surfactants (1.0mL, 1%) were conducted at 125 rpm for 30 minutes. The sum of phenanthrene concentration recovery

was equal to that in the solution (empty bar) plus that in the residual sand surface (lined bar). The results showed all the phenanthrene concentration recovery of 6 surfactants reach above 90%. Figure 2 shows the second example at the 4% surfactant concentration at 0 rpm for 30 minutes.

The parameters such as the time, mixing speeds, surfactant concentrations, and W/S ratios were tested for the four non-ionic surfactants in section 5.1.1. The optimum non-ionic surfactant was obtained from this section. It was compared with the ionic surfactants in section 5.1.2. The results are shown in the following figures (Figure 3 to 20). The ordinate represents the residual phenanthrene concentration percentage (R%) by HPLC analysis. The abscissa indicates the various parameters such as the time, mixing speeds, surfactant concentrations and quantities (as W/S ratios).

5.1.1 Four Non-ionic Surfactants

Four non-ionic surfactants were Brij 30 (BR), Triton X-100 (TR), Tergitol NP-10 (TE), and Igepal CA-720 (IG).

Time effect

10, 20, 30, and 60 minutes were tested in order to find out the optimum reaction time. The concentration in 4% and the shaking speed in 200rpm were fixed. Figure 3 shows that the four non-ionic surfactants are capable to extract the phenanthrene from the spiked sand under certain conditions because the residual phenanthrene concentration percentages (R%) reduces with time. In the first 10 minutes, the curves drop sharply. Then, they slowly decrease until 20 minutes. After 20 minutes, the curves tend very smoothly and reach equilibrium until 60 minutes. For a safety reason, the time of 30 minutes was chosen as optimum reaction time for the following experiments. At 30 minutes, the residual phenanthrene concentration percentage (R%) values are about 50% except BR. It is about

70%. Therefore, the extraction effects of the surfactants reach about 50% under this conditions.

Mixing speeds

Various mixing speeds were tested such as 0 rpm, 50rpm, 125rpm, 150rpm and 200rpm. The 4% surfactants were added to the sand and shaken for 30 minutes. At 0rpm (without mixing), the 1 mL surfactant solutions were poured into the sample vials very slowly and carefully to prevent bubbles. Then, the sample vials were kept in the rack without shaking for 30 minutes. The reason for testing the 0rpm was to check the diffusion effect while the phenanthrene dissolving into the surfactant solutions. The other shaking speeds were designed in order to find out the optimum condition. Figure 4 shows that the curves are approaching the lowest points of the R% at 125rpm. However, the higher speeds at 150rpm and 200rpm do not enhance the treatment efficiencies compared with that at 125rpm. Therefore, the mixing speed at 125rpm can be considered economically as the optimum condition. Under this conditions, the residual phenanthrene concentration percentage (R%) is about 40-50%. However, the R% of BR is about 70%. The diffusion effect at 0 rpm, the R% is about 60-70% but R% of BR is about 90%. Therefore, by comparing with the R% values at 125rpm and 0 rpm, shaking effects are about 20% for the four non-ionic surfactants.

Surfactant concentrations

Five surfactant concentrations: 0.1%, 1.0%, 4.0%, 6.0%, and 10.0 % (vol./vol.) were made. 1 mL surfactant solutions were added to the sand and shaken for 30 minutes at 0 rpm or 125 rpm. The diffusion effects at 0 rpm is shown in Figure 5. The extraction effects at 125rpm are shown in Figure 6. In Figure 5, the residual phenanthrene concentration percentage (R%) values are about 80% at surfactant concentrations of 0.1% and 1%. The curves are decreasing while the concentrations were increased in 4%. The R% values

reduces to about 70% except BR. The R% values of the higher concentrations in 6% and 10% are similar to that in 4%. The higher concentrations of the surfactants did not enhance the extraction effects much. Therefore, the concentration of 4% can be chosen as the optimum condition economically. Besides, the concentration effect did not change much of BR. Figure 6 shows the curves decrease until the concentration higher than 4% at 125 rpm. Under this condition, the residual phenanthrene concentration percentage (R%) values are about 40-50%. BR reaches about 70%. Therefore, by comparing with the diffusion effects at 0 rpm, the extractions effects of the non-ionic surfactants are about 25% but BR only reaches about 10%. Besides, the mixing effect at 0 rpm and 125 rpm under different TE concentrations is shown in Figure 7. The R% between 0 rpm and 125rpm is increasing as the surfactant concentrations increasing from 0.1%, to 4%. However, higher than 4%, the enhancement is similar about 25% among 4%, 6% and 10%. Therefore, the concentration of 4% is more economical. The other surfactants (BR, TR and IG) are shown at 4% in the Figure 8, 9 and 10, respectively. In Figure 8, by comparing the extraction effect at 125 rpm with 0 rpm for BR is about 24%. In Figure 9, the extraction effect of TR is about 24%. In Figure 10, the extraction effect of IG is about 26%. The summary is shown in Table 3.

Table 3 The enhancement of mixing speeds for the four non-ionic surfactants (at surfactant concentration of 4%)

	TE	BR	TR	IG
0 rpm	65.4%	86.9%	63.7%	70.3%
125 rpm	40.7%	62.7%	39.5%	44.6%
enhancement	24.7%	24.2%	24.2%	25.7%

W/S ratios

The W/S (water/solid) ratios were tested by fixing the sand weights (2.0g), and adjusting the volume of surfactants as 1.0mL, 2.0mL, and 3.0mL. The 4% surfactants were mixed with sand at 0 or 125 rpm for 30 minutes. Figure 11 shows the diffusion effects at 0 rpm. Figure 12 shows the extraction effects at 125 rpm. In Figure 11, the residual concentration percentage of phenanthrene (R%) is about 60-70% except BR reaching 90% while 1.0 mL surfactants adding. The curves drop to about 40% but BR is about 50% while 2.0 mL surfactants are added. The higher W/S can enhance the diffusion effect (about 20%) by comparing with 1.0 mL and 2.0 mL surfactants adding. However, 3.0 mL surfactants can not enhance more diffusion effects because the R% values are similar to that of adding 2.0 mL surfactants. It indicates the more quantities of surfactants (more than 2.0 mL) can not obtain the linear relations of the higher treatment efficiencies. In Figure 12, R% is about 40%, except BR is about 70% when 1.0 mL surfactants are added. The curves drop to about 20-30%, but the curve of BR drop to about 20% while 2.0 mL surfactants adding. Therefore, the extraction effects are enhanced about 10-20% from 1.0 mL to 2.0 mL surfactants adding. The extraction effect of BR is higher about 50%. However, when adding 3.0mL surfactants, the R% values do not give better results than 2.0mL. Although 2.0 mL of surfactant is more efficient than 1.0 mL at 0rpm and 125rpm, 1.0 mL is selected for economic reasons.

5.1.2 Non-ionic and Ionic Surfactants

The Tergitol NP-10 (TE) was chosen as the optimum non-ionic surfactant to compare with the anionic (SDS) and cationic (HTAB) surfactants. The parameters tested were the time, mixing speeds, surfactant concentrations, and W/S ratios. Figure 13 shows the time effect for 10, 20, 30 and 60 minutes. The curves drop sharply in the first 10 minutes, then slowly decrease until 20 minutes. After 20 minutes, they are almost constant. Therefore, 30 minutes is selected as the optimum extraction time for the following tests. Figure 14

shows the mixing speed effects at 0rpm, 50rpm, 125rpm, 150rpm and 200rpm. At 125rpm, the residual phenanthrene concentration percentage (R%) values reduce to the lowest points for TE and SDS. Though the R% of HTAB is continuously decreasing at 150 rpm and 200 rpm, the R% differed in 5%. So, the optimum condition of mixing speed is chosen at 125rpm. The residual phenanthrene concentration percentages are about 40% under this condition. The surfactant concentration effects in 0.1%, 1.0%, 4.0%, 6.0% and 10.0% for the diffusion effects at 0 rpm show in Figure 15. the curves decrease at low surfactant concentrations. When the concentrations higher than 4%, the curves remain stable. Therefore, concentration of 4% is selected as the optimum condition. Meanwhile, the R% values of TE, SDS and HTAB are about 68%, 58%, and 45%, respectively. Figure 16 shows the extraction effects of surfactants at 125 rpm while the surfactant concentrations in 4%. Under this condition, the R% values of the three different surfactants are almost the same about 43%. Therefore, the extraction enhancements from 0 rpm to 125 rpm for TE, SDS and HTAB are about 24.7%, 13.8% and 3.4%, respectively (see Figure 17 and Figure 18). The summary is given in Table 4. The W/S ratios are the ratios of surfactant quantities to sand weights. Figure 19 shows the surfactant quantities at 0rpm for diffusion effects. The residual phenanthrene concentration percentage (R%) values of TE, SDS and HTAB are about 68%, 52%, and 42%, respectively while adding 1.0 mL surfactants. The R% values are similar while adding 2.0 mL and 3.0 mL. They are about 40%. Figure 20 shows the W/S ratio effects at 125 rpm. The R% values are about 40%, 20-30%, and 20% while 1.0 mL, 2.0 mL and 3.0 mL surfactants adding, respectively. For economic considerations, the 1.0 mL is chosen as the optimum volume.

Table 4 The enhancement of removal at different mixing speeds for the non-ionic and ionic surfactants (at surfactant concentration of 4%)

	TE	SDS	HTAB
0 rpm	65.4%	53.4%	42.9%
125 rpm	40.7%	39.6%	39.5%
enhancement	24.7%	13.8%	3.4%

5.2 Fenton's Reactions

The Fenton's reactions occurred when Fe(II) and H₂O₂ solutions were added into the sand to chemically react with the target compound. In this study, there are five different concentrations of Fe(II) solutions and five H₂O₂ concentrations tested. Since the Fenton's reagents are capable to decompose the phenanthrene, the sum of phenanthrene recovery efficiency from the dissolved parts in the solutions and the residual parts in sand can not obey the mass balance rule. The treatment efficiencies can be obtained by the residual phenanthrene concentration percentage (R%) in sand. Parameters such as the time, mixing effects with Fe(II) concentrations, and H₂O₂ concentrations were tested.

5.2.1 Time Effect

Reaction times such as 5, 10, 20, 30, 40, 50 and 60 minutes were tested in order to obtain the optimum condition. In Figure 21, the concentrations of Fenton's reagents are [Fe(II)]=0.1, 0.4 and 4g/L; and [H₂O₂]=0.7% and the mixing speed is at 150 rpm. The curves drop steeply and sharply in the first 10 minutes. After 10 minutes, the curves slowly decrease and smoothly approach to 60 minutes. This implies that the chemical reactions are very rapid and spontaneous as soon as the Fenton's reagents react with the phenanthrene on the spiked sand surface. Therefore, the time of 30 minutes is chosen as the optimum reaction time by considering the safety factor for the following reactions.

5.2.2 Mixing Speeds, Fe(II) and H₂O₂ Concentration Effects

The mixing speeds were adjusted at 50rpm, 100rpm, 150rpm and 200rpm, for 30 minutes while the Fenton's reagents were added into the sand samples. Figure 22 shows the effects of different [Fe(II)] (0, 0.4, 2, 4, 6, and 8g/L) at 50rpm while [H₂O₂]=0.035%, 0.07%, 0.14%, 0.7% and 1.4%. Under the same H₂O₂ concentration conditions, the Fe(II) concentration effects are shown in Figures 23, 24 and 25 at 100, 150 and 200 rpm, respectively. In Figure 22, the H₂O₂ concentrations are in log scale. The curves tend decreasing as the H₂O₂ concentrations increasing except the [Fe(II)]=0g/L curve (without Fe(II) solutions, only adding the H₂O₂ solutions). The residual phenanthrene concentration percentage (R%) of the [Fe(II)]=0g/L curve only fluctuate by 5% so that it is almost independent of the H₂O₂ concentrations. The [Fe(II)]=2g/L curve shows an optimum value at [H₂O₂]=0.7% while the R% was higher at [H₂O₂]=1.4%. While [H₂O₂] between 0.14% and 0.7%, the differences of the R% values are about 20%. Therefore, the optimum H₂O₂ concentration can be 0.7% in the certain conditions for the economic consideration. Moreover, the [Fe(II)]= 2g/L curve can reach the lowest R% about 38% while [H₂O₂]= 0.7%. The best Fe(II) concentration can be 2 g/L to approach the best treatment efficiencies. However, the R% values are about 90% in the same H₂O₂ concentration conditions while the [Fe(II)]=0g/L and [Fe(II)]=0.4g/L. Therefore, the low Fe(II) concentrations can initialize fewer radicals for the Fenton's reactions. The treatment efficiencies are hardly enhanced without or in low Fe(II) concentrations in the certain conditions. The similar situations are shown in Figures 23, 24 and 25 at different mixing speeds. In Figure 23, the lowest R% is about 30% while [Fe(II)]=8 g/L and [H₂O₂]= 0.7% at 100 rpm. The R% value of [Fe(II)]=0 g/L curve is lower about 75%. Figure 24 shows the lowest R% of [Fe(II)] is 4g/L at 150 rpm. The lowest R% is about 33% in Figure 25 while [Fe(II)]=4g/L and [H₂O₂]=0.7%. The concentration effects of [Fe(II)] are summarized in Table 5.

Table 5 The optimum Fe(II) concentrations at different mixing speeds while $[H_2O_2]=0.7\%$

rpm	50	100	150	200
R%	38%	30%	36%	33%
Fe(II), g/L	2	8	4	4

The mixing speed effects are shown in Figures 26, 27, 28, 29, 30 and 31 by adjusting the Fe(II) concentrations while the five different H_2O_2 concentrations are fixed. In Figure 26, there is no Fe(II) solutions added. The 0.5 mL Fe(II) solutions are replaced by the distilled water. Therefore, 0.5 mL distilled water and the 0.5 mL H_2O_2 solutions are added to the sand samples. The R% values (about 73% to 78%) are fluctuated in 5% differences only among 100rpm, 150rpm and 200rpm. However, at 50rpm, the R% values are about 90% by increasing H_2O_2 concentrations. This indicates the residual phenanthrene concentrations are H_2O_2 concentration independent. Besides, the R% values are about 70-80% among 100, 150 and 200 rpms. Therefore, the higher mixing speeds do not enhance the treatment efficiencies. In Figure 27, the Fe(II) concentration=0.4 g/L. The 150rpm curve shows the lowest R% about 50% while $[H_2O_2]=0.7\%$. The lowest R% is located about 60%, and 70% at 100rpm and 200 rpm, respectively. At 50rpm, the lowest R% is about 90%. Therefore, 150rpm can be the optimum mixing speed under these conditions. In Figure 28, $[Fe(II)]=2g/L$, the curves decrease with the increasing H_2O_2 concentrations. The R% values are about 40% to 50% of the four curves while $[H_2O_2]$ in 0.7%. This implies the mixing speeds do not affect the R% values much. The R% values are lower than 50% at the four mixing speeds. This indicates that there is only about half amount of the target compound left in sand under these conditions. In Figure 29, $[Fe(II)]=4g/L$, the curves decrease until the $[H_2O_2]=0.7\%$ while the R% values are about 32% to 35% at 100, 150 and 200 rpms. At 50rpm, the R% can reach about 48%. The higher concentration of H_2O_2 in 1.4% do not enhance much of the treatment efficiencies. In

Figure 30 and 31, the curves reduce as the H_2O_2 concentrations increasing. From Figure 30, $[Fe(II)] = 6g/L$, the R% value is about 37% at 150 rpm while $[H_2O_2] = 0.7\%$. In Figure 31, $[Fe(II)] = 8g/L$, the R% value is about 38% , and 32% at 150 rpm and 100 rpm, respectively while $[H_2O_2] = 0.7\%$. Therefore, the R% values can reach about 30% with the addition of Fe(II) solutions of 4g/L to 6g/L and 8g/L while $[H_2O_2] = 0.7\%$. For economic considerations, the 4g/L of Fe(II) solutions with $[H_2O_2]$ in 0.7% are chosen as the optimum conditions. The optimum mixing speeds are summarized in Table 6. Therefore, the optimum conditions of Fenton's reactions could be obtained while $[Fe(II)] = 4g/L$, $[H_2O_2] = 0.7\%$, at 50rpm for 30 minutes.

Table 6 The optimum mixing speeds at different $[Fe(II)]$ while $[H_2O_2] = 0.7\%$

Fe(II), g/L	0.4	2	4	6	8
R%	50%	40-50%	30-40%	30-40%	30-40%
rpm	150	50,100, 150,200	100,150, 200	150, 200	100, 150

5.3 Combined Effects

From section 5.1, the surfactants can extract phenanthrene from the spiked sand under certain conditions. The sum of the recovery efficiency of that dissolved in surfactant solutions and that in sand should obey the mass balance rule approaching to above 90%. Therefore, the sum should be almost equal to the initial concentrations of phenanthrene (20mg/L) except the acceptable errors. However, the surfactant extractions resulted in the second disposal problems need to be further treated. The phenanthrene was actually transferred from sand to the surfactant solutions. However, Fenton's reactions proved that the phenanthrene was effectively decomposed from the spiked sand. Therefore, this chemical reaction was able to decrease the phenanthrene concentration on the sand surface. Since the Fenton's reactions were effective for the decomposition of the

phenanthrene, the series of Fenton's reactions were employed to enhance the treatment efficiencies. The combination of surfactant extractions and Fenton's reactions was conducted to compare the treatment efficiencies.

The series of Fenton's reactions were tested in three stages in Figure 32. The concentrations were in $[\text{Fe(II)}]=4\text{g/L}$, and $[\text{H}_2\text{O}_2]=0.7\%$ at 150rpm for 30 minutes. The residual phenanthrene concentration percentage (R%) is about 43% after the first stage in the certain conditions. The R% reduces to about 17% after the second stage. Additionally, the R% reduce continuously to about 7%, after the third stage. Therefore, the additional effects of the Fenton's reactions in three stages can efficiently decompose the phenanthrene over 90%. Therefore, the series of reactions proved more effective than a single reaction.

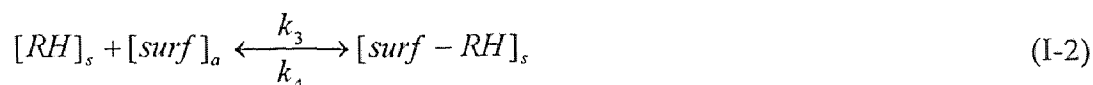
The combinations of surfactant, TE (in 4%) and Fenton's reagents ($[\text{Fe(II)}]=4\text{g/L}$, $[\text{H}_2\text{O}_2]=0.7\%$) were conducted to compare the treatment efficiency with the addition of surfactant only. There were two combination methods. The first method was used to mix TE with Fenton's reagents in sand at the same time at 150 rpm for 30 minutes. The second method was used to add TE into sand first and shake at 150 rpm for 30 minutes, then add Fenton's reagents at 150rpm for 30 minutes. Figure 33 shows almost no differences between these two combination methods by comparing with the residual phenanthrene concentration in sand and in solution. The phenanthrene concentrations in surfactant or mixed solutions among the three groups of figures were similar about 44-46%. However, comparing the residual phenanthrene concentrations in sand, the R% values of two combinations (18% and 20%) are lower than that adding surfactant only (about 48%). The sums of phenanthrene concentrations in two combinations (about 63%) are also lower than that adding surfactant only (92%). This implies that two combinations obtain the similar effects. Fenton's reagents can be added with the surfactant at the same time or in sequence. Meanwhile, in the combinations, Fenton's reagents can decompose the residual phenanthrene on the sand surface. This results in lower residual phenanthrene

concentrations in sand in the combinations than that of adding the surfactant only. The major concern of the residual phenanthrene concentration in sand under certain conditions is showed in Figure 34. The R% value of single Fenton's reaction is about 32% (see Figure 32). The R% is about 48% and 20% for adding surfactant only and the combination, respectively. This implies the combination can enhance the residual phenanthrene concentration reduction by comparing with adding surfactant only.

5.4 Modeling

5.4.1 Dissolving of Phenanthrene from Sand Surface by Surfactants

From the model described in chapter 3,



$$\frac{d[surf - RH]_a}{dt} = k_5[surf - RH]_s \quad (I-6)$$

- (1) The time zone from $t = 0$ to the time when Equation (I-2) reaches its steady state ($t = 0$ to 20 minutes): In this time zone, the large values of initial $[RH]_s$ and $[surf]_a$ yields high value of $[surf-RH]_s$ forming rate as indicated in Equation (I-2). Thus, it causes a large disappearance rate of phenanthrene from sand surface as indicated by Equation (I-6). The model expressions could be corroborated by the experimental results shown in Figure 3 and 13. In the first 20 minutes, the residual phenanthrene concentrations dropped sharply.
- (2) After a certain time, the whole system reaches its equilibrium ($t= 30$ or more minutes). The curves decreased monotonically reaching equilibrium after 30 minutes in Figure 3 and 13.

$$\frac{[RH]_{s0} - m[surf - RH]_a}{[RH]_{s0}} = 1 - m \frac{k_5[RH]}{k_6[RH]_{s0}} [surf]_a \quad (I-11)$$

Equation (I-11) may be used to interpret the effects of surfactant concentration and mixing speed on the equilibrium value of residual phenanthrene concentration in sand.

Under equilibrium condition, $[surf]_a$ should increase with respect to initial surfactant concentration $[surf]_{a0}$ at low $[surf]_{a0}$. When $[surf]_{a0}$ is larger than a certain critical value, micelles will form and $[surf]_a$ becomes independent of $[surf]_{a0}$. The residual phenanthrene concentration is affected accordingly. The effects of surfactant concentration for the four nonionic surfactants are show in Figure 5. The residual phenanthrene concentration percentages are decreasing as surfactant concentrations increase when the concentrations are smaller than 4% at 0 rpm. When surfactant concentrations are greater than 4%, the residual phenanthrene concentration percentages are independent of surfactant concentrations. Figure 6 shows the same situation at 125 rpm. Figure 15 and 16 show the same effects for the ionic surfactants.

Under equilibrium condition, the mixing speed causes the reverse reaction of Equation (I-1). Therefore, higher mixing speed will increase the value of k_2 and thus, the value of equilibrium $[surf]_a$ and lower the value of residual phenanthrene concentration in sand. For the four non-ionic surfactants, Figure 4 and 14 show the residual phenanthrene concentration percentages decreased as the mixing speed increases up to 125 rpm. However, at the higher mixing speed, greater than 125 rpm, no further reduction in phenanthrene concentration occurs. Figure 7 shows the mixing effect from 0 rpm to 125rpm with different surfactant concentrations for Tergitol NP-10. The same effects are shown in Figure 8 for Brij 30, Figure 9 for Triton X-100 and Figure 10 for Igepal CA-720. Figures 11 and 12 also show that mixing effects decrease the residual phenanthrene concentration from 0 rpm to 125 rpm. Mechanical mixing enhances the dissolution of phenanthrene into the surfactant solutions. Thus, the residual phenanthrene concentration

in sand decreases. Similar effects of mixing speeds are seen in Figure 14, 15, 16, 17, 18, 19 and 20 for the ionic surfactants.

5.4.2 Fenton's Reaction with Phenanthrene on the Sand Surface

$$-\frac{d[RH]_s}{dt} = k_9[RH]_s \frac{K_p \{ [Fe^{+2}]_0 - [Fe^{+3}] \} [H_2O_2]}{[OH^-][Fe^{+3}]} \quad (\text{II-4})$$

At the beginning of the reaction; $t \rightarrow 0$, $[Fe^{+3}]$ is small :

$$-\left. \frac{d[RH]_s}{dt} \right|_{t=0} = k_9[RH]_s \frac{K_p [Fe^{+2}]_0 [H_2O_2]}{[OH^-][Fe^{+3}]} \quad (\text{II-5})$$

Equation (II-5) shows that the initial rate of phenanthrene reduction in sand increases as $[Fe^{+2}]_0$ increases. Experimental results are shown in Figure 21. The phenanthrene reduction rate in sand is drastically decreased, when the reaction time passes ten minutes. The rate is independent of $[Fe^{+2}]_0$. From Equation (II-4), the residual phenanthrene concentration in sand reaches steady state after 10 minutes.

After 10 minutes, $-\frac{d[RH]_s}{dt} = 0$, as the interphase reaction also reaches equilibrium,

$$[RH]_s = \frac{k_{10}[OH^-]^2[Fe^{+3}]^2}{k_9 K_p [Fe^{+2}][H_2O_2]} \quad (\text{II-8})$$

Equation (II-8) shows that the residual phenanthrene on sand surface will become smaller when a larger dose of $[Fe^{+2}]_0$ is used. Also, Equation (II-8) shows the same effect

when a larger dose of $[H_2O_2]$ is used. Figures 22, 23, 24 and 25 show the experimental results at 50 rpm, 100 rpm, 150 rpm and 200 rpm.

The residual phenanthrene concentration on sand surface is mostly affected by three factors, i.e., mixing speed, initial Fe(II) concentrations and initial concentrations of H_2O_2 . Experimental results in Figures 27, 28, 29, 30 and 31 show that mixing speed and H_2O_2 concentrations affect residual phenanthrene concentrations as a function of different Fe(II) concentrations.

5.4.3 Combination Effects of the Surfactant and Fenton's Reaction on the Removal of Phenanthrene on Sand Surface

Under equilibrium condition, the residual phenanthrene concentration in sand (RPCPIS) can be expressed :

$$RPCPIS = -\frac{k_3 k_5 m [RH]_s [surf]_a}{k_4 k_6 [RH]_{s0}} + \frac{k_{10} k_{12} [ROH] [Fe^{+3}]^2 [OH^-]^2}{[RH]_{s0} k_9 k_{11} k_p^2 [Fe^{+2}]^2 [H_2O_2]^2}$$

$$=-A+B \quad (\text{note: } B>A)$$

where A is $\frac{k_3 k_5 m [RH]_s [surf]_a}{k_4 k_6 [RH]_{s0}}$, and B is $\frac{k_{10} k_{12} [ROH] [Fe^{+3}]^2 [OH^-]^2}{[RH]_{s0} k_9 k_{11} k_p^2 [Fe^{+2}]^2 [H_2O_2]^2}$

when A is large, more $[RH]_s$ is going into aqueous phase due to the surfactant. So RPCPIS will be small. When $[H_2O_2]$ is large, B is small, so RPCPIS is small. When $[Fe^{+2}]$ is large, B is small, so RPCPIS is small. Figures 33 and 34 show that the two mechanisms for removal of phenanthrene from the sand surface do not seem to interfere with each other. One can see that (1) the concentration of RH in solution is identical in cases 1, 2 and 3 as shown in Figure 33. (2) the decrease in RH concentration by case 2 and case 3 are identical as shown in in Figures 33 and 34.

CHAPTER 6

CONCLUSIONS

From experimental results, both the extractions with the surfactants and chemical reactions by the Fenton's reagents were effective to treat the phenanthrene-spiked sand samples. The optimum conditions were considered, including the safety factors and economic considerations. The conclusions are as follows:

6.1 Extractions

The parameters such as the time, mixing speeds, surfactant concentrations and quantities were tested in order to find the optimum conditions. The sums of the phenanthrene concentration recoveries should match the mass balance rule up to 100% including what in the surfactant solutions and what in the residual sand samples. Figure 1 and 2 were the examples. The extractions by surfactants were divided into two parts: (1) Non-ionic and (2) Non-ionic and ionic.

6.1.1 Four Non-ionic Surfactants

The four non-ionic surfactants were Brij30 (BR), Triton X-100 (TR), Tergitol NP-10 (TE), and Igepal CA-720 (IG).

Time effect

In Figure 3, the surfactant concentrations were in 4% at mixing speed of 200 rpm. The residual phenanthrene concentration percentage (R%) values after 20 minutes (to 60 minutes) are fluctuated between 40-50%, so the R% of 20, 30 and 60 minutes were similar. Therefore, 30 minutes can be the optimum extraction time for a safety reason.

Mixing speed

In Figure 4, the mixing speeds at 0 rpm, 50 rpm, 125 rpm, 150 rpm and 200 rpm were tested at surfactant concentrations of 4% for 30 minutes. In these conditions, the lowest residual phenanthrene concentration percentage (R%) was about 40-50% at 125 rpm, except that with BR was about 70%. Therefore, 125 rpm was chosen as the optimum mixing speed for obtaining the lowest residual phenanthrene concentration in the sand samples after extractions by the surfactants.

Surfactant concentrations

In Figure 5 and 6, at 0 rpm and 125 rpm for 30 minutes, the residual phenanthrene concentration percentage (R%) values were improved while the concentration of surfactants were in 4%, 6% and 10%. There were small differences in the R% values among the three different concentrations. Therefore, the concentrations in 4% were chosen as the optimum condition for the economic considerations. The residual phenanthrene concentration percentage can be improved by increasing the mixing speed from 0 rpm to 125 rpm. For examples, TE was enhanced about 25%, BR was about 25%, TR was about 24% and IG was about 26% in Figure 7, 8, 9 and 10. The enhancement effects were similar among the four non-ionic surfactants.

W/S ratios

The W/S (water to sand) ratio was varied to see if the more surfactant volumes (2 or 3 mL) can enhance the extraction effects or not. From the results in Figure 11 and 12, the better residual phenanthrene concentration percentage (R%) can be obtained by adding 2 mL than 1 mL surfactants. However, the R% values were similar between adding 2 mL or 3 mL surfactants. Since the surfactants mainly transferred the phenanthrene from sand to the solutions, a second disposal problem arises. A minimum of surfactants should be added, so 1.0 mL of surfactants, were then chosen as the optimum conditions.

6.1.2 Non-ionic and Ionic Surfactants

The Tergitol NP-10 (TE) was the typical non-ionic surfactant which was chosen to compare with the anionic (SDS) and cationic (HTAB) surfactants. The tested parameters were time, mixing speed, surfactant concentration and W/S ratio. The time effect at 30 minutes was chosen as the optimum condition because that the curves were near to be constant after 20 minutes. Therefore, 30 minutes was selected for safety considerations. Besides, in these conditions, for 30 minutes, the residual phenanthrene concentration percentage (R%) of TE (non-ionic) was about 50%, SDS (anionic) was about 48%, HTAB (cationic) was about 33%. This implied the ionic surfactants were better able to extract the phenanthrene than non-ionic one in these conditions. The mixing speed of 125rpm was chosen as the optimum, since the R% values were best for TE and SDS. Though HTAB was continuously decreasing at 150rpm and 200rpm with small differences. Meanwhile, the residual phenanthrene concentration percentage values were almost the same for these three surfactants about 40%. The concentration effects of surfactants in unstirred solution were tested in order to check the diffusion effects. At the concentrations of 4%, the lowest residual phenanthrene concentration percentage (R%) of TE was about 68%, SDS was about 58%, and HTAB was about 45%. For the phenanthrene diffusion from sand into solution at 0 rpm, the cationic surfactant was the better one. At 125 rpm, the surfactant concentration of 4% was chosen as the optimum condition. The residual phenanthrene concentration percentage values were about the same at 43%. Therefore, the extraction effects are about the same among these surfactants. However, the extraction enhancements from 0 rpm to 125 rpm for TE was about 25%, SDS is about 18% and HTAB is about 3%. Therefore, the enhancement of the non-ionic was better than that of the ionic. The W/S ratios showed at 0 rpm in 4% for diffusion. The residual phenanthrene concentration percentage (R%) of TE was about 68%, SDS was about 58%, and HTAB was about 45% while adding 1.0 mL surfactants. The R% values were about 40% while adding 2.0 mL and 3.0 mL surfactants. Therefore,

greater amounts of surfactants can enhance the diffusion effects. However, for economic considerations and fewer disposal problems, 1.0 mL was chosen as the optimum volume. At 125 rpm and concentrations at 4%, the R% values of three surfactants were about 40% while 1.0 mL of surfactants adding, 20-30% while 2.0 mL adding, and 20% while 3.0 mL adding. The extraction effects were about the same for the three surfactants at the tested conditions. Therefore, the optimum volume was selected as 1.0 mL for safety considerations.

6.2 Fenton's Reactions

The Fenton's reactions were employed in this study by testing five different concentrations of Fe(II) solutions and five H₂O₂ concentrations to find out the optimum amounts for both Fe(II) and H₂O₂. The other tested parameters were time, mixing effects, Fe(II) and H₂O₂ concentrations. The optimum conditions can be obtained by considering the lower residual phenanthrene concentration percentage (R%) values and less amounts of the reagents.

6.2.1 Time Effect

In Figure 13, the optimum reaction time can be obtained at 30 minutes while [Fe(II)]=4g/L and [H₂O₂]= 0.7% at 150 rpm. After 10 minutes, the curve slowly descended and smoothly approached to steady state until 60 minutes. The residual phenanthrene concentration percentage (R%) varied from 35% to 40%. This indicated the chemical reactions were spontaneous and very fast in the first 10 minutes. The Fenton's reagents reacted with the phenanthrene on the spiked sand in a very short time, then the reaction slowed. Therefore, by considering the safety factor, 30 minutes of the reaction time was chosen as the optimum condition.

6.2.2 Mixing Speeds, Fe(II) Concentrations and H₂O₂ Concentration Effects

In Figure 22, at 50 rpm, the effects of different Fe(II) concentrations with five H₂O₂ concentrations were employed. Most of the curves showed decreasing trend as the H₂O₂ concentrations increasing. The [Fe(II)]=2g/L curve gave an optimum value for R% of 38% while [H₂O₂] was 0.7%. The residual phenanthrene concentration percentage (R%) was getting higher after 0.7% and 1.4%. For the economic considerations, the optimum H₂O₂ concentration was selected as 0.7%. The optimum conditions of the Fe(II) concentration effects was as follows while [H₂O₂] was 0.7%. At 100 rpm, the lowest R% was about 30% while [Fe(II)]=8 g/L. At 150 rpm and [Fe(II)]= 4g/L, the lowest R% was about 36%. At 200 rpm, the optimum [Fe(II)] was 4g/L and the R% was about 33%. Therefore, the conditions of [Fe(II)]=4g/L and [H₂O₂]=0.7% at 150 rpm for 30 minutes were chosen as the optimum operating conditions.

By fixing the concentrations of the Fe(II) solutions and the H₂O₂, the mixing speed effects can be obtained. While [Fe(II)] =0g/L (Fe(II) solution was replaced by the distilled water), the reactions are H₂O₂ concentration independent. Besides, the R% values were fluctuated in 5% (about 73% to 78%) while at 100 rpm, 150 rpm and 200 rpm except about 90% at 50 rpm. Therefore, the higher mixing speeds did not enhance the treatment efficiencies.

When the [Fe(II)]=0.4 g/L 150 rpm provided the lowest residual phenanthrene concentration percentage (R%), about 50% among the curves. Therefore, 150 rpm can be the optimum condition. In 2g/L of the Fe(II), the R% values were about 40% to 50% in the four curves when [H₂O₂] was 0.7%. This indicated the mixing speeds did not affect the R% very much. At Fe(II)=4g/L, the R% values were about 32%-35% at 100 rpm, 150rpm and 200 rpm except that 50 rpm (about 48%). Therefore, while [Fe(II)]=4g/L, the R% values can reach about 30%. The treatment effects were fairly acceptable. At [Fe(II)]=6g/L, the lowest R% value was about 37% at 150 rpm. At [Fe(II)]=8g/L, the R% value was about 38% at 150 rpm and about 32% at 100 rpm. Therefore, the R% values

can reach about 30% when $[H_2O_2]=0.7\%$ and Fe(II) solutions were in 4g/L, 6g/L to 8 g/L. For the economic considerations, $[Fe(II)]=4g/L$ with $[H_2O_2]=0.7\%$ at 150 rpm for 30 minutes were chosen as the optimum operating conditions.

6.3 Combined Effects

Although the surfactants can extract the phenanthrene from the sand samples, there were the further disposal problems. This is because the phenanthrene was not degraded by surfactants. The dissolved phenanthrene in the surfactant solutions needed to be further treated. However, the Fenton's reagents can effectively decompose the phenanthrene from the spiked sand. For further enhancement, the series of Fenton's reactions, or the combinations of surfactant extractions and Fenton's reactions were employed. There were three stages for the series of the Fenton's reactions. The Fenton's reagents were added into the spiked sand three times. The reagent conditions were applied in $[Fe(II)]=4g/L$ and $[H_2O_2]=0.7\%$ at 150 rpm for 30 minutes. The residual phenanthrene concentration percentage (R%) decreased stage by stage from about 32% to 18%, to about 7% in the third stage. Therefore, the series of the Fenton's reactions can efficiently decompose over 90% of the phenanthrene.

The second disposal problems needed to be handled for the dissolved phenanthrene in the surfactant extractions from the spiked sand. Therefore, the combinations of surfactant solutions and the Fenton's reagents were employed. The concentrations of Fenton's reagents were $[Fe(II)]=4g/L$ and $[H_2O_2]=0.7\%$. The concentration of TE was at 4%. Two different combination methods were employed: (1) TE and Fenton's reagents were mixed at the same time, and (2) TE was added first, followed by the addition of Fenton's reagents. By comparing these two methods, the phenanthrene concentrations in the solutions were similar, about 44-46%. The residual phenanthrene concentration percentage in the spiked sand of the two combinations (18% and 20%) were also similar. This implied that the two combinations resulted in similar effects. Therefore, the surfactant

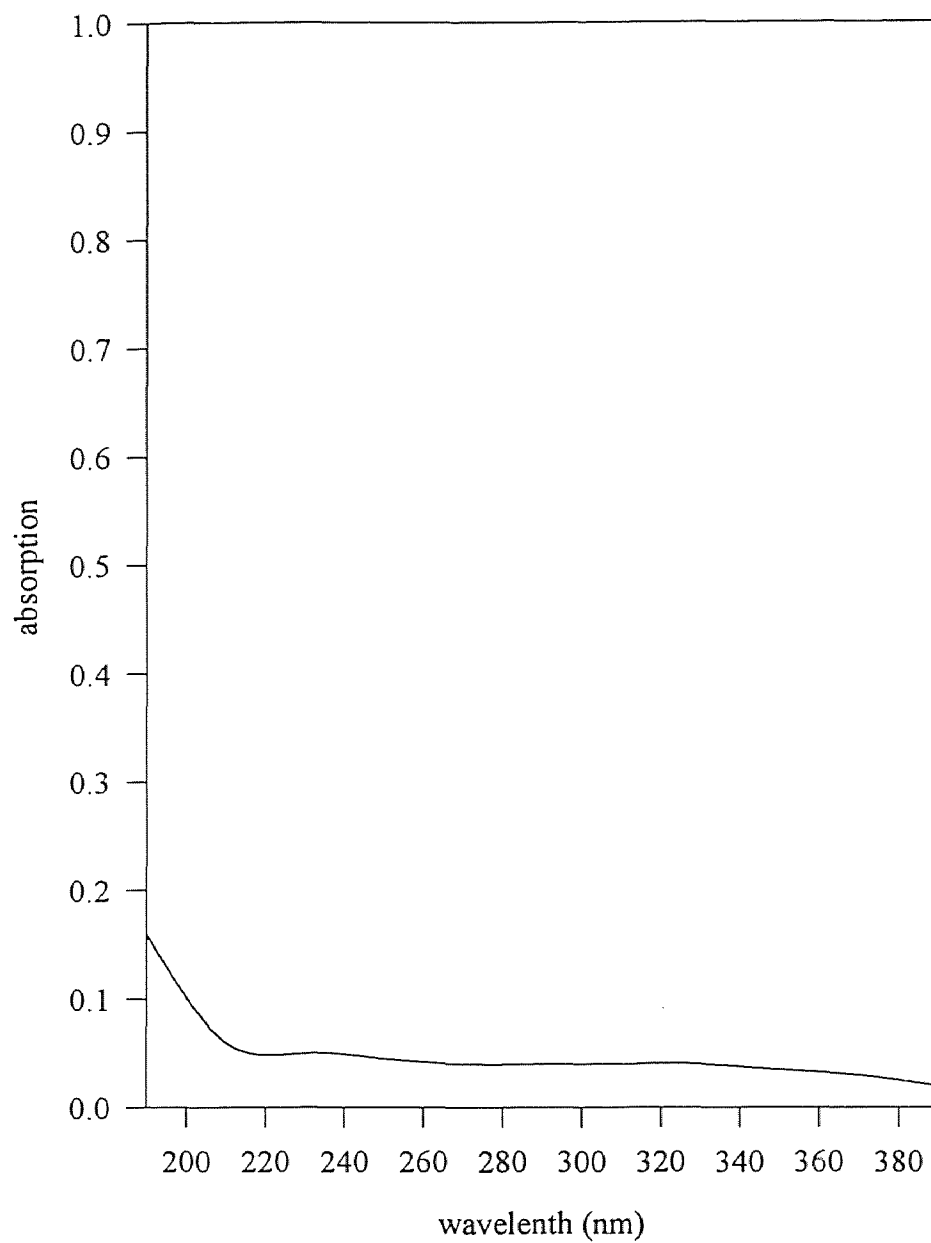
solutions and Fenton's reagents can be added to the sand samples at the same time or in sequences. The combinations of surfactant and Fenton's reagents were found to be better than by the addition of surfactant only. In the combinations, the residual phenanthrene concentrations in the sand samples and the sums of both phenanthrene concentrations in solutions and the residual in the sand samples were lower than that of adding the surfactant only. However, the phenanthrene concentrations in the solutions were about the same for both the combinations and only surfactant. This implied, in the combinations, the Fenton's reagents could continuously decompose the phenanthrene on the sand surfaces. Therefore, using the combinations of surfactants and Fenton's reagents can enhance the treatment efficiencies.

6.4 Modeling

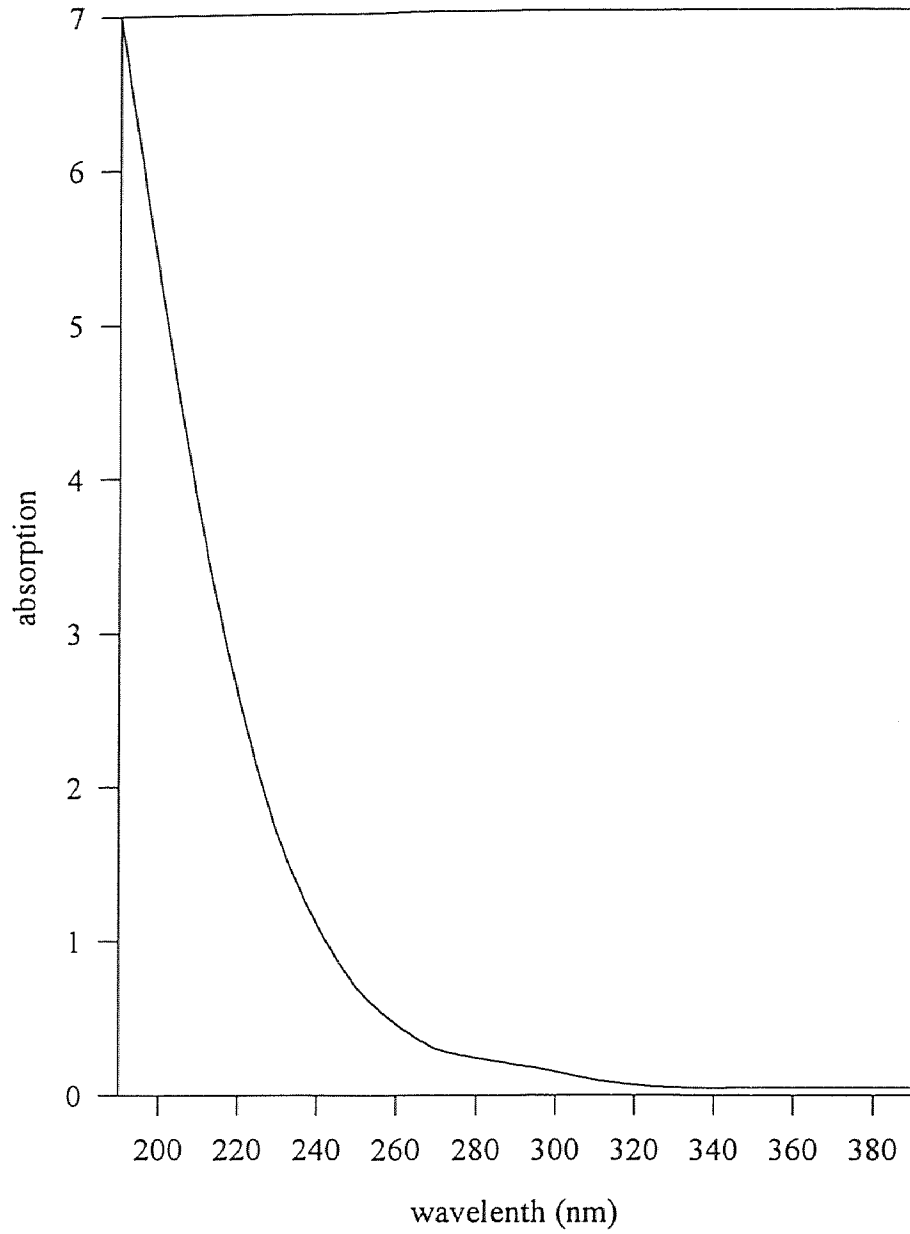
The model was developed (in Chapter 3) that can qualitatively predict the residual phenanthrene concentration on sand surface as a function of time, mixing speed, and concentrations of surfactant or Fenton's reagents. The model included three parts: (1) dissolving of phenanthrene from sand surface by surfactants; (2) Fenton's reaction with phenanthrene on sand surface; and (3) the combination effects of the surfactants and Fenton's reaction on the removal of phenanthrene on sand surface. The model was in good agreement with the experimental results.

APPENDIX 1
MODEL ASSUMPTION

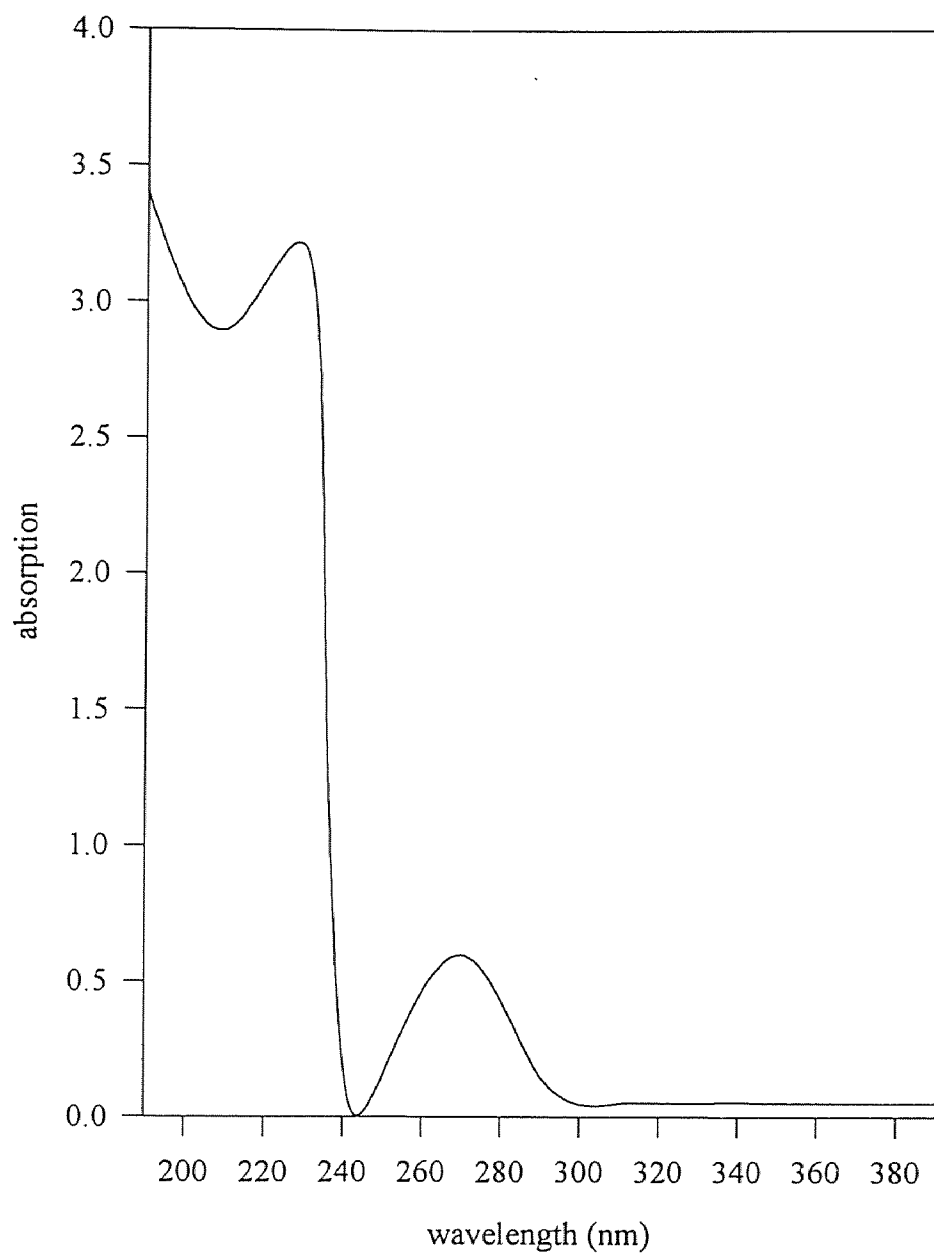
In order to prove that the surfactant is not oxidized by Fenton's reagents, the following experiments were conducted. The Fe(II) solution, H₂O₂ reagent, pure surfactant TE and the mixture (after the TE was mixed with Fenton's reagents at 125rpm for 30 minutes) were scanned in the UV-Visible range using Varian DMS 300 UV-Visible spectrophotometer. The spectra are shown in the following pages. Fe(II) shows low absorption in the range. H₂O₂ shows a bulk absorption below 270nm. Pure surfactant, TE, has a characteristic absorption of 0.748 at 276.9nm. The mixture shows the characteristic absorption of 0.782 at 276.3nm. By comparing TE and mixture, the surfactant property did not seem to be changed by the Fenton's reaction. Therefore, we assumed that the surfactant is not oxidized by Fenton's reagents.



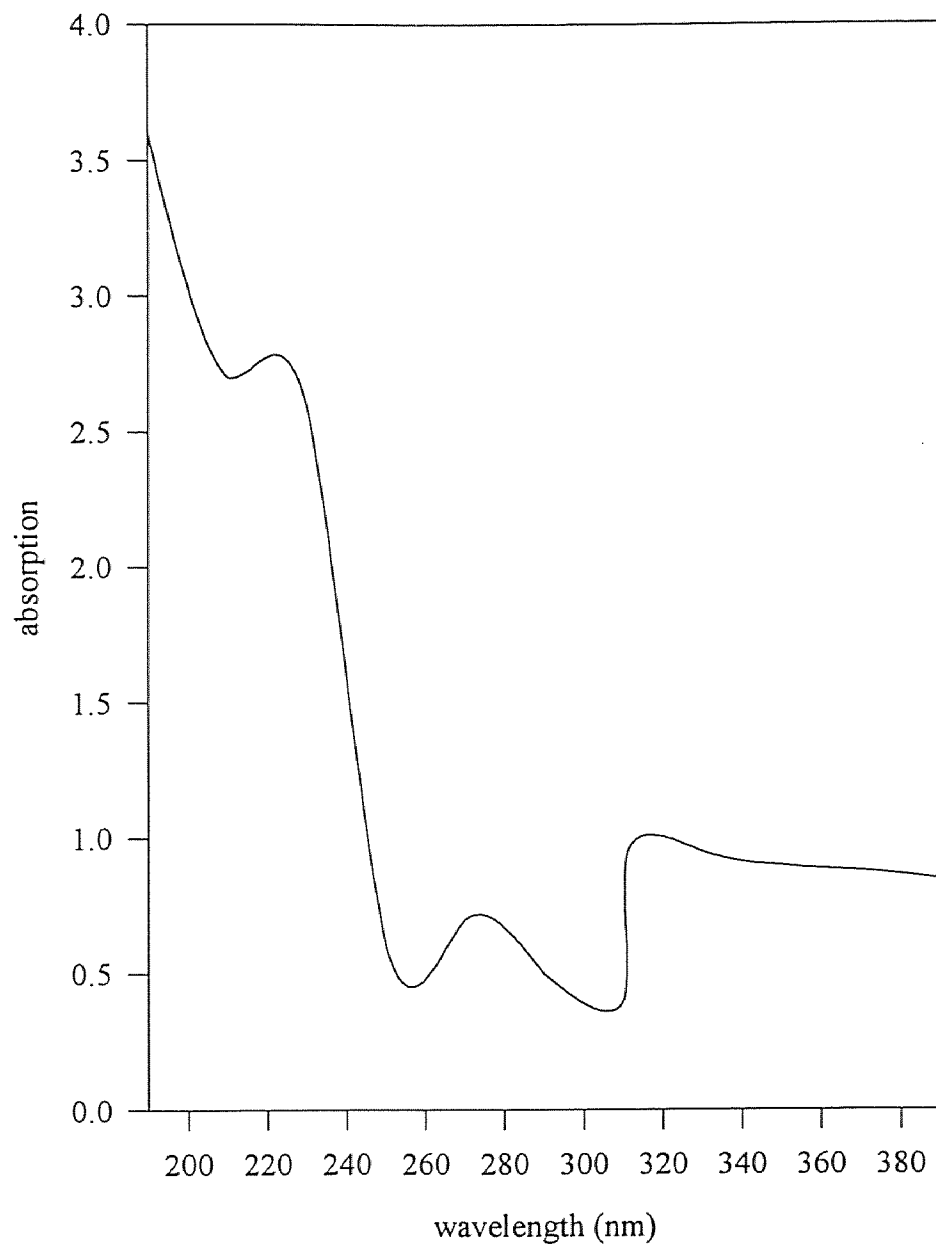
Spectrum of Fe(II) solution



Spectrum of H₂O₂ reagent



Spectrum of Tergitol NP-10 (TE) solution



Spectrum of mixture of TE and Fenton's reagents

APPENDIX 2
FIGURES

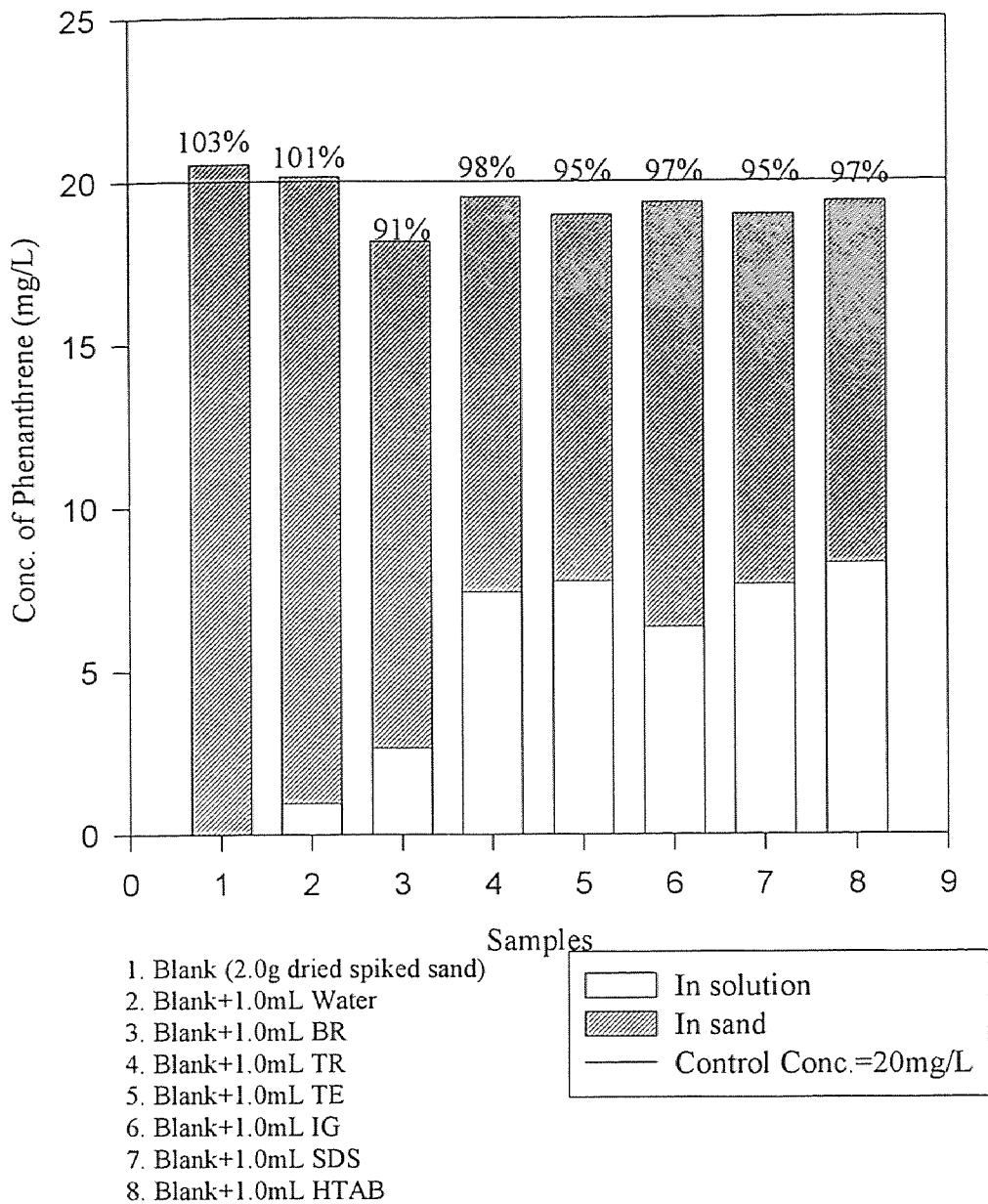


Figure 1 The recovery efficiencies of surfactants in 1% at 125 rpm for 30 minutes

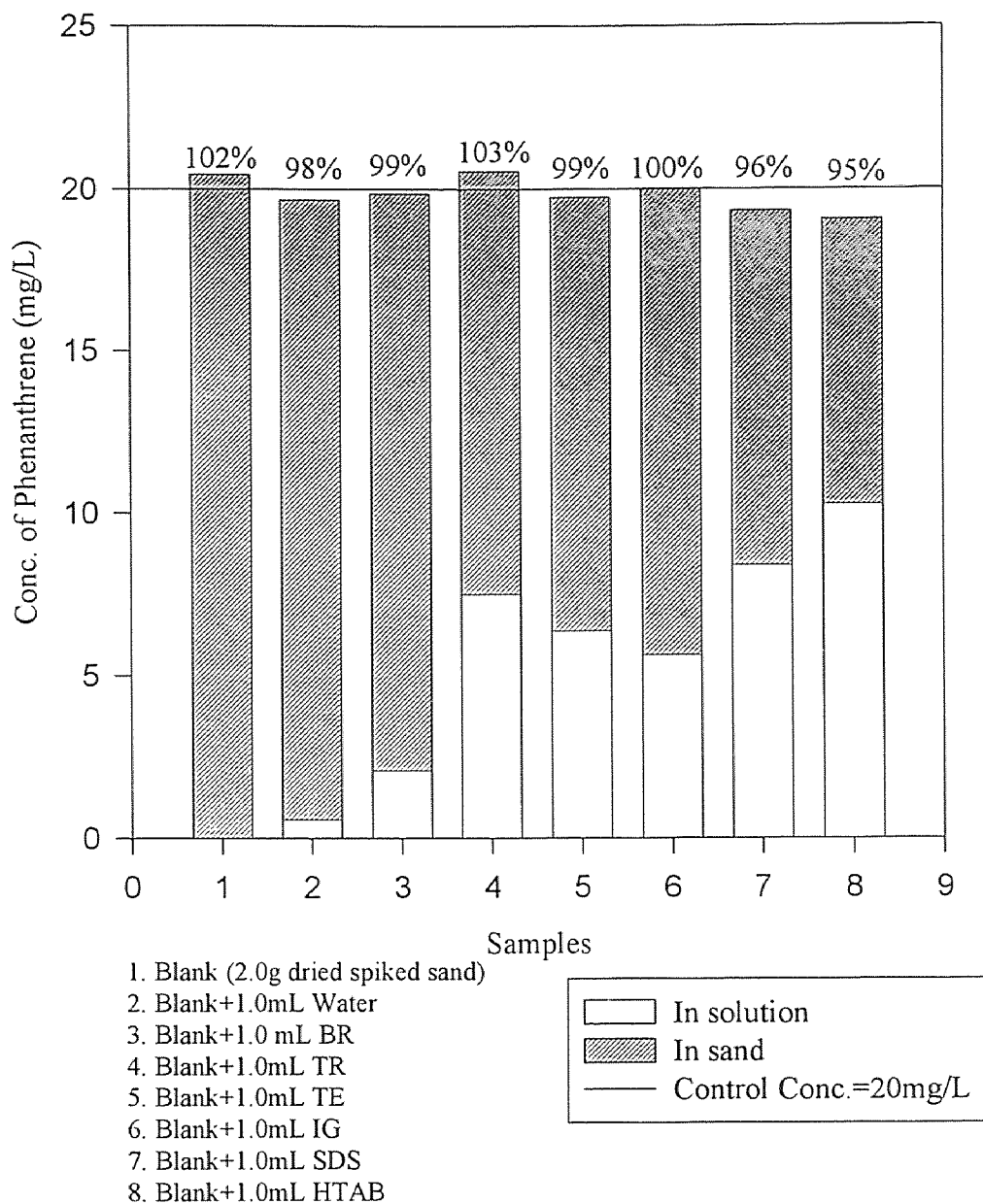
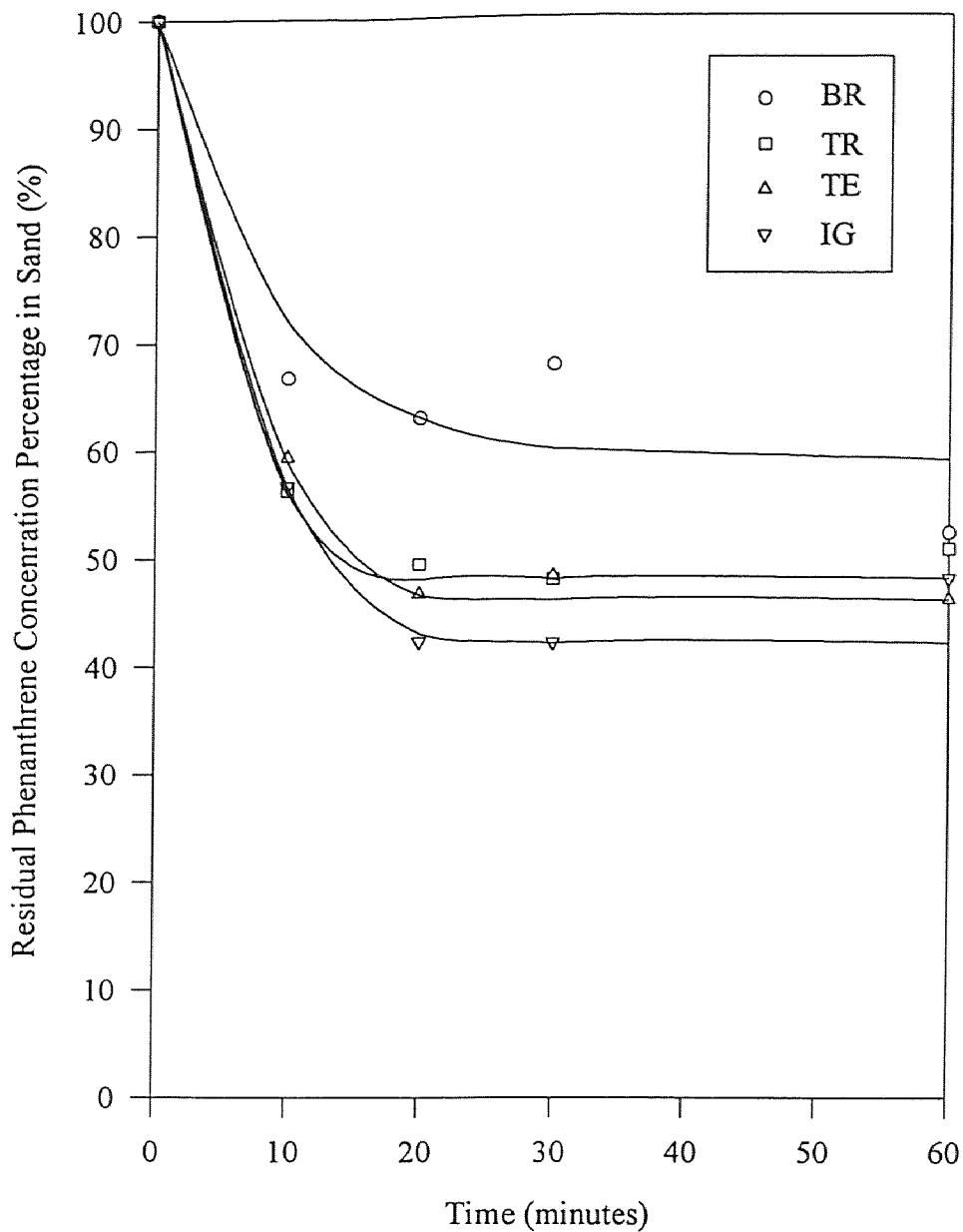
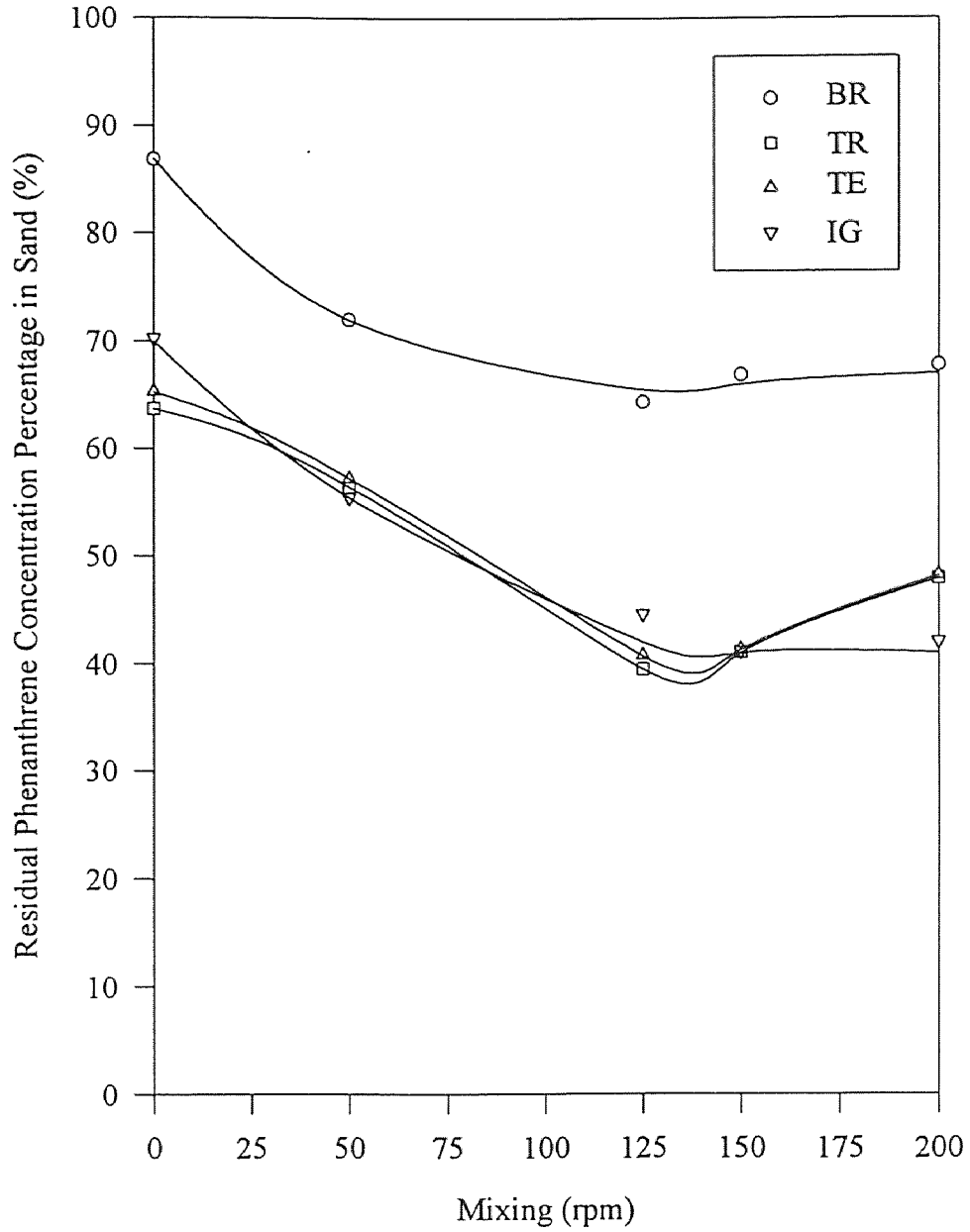


Figure 2 The recovery efficiencies of surfactants in 4% at 0 rpm for 30 minutes



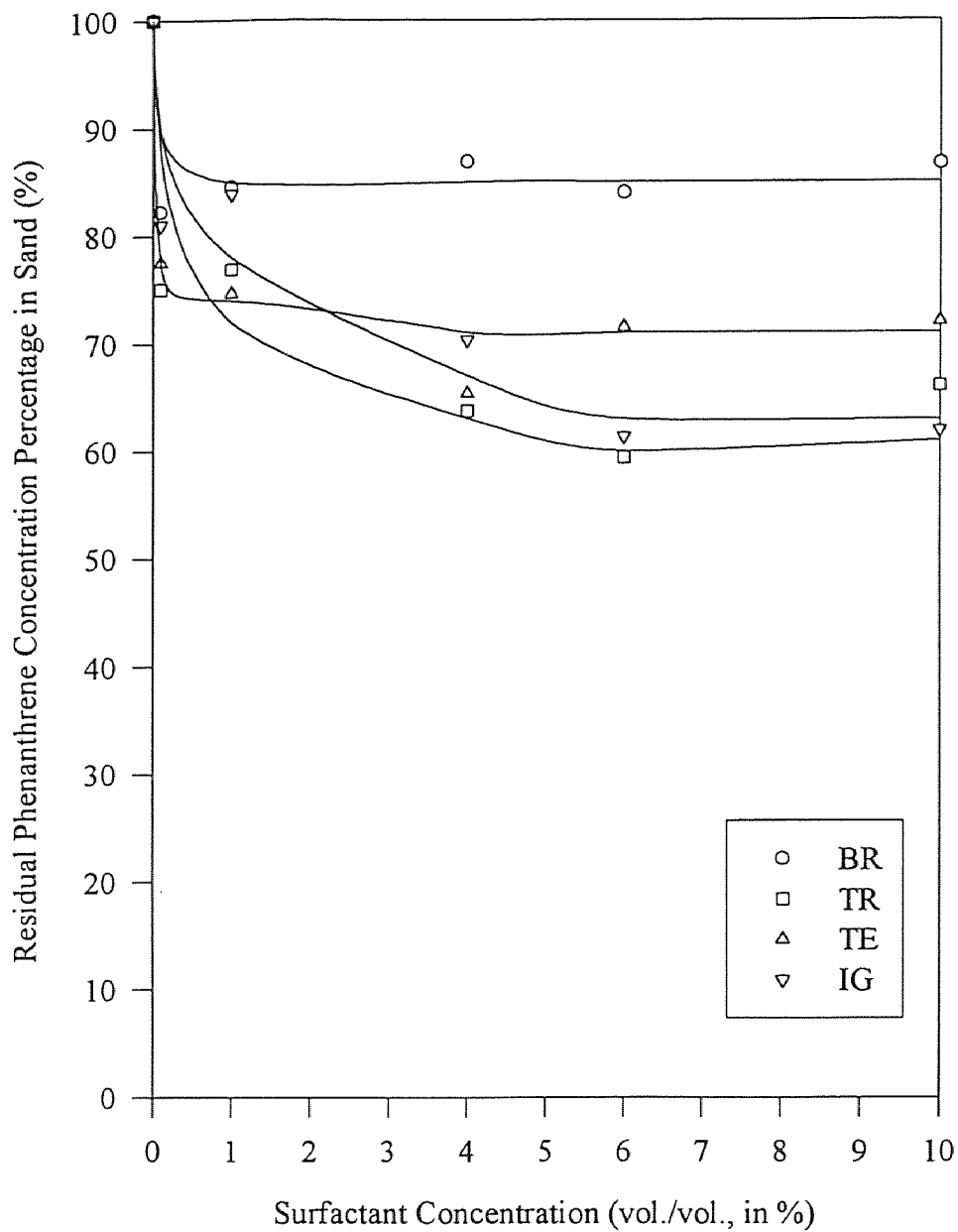
*2.0g spiked sand (100mg/Kg) + 1.0 mL 4% surfactants, at 200 rpm.

Figure 3 Time effects of the four non-ionic surfactants



*2.0g spiked sand (100mg/Kg) + 1.0 mL 4% surfactants, for 30 minutes.

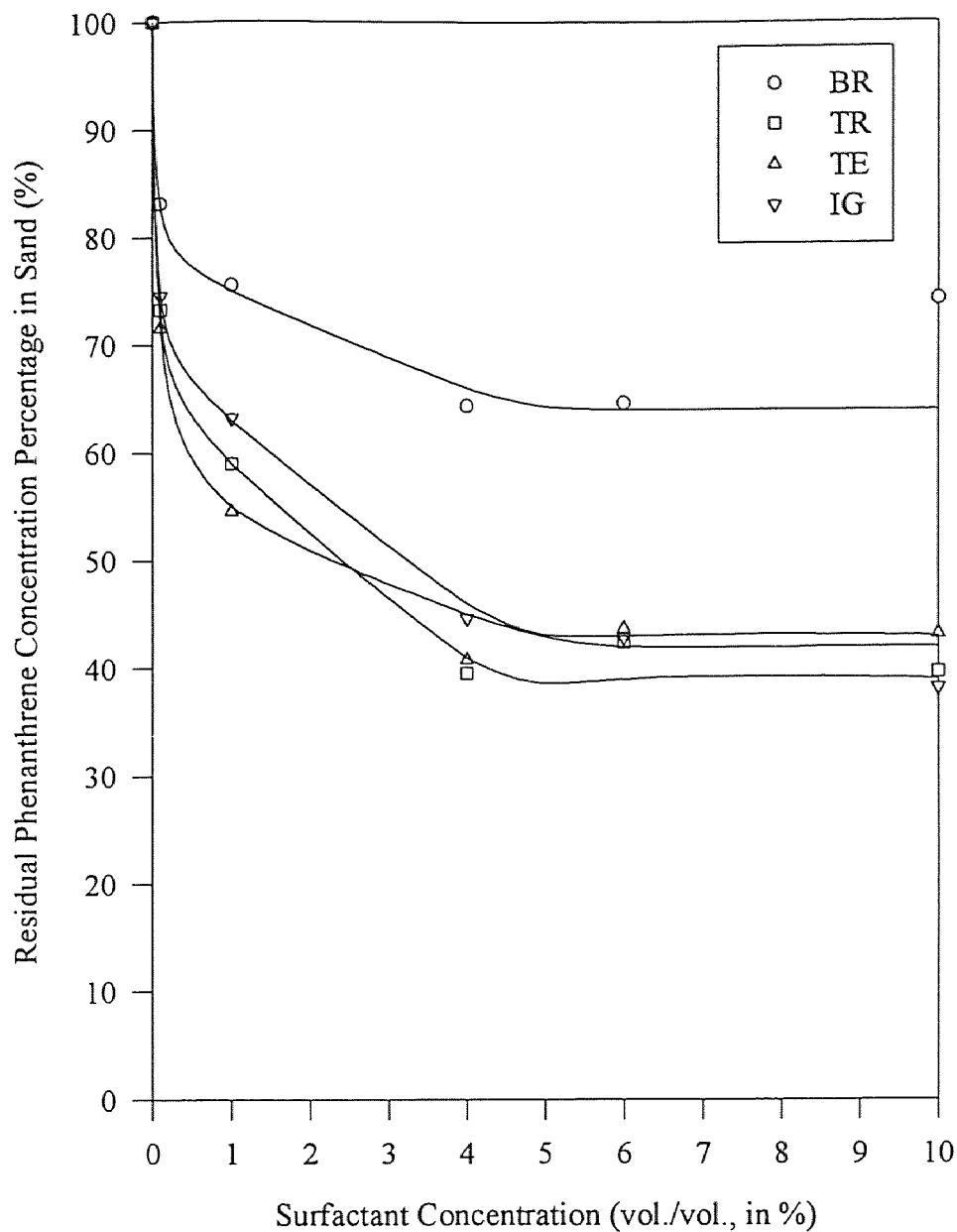
Figure 4 Mixing effects on the four non-ionic surfactants



* vol./vol. in % : surfactants (in mL) were diluted into 100 mL by distilled water.

*2.0g spiked sand (100mg/Kg) + 1.0 mL surfactants, at 0 rpm, for 30 minutes.

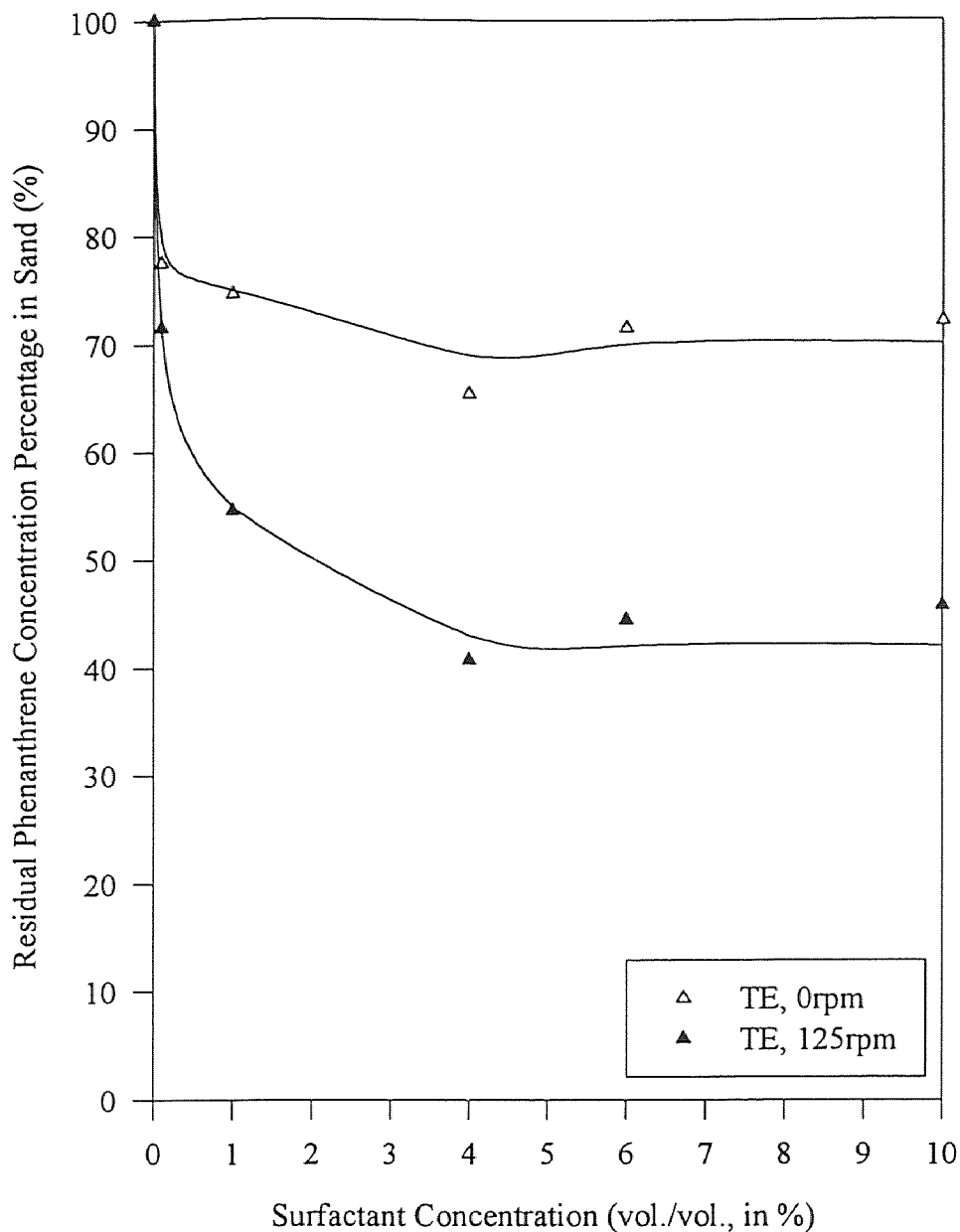
Figure 5 Surfactant concentration effects of the four non-ionic surfactants at 0rpm



* vol./vol. in % : surfactants (in mL) were diluted into 100 mL by distilled water.

*2.0g spiked sand (100mg/Kg) + 1.0 mL surfactants, at 125 rpm, for 30 minutes.

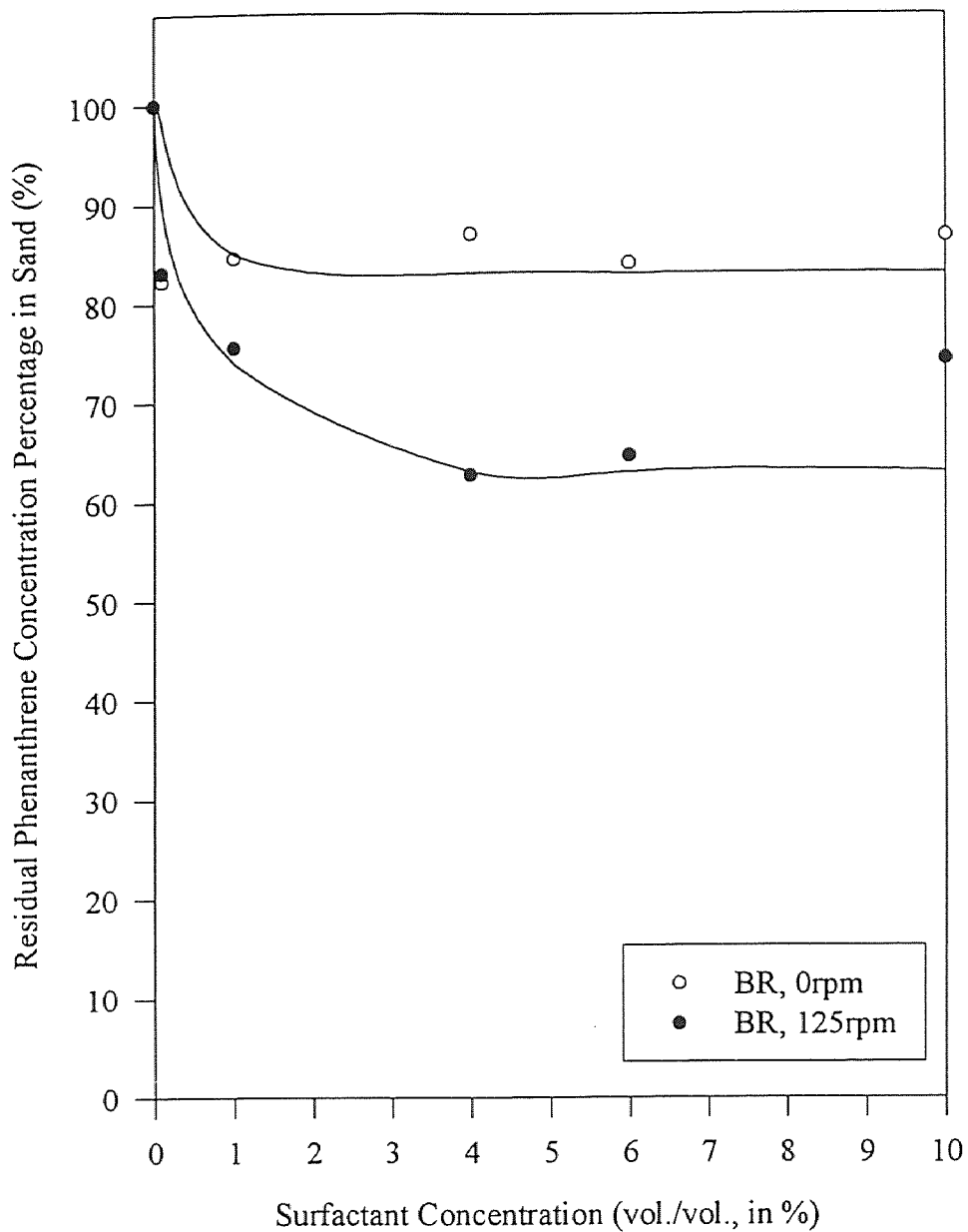
Figure 6 Surfactant concentration effects of the four non-ionic surfactants at 125rpm



* vol./vol. in % : surfactants (in mL) were diluted into 100 mL by distilled water.

*2.0g spiked sand (100mg/Kg) + 1.0 mL TE, for 30 minutes, at 0 and 125 rpm.

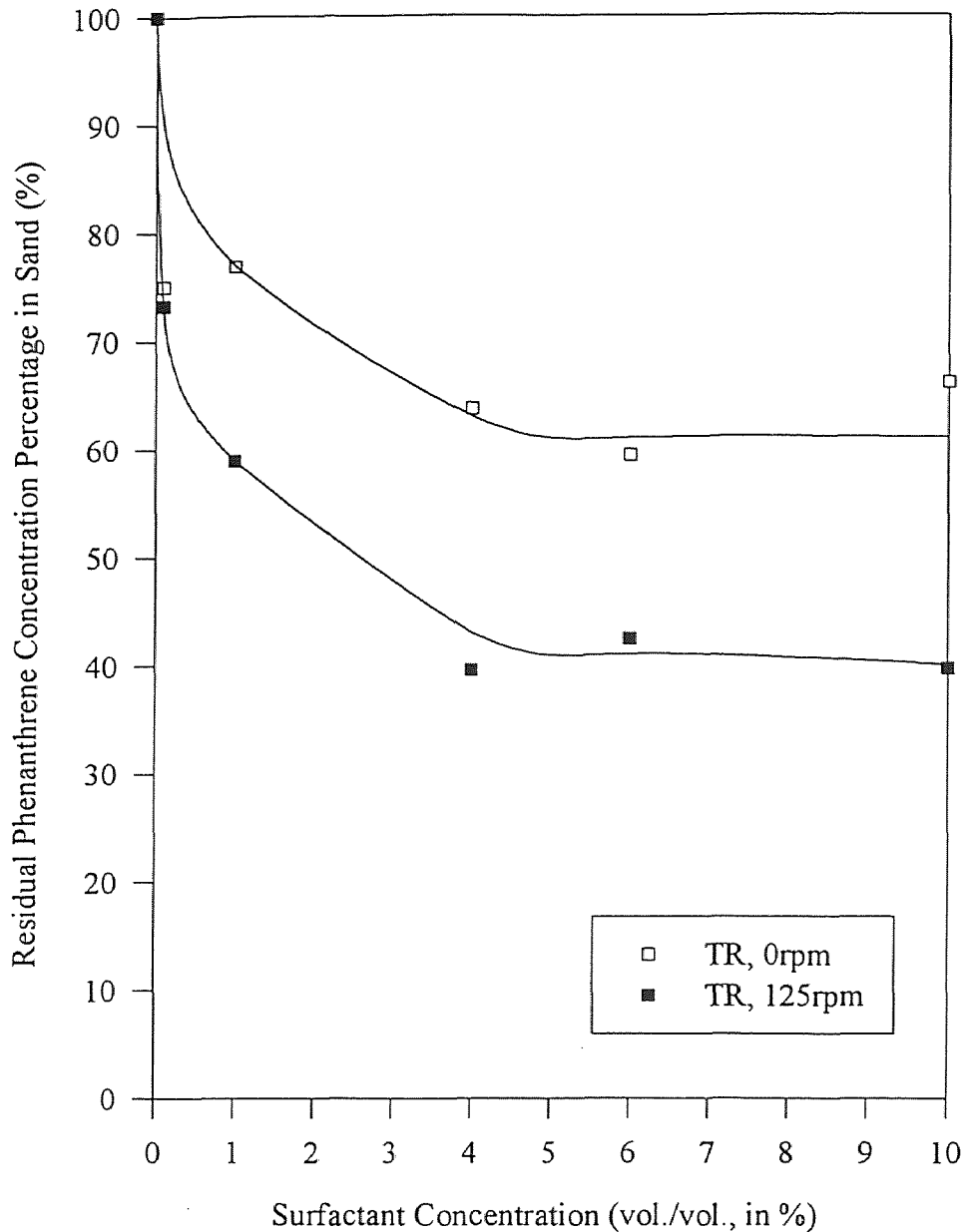
Figure 7 The comparison of Tergitol NP-10 (TE) concentration effects at 0rpm and 125rpm



* vol./vol. in % : surfactants (in mL) were diluted into 100 mL by distilled water.

*2.0g spiked sand (100mg/Kg) + 1.0 mL BR, for 30 minutes, at 0 and 125 rpm.

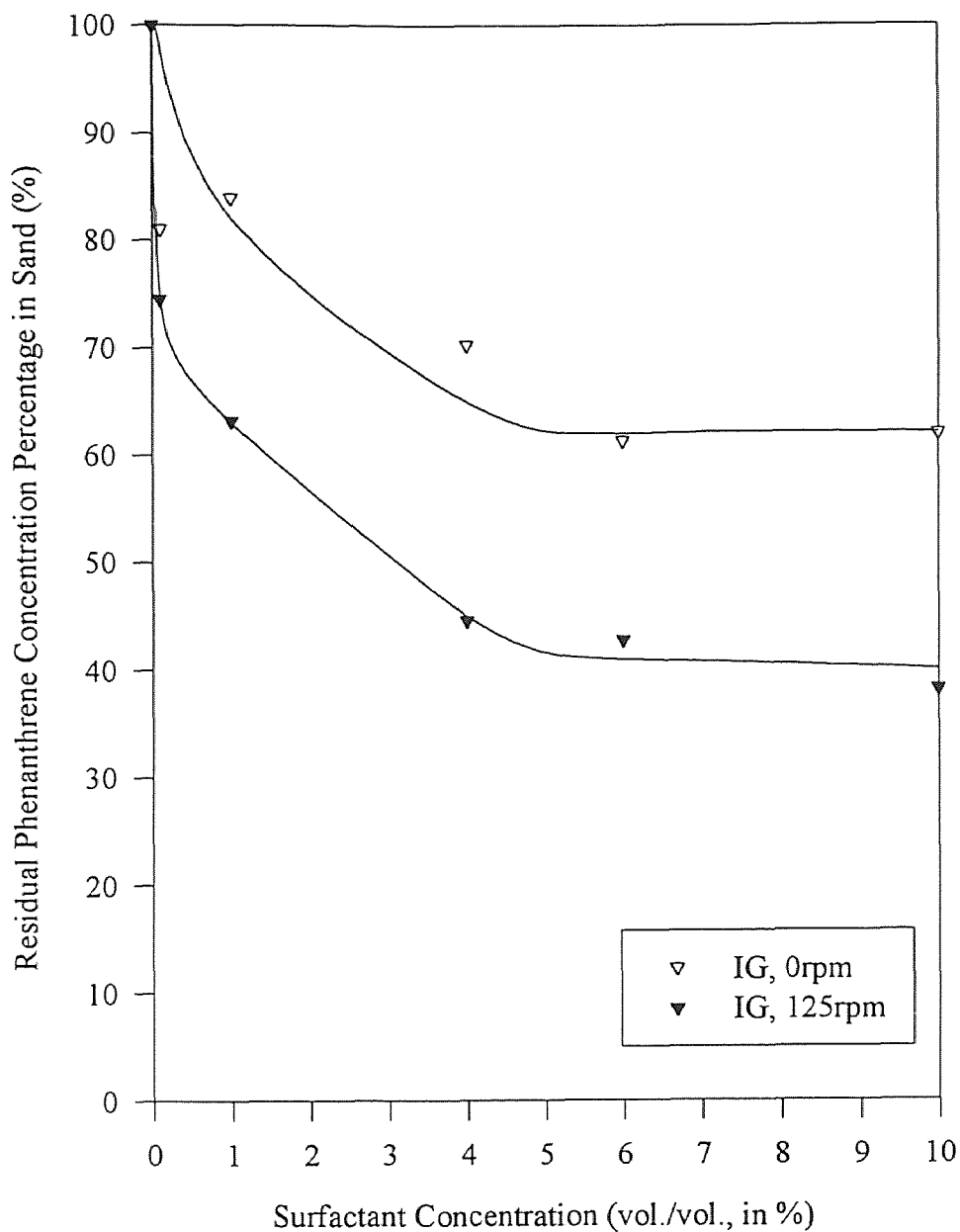
Figure 8 The comparison of Brij 30 (BR) concentration effects at 0rpm and 125rpm



* vol./vol. in % : surfactants (in mL) were diluted into 100 mL by distilled water.

*2.0g spiked sand (100mg/Kg) + 1.0 mL TR, for 30 minutes, at 0 and 125 rpm.

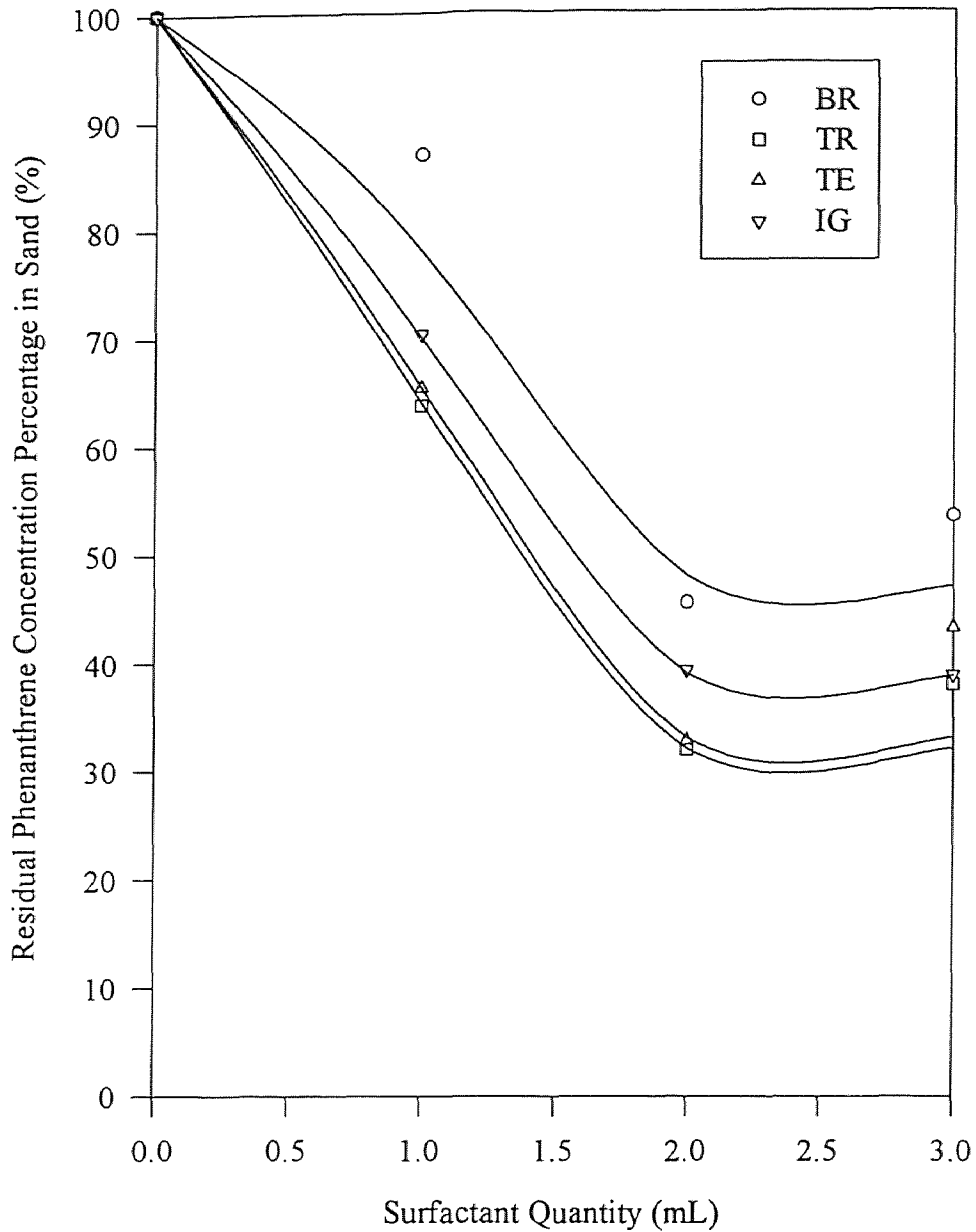
Figure 9 The comparison of Triton X-100 (TR) concentration effects at 0rpm and 125rpm



* vol./vol. in % : surfactants (in mL) were diluted into 100 mL by distilled water.

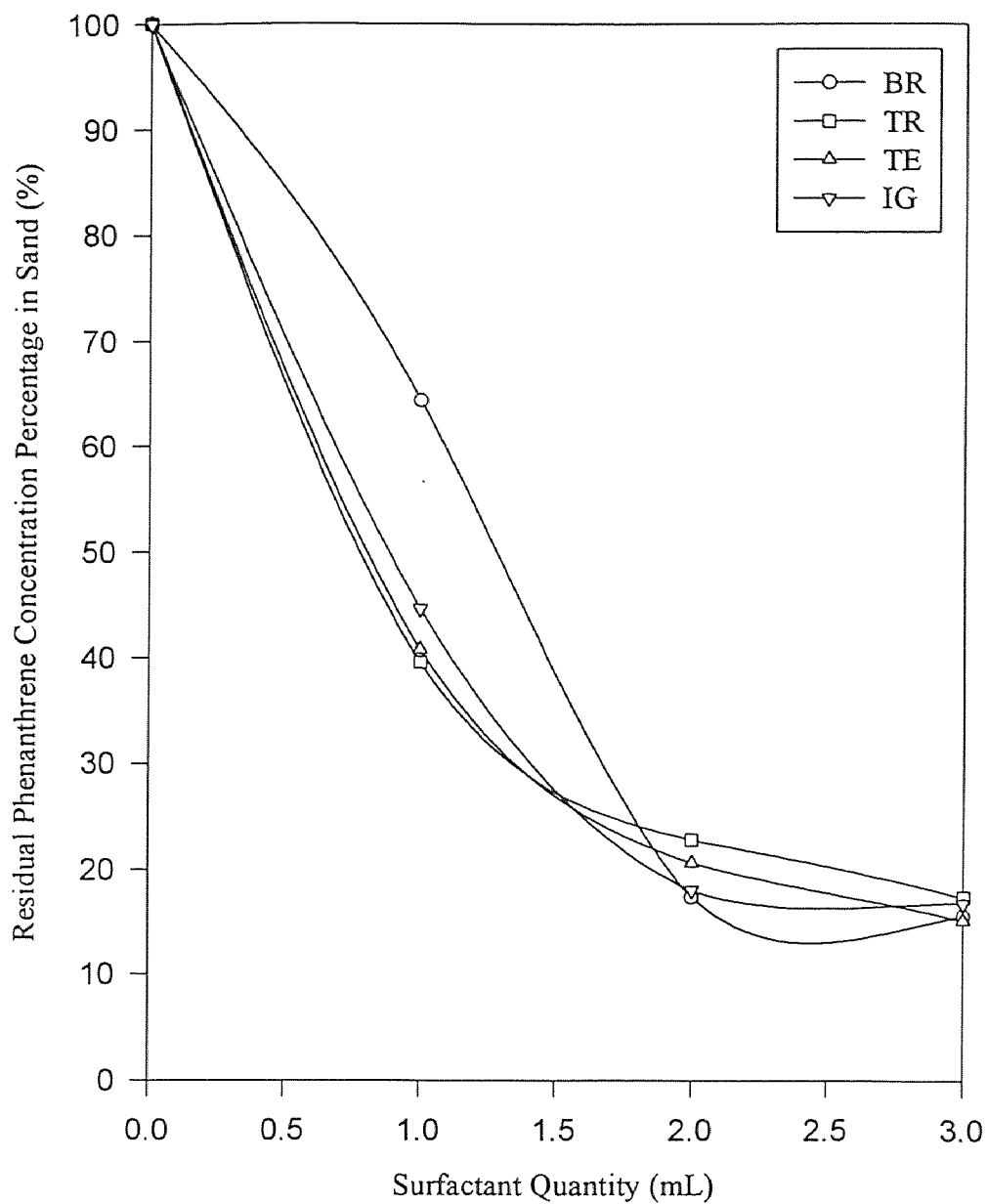
*2.0g spiked sand (100mg/Kg) + 1.0 mL IG, for 30 minutes, at 0 and 125 rpm.

Figure 10 The comparison of Igepal CA-720 (IG) concentration effects at 0rpm and 125rpm



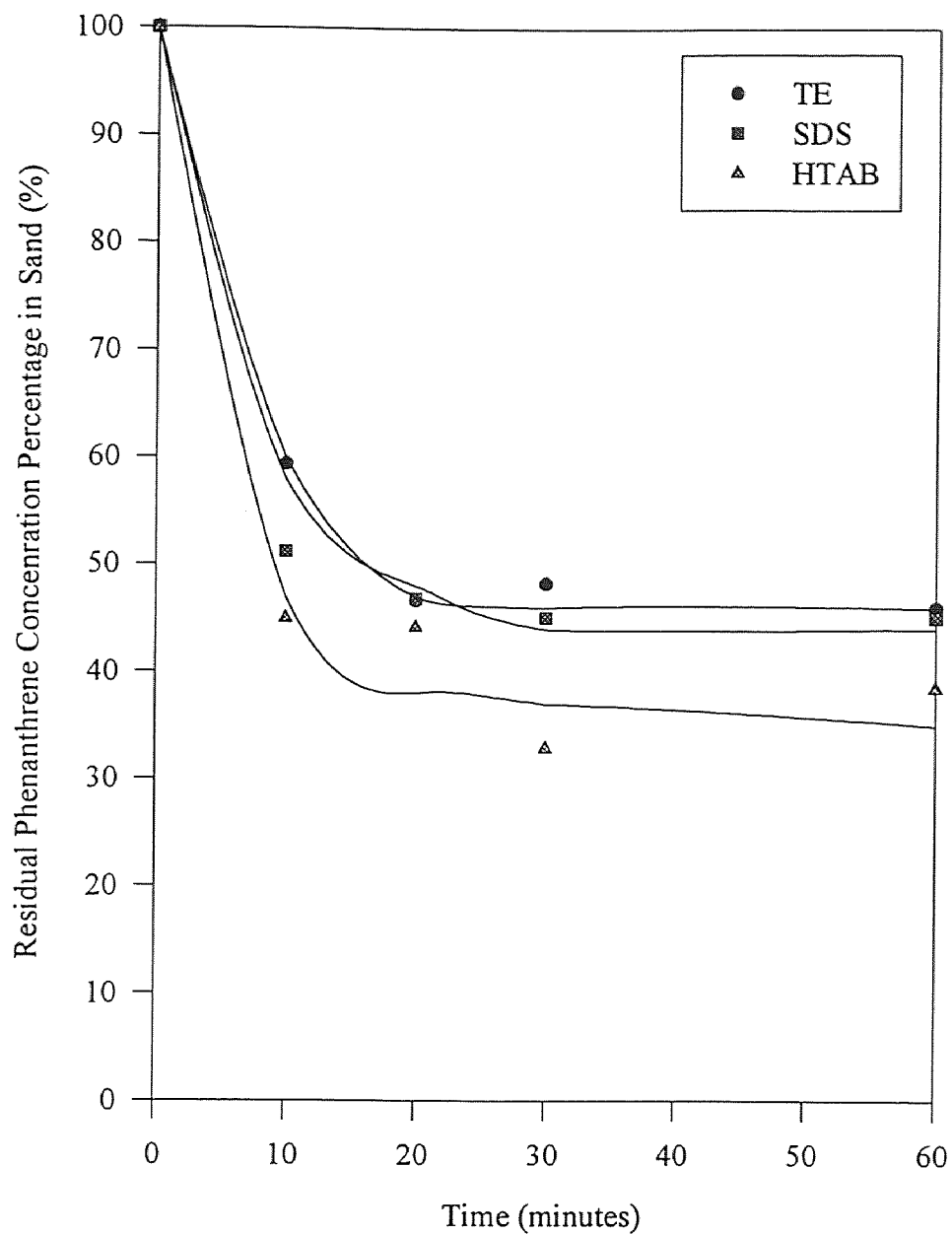
*2.0g spiked sand (100mg/Kg) + surfactants, for 30 minutes, at 0 rpm.

Figure 11 Surfactant quantity effects of the four non-ionic surfactants at 0rpm



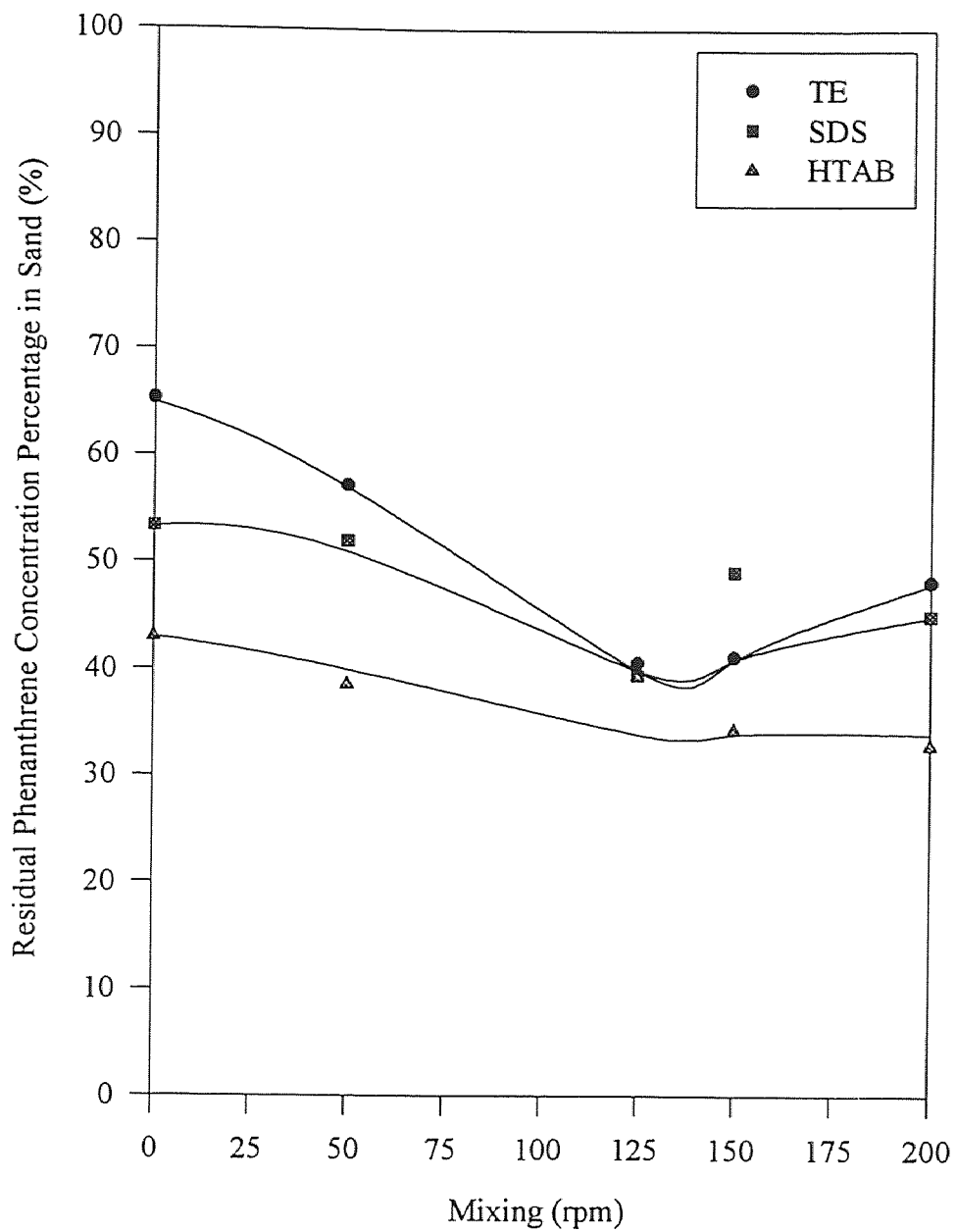
*2.0g spiked sand (100mg/Kg) + surfactants, for 30 minutes, at 125 rpm.

Figure 12 Surfactant quantity effects of the four non-ionic surfactants at 125rpm



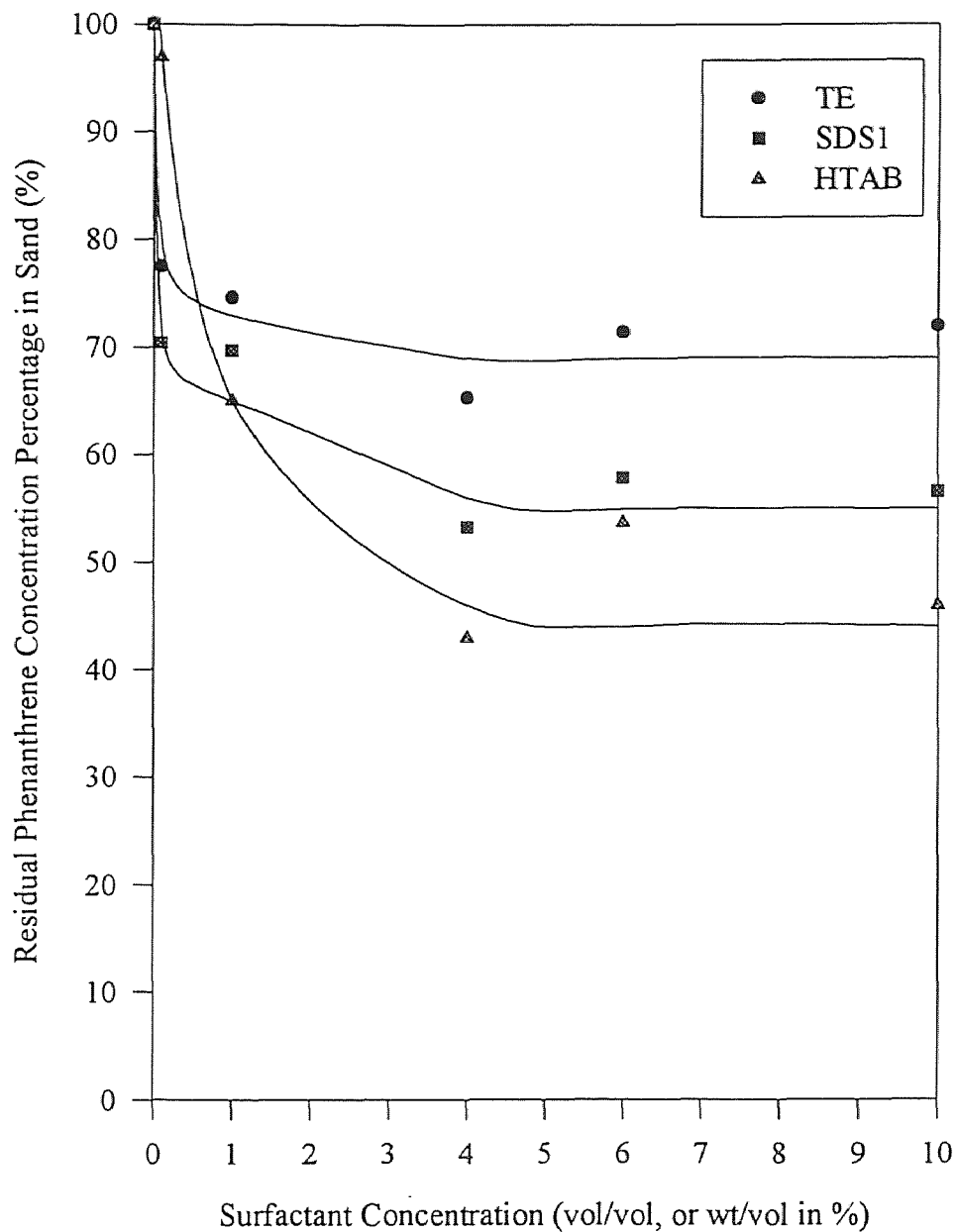
*2.0g spiked sand (100mg/Kg) + 1.0 mL surfactants, in 4%, at 200 rpm.

Figure 13 Time effects of TE, SDS and HTAB



*2.0g spiked sand (100mg/Kg) + 1.0 mL surfactants, in 4%, for 30 minutes.

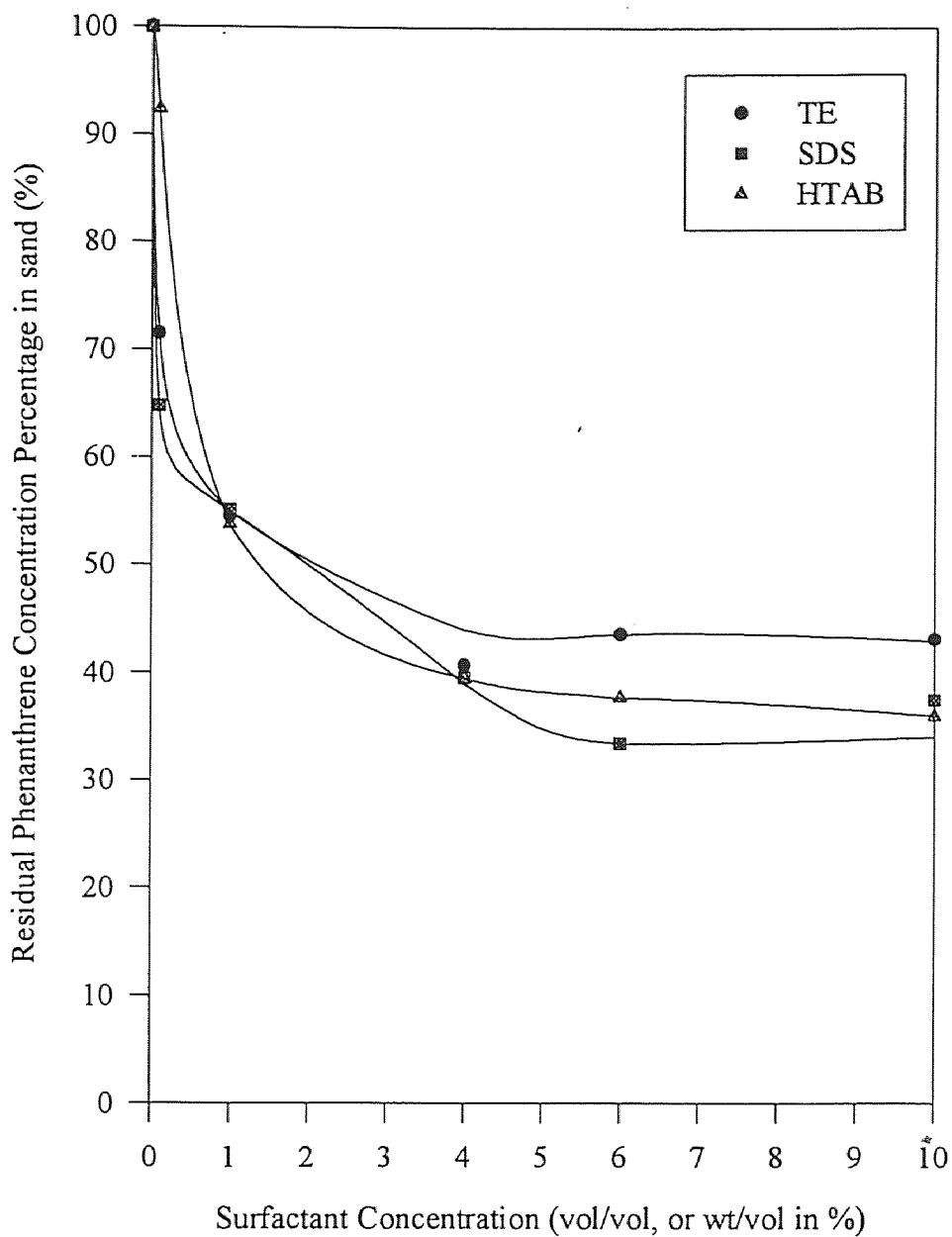
Figure 14 Mixing effects of TE, SDS and HTAB



* wt./vol. in % : surfactants (in mg) were diluted into 100 mL by distilled water.

*2.0g spiked sand (100mg/Kg) + 1.0 mL surfactants, at 0 rpm, for 30 minutes.

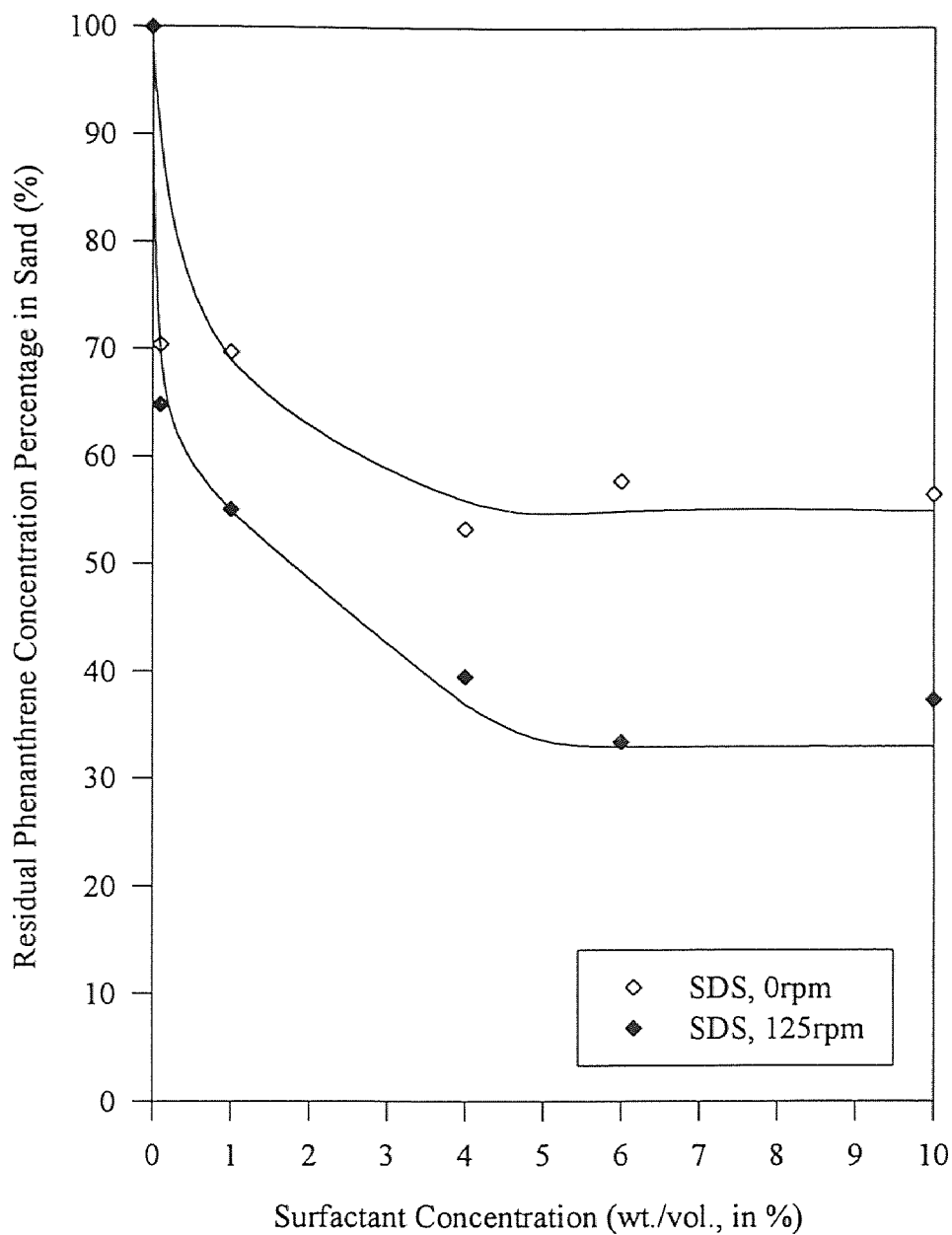
Figure 15 Surfactant concentration effects of TE, SDS and HTAB at 0rpm



* wt./vol. in % : surfactants (in mg) were diluted into 100 mL by distilled water.

*2.0g spiked sand (100mg/Kg) + 1.0 mL surfactants, at 125 rpm, for 30 minutes.

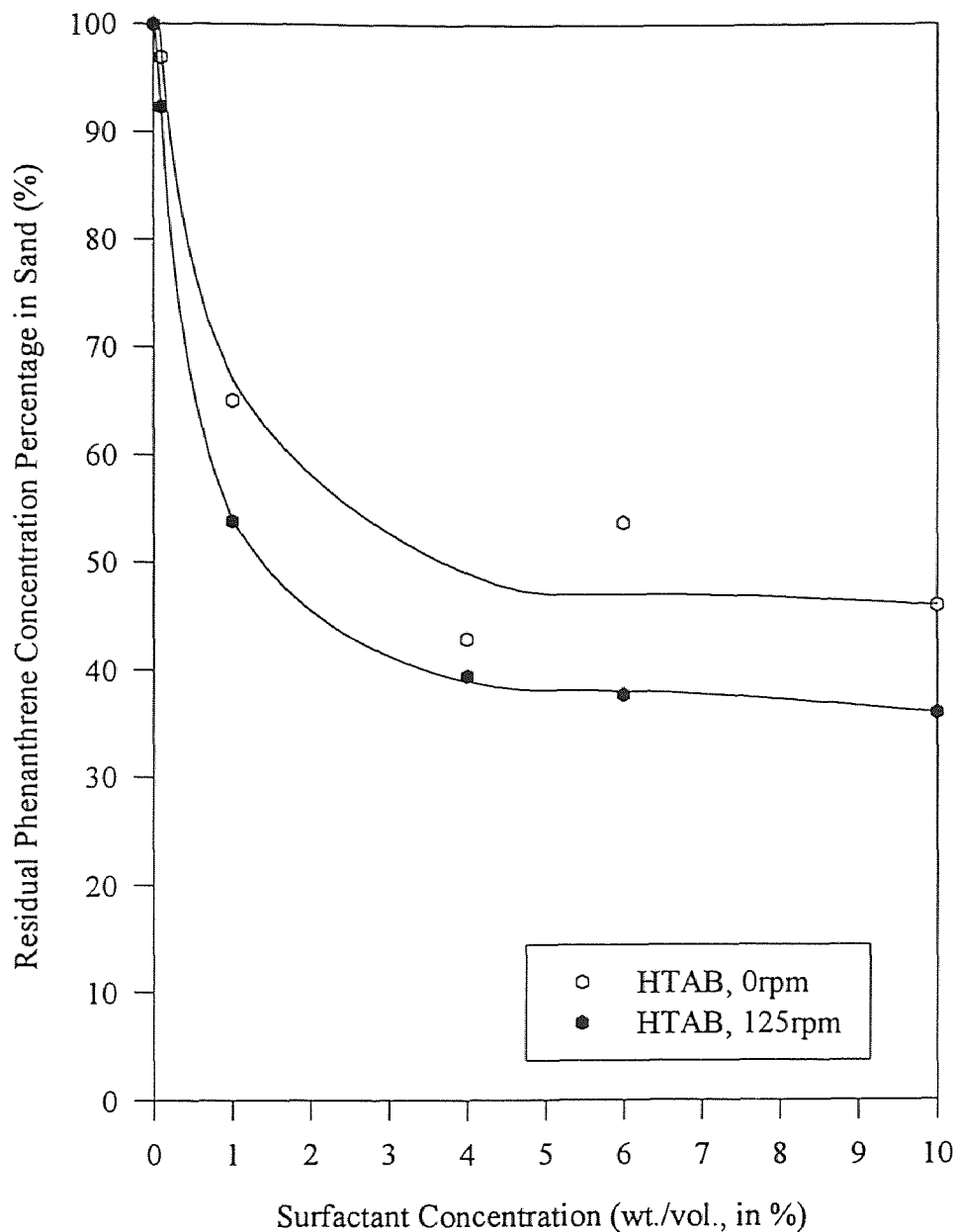
Figure 16 Surfactant concentration effects of TE, SDS and HTAB at 125rpm



* wt./vol. in % : surfactants (in mg) were diluted into 100 mL by distilled water.

*2.0g spiked sand (100mg/Kg) + 1.0 mL SDS, for 30 minutes, at 0 and 125 rpm.

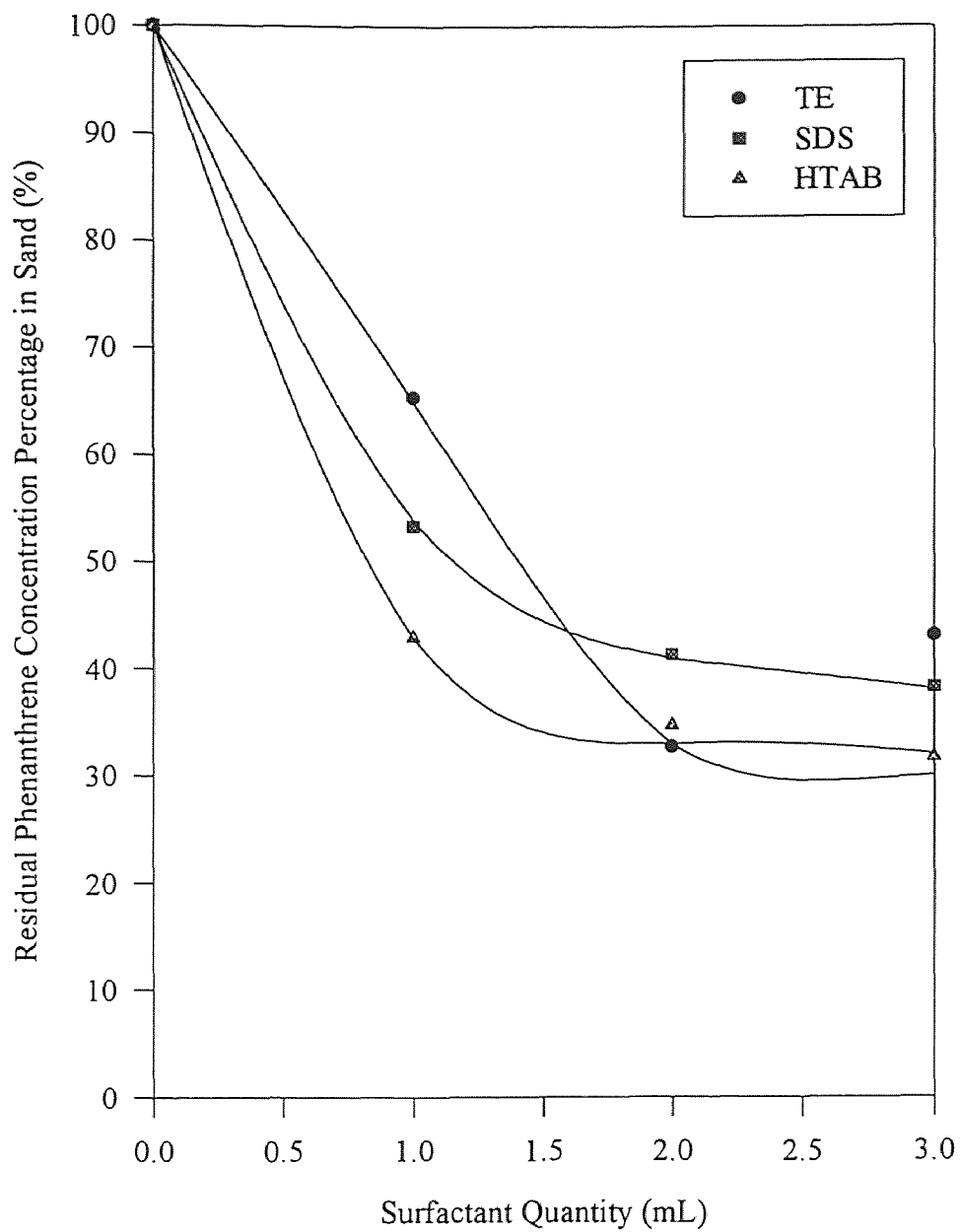
Figure 17 The comparison of Sodium Dodecyl Sulfate (SDS) concentration effects at 0rpm and 125rpm



* wt./vol. in % : surfactants (in mg) were diluted into 100 mL by distilled water.

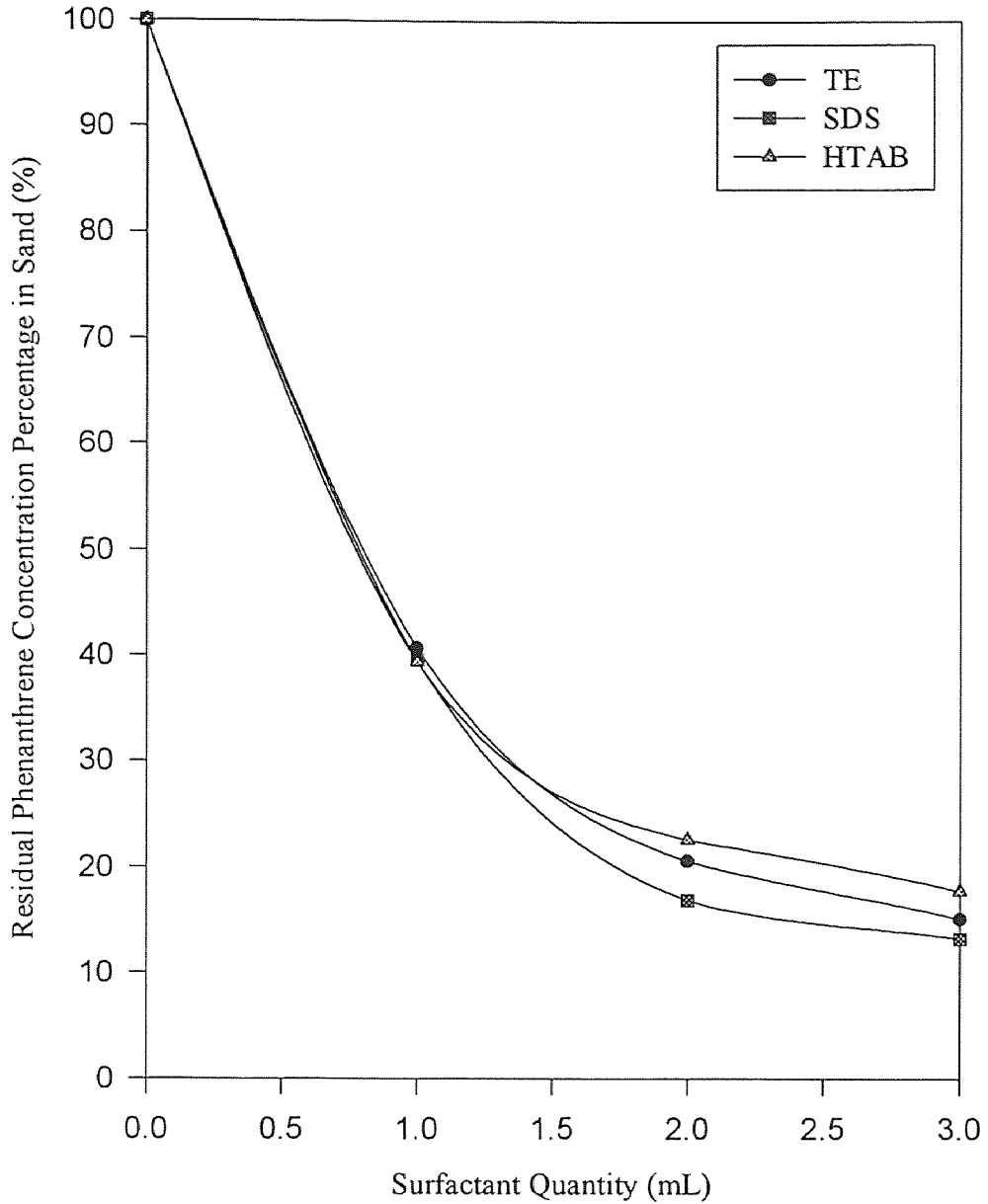
*2.0g spiked sand (100mg/Kg) + 1.0 mL HTAB, for 30 minutes, at 0 and 125 rpm.

Figure 18 The comparison of Hexadecyl Trimethyl Ammonium Bromide (HTAB) concentration effects at 0rpm and 125rpm



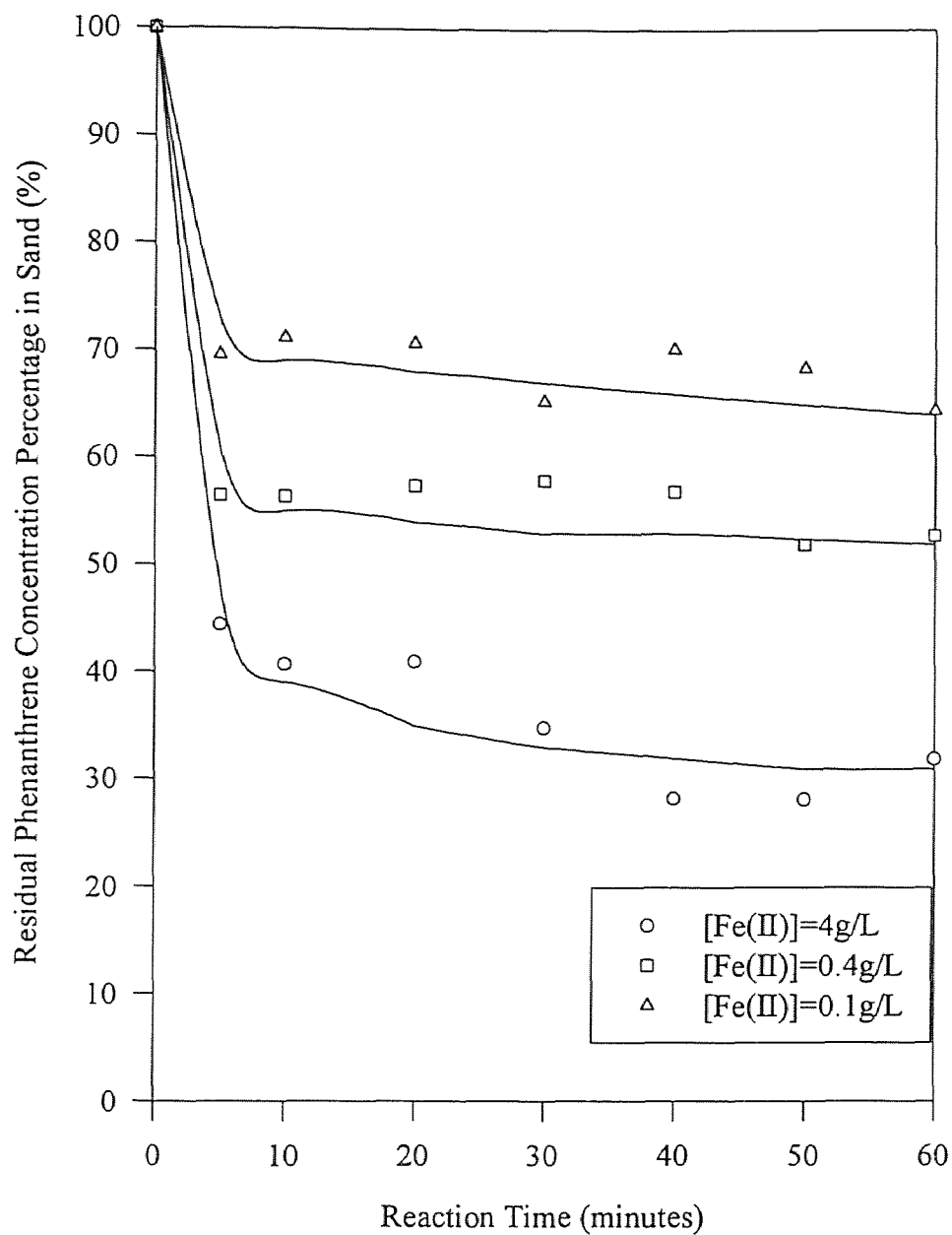
*2.0g spiked sand (100mg/Kg) + surfactants in 4%, for 30 minutes, at 0 rpm.

Figure 19 Surfactant quantity effects of TE, SDS and HTAB at 0rpm



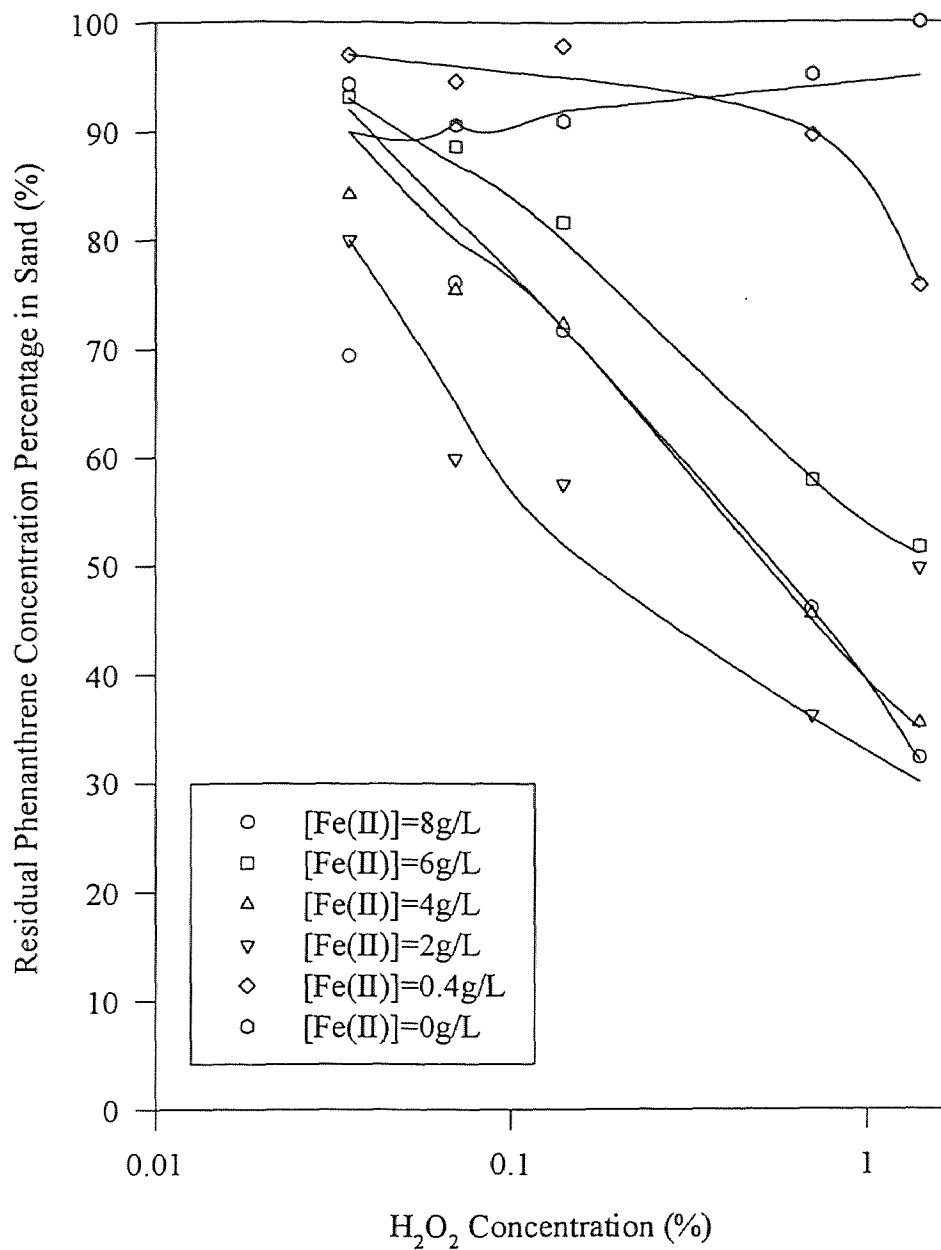
*2.0g spiked sand (100mg/Kg) + surfactants in 4%, for 30 minutes, at 125 rpm.

Figure 20 Surfactant quantity effects of TE, SDS and HTAB at 125rpm



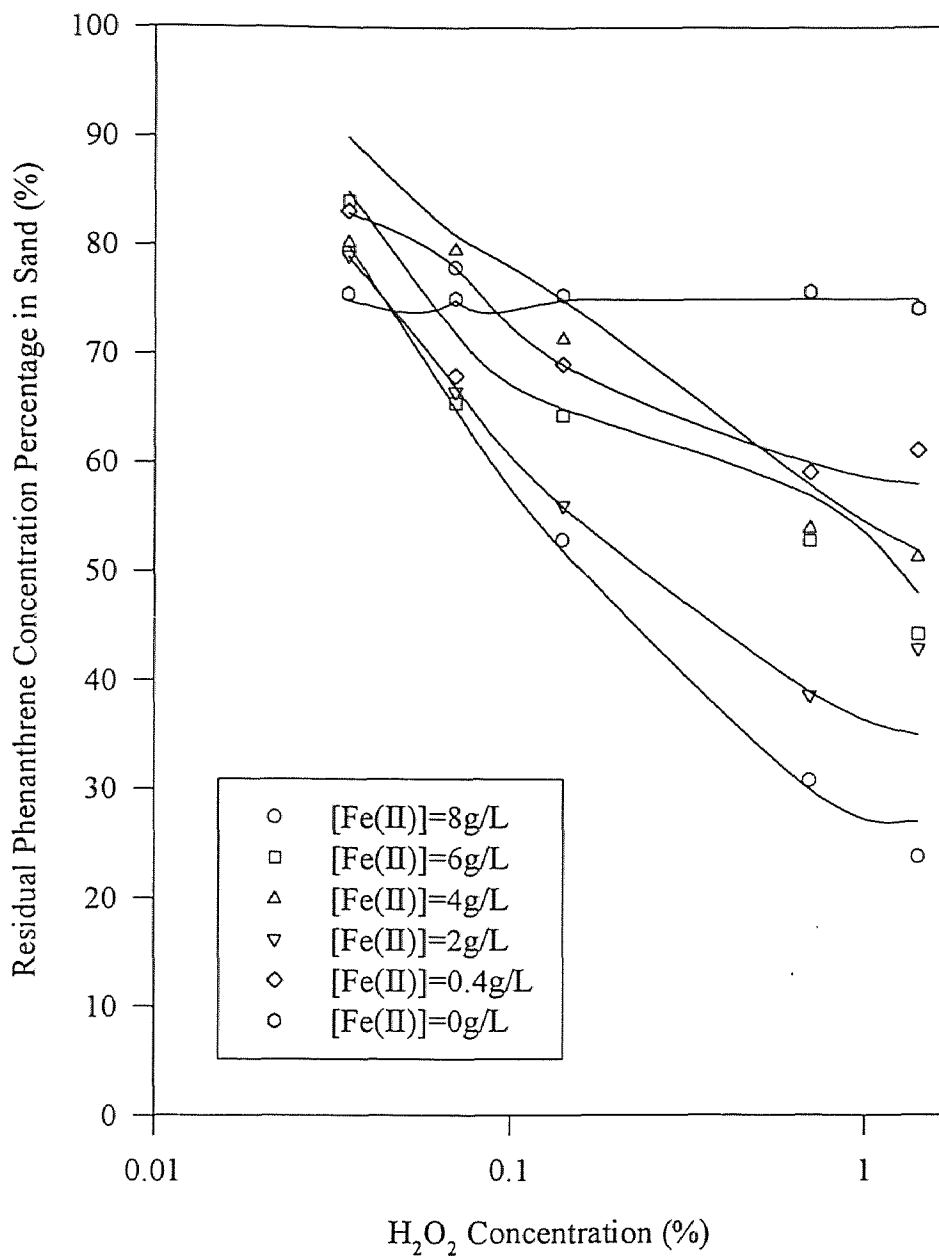
* 2.0g spiked sand (100mg/Kg) + 1.0 mL reagents (0.5 mL Fe⁺² + 0.5 mL H₂O₂), [H₂O₂]= 0.7%, at 150 rpm.

Figure 21 Time effects of the Fenton's reactions



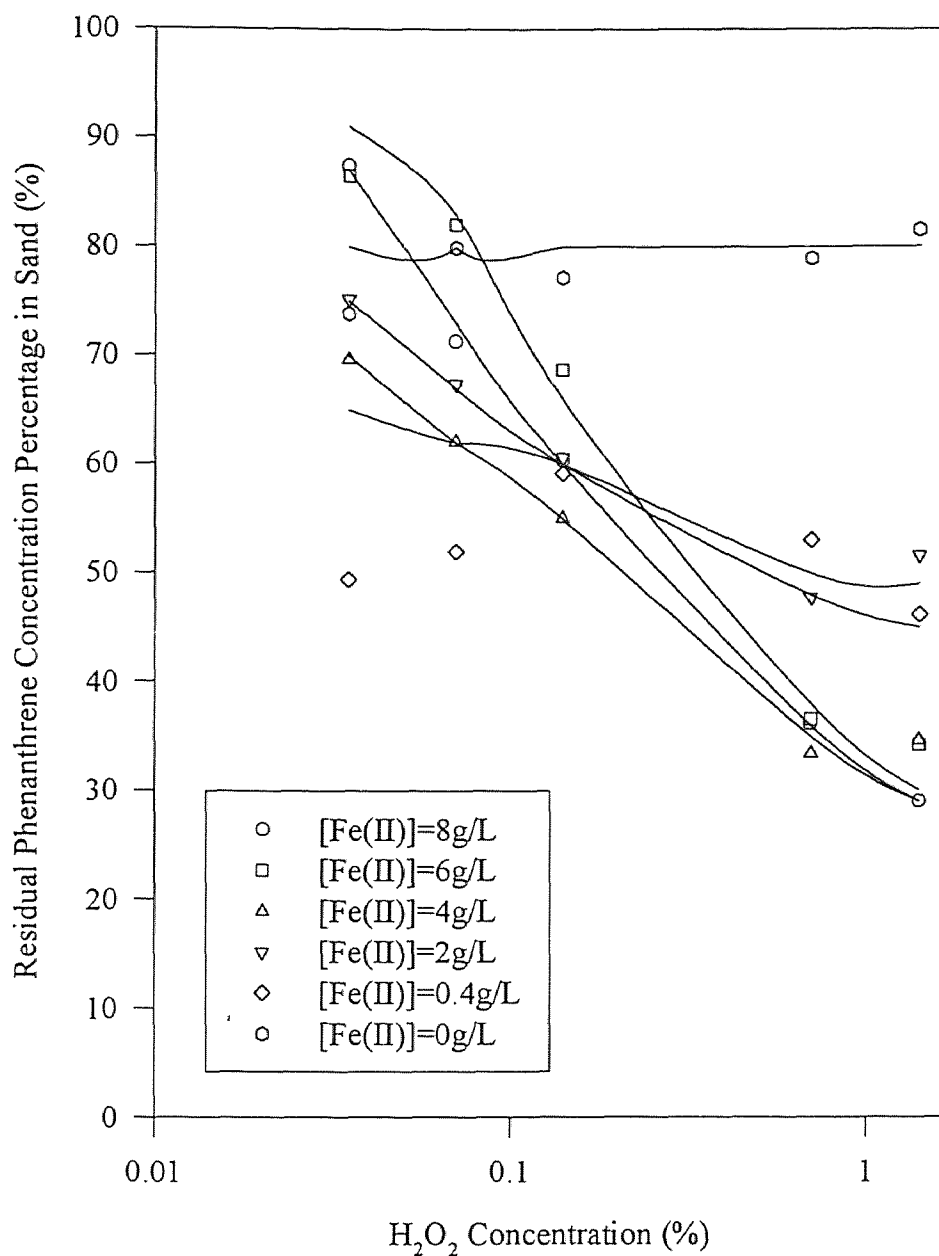
* 2.0g spiked sand (100mg/Kg) + 1.0 mL reagents (0.5 mL Fe⁺² + 0.5 mL H₂O₂), [H₂O₂]= 0.7%, at 50 rpm, for 30 minutes.

Figure 22 The Fenton's reagent concentration effects at 50 rpm



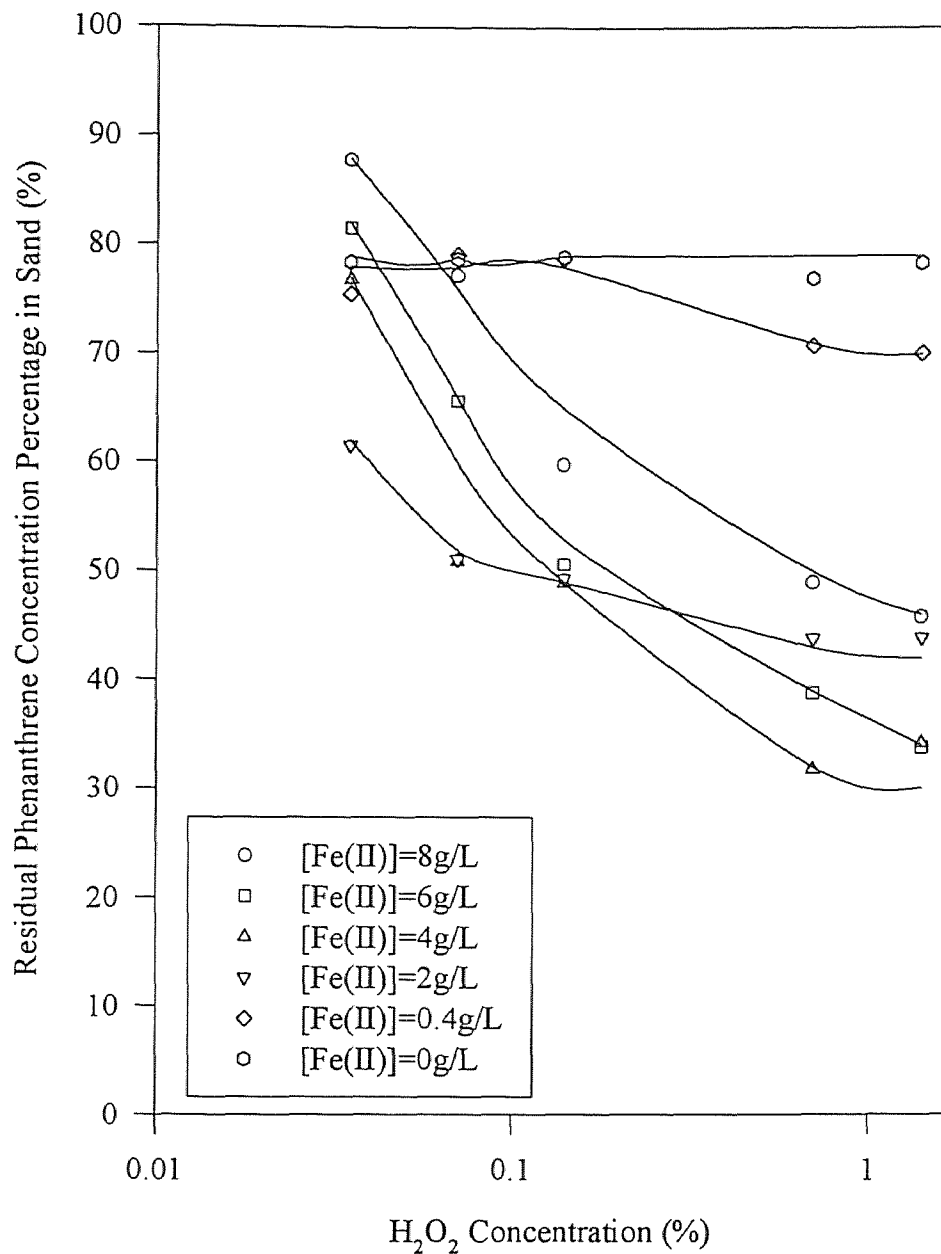
* 2.0g spiked sand (100mg/Kg) + 1.0 mL reagents (0.5 mL Fe⁺² + 0.5 mL H₂O₂), [H₂O₂]= 0.7%, at 100 rpm, for 30 minutes.

Figure 23 The Fenton's reagent concentration effects at 100 rpm



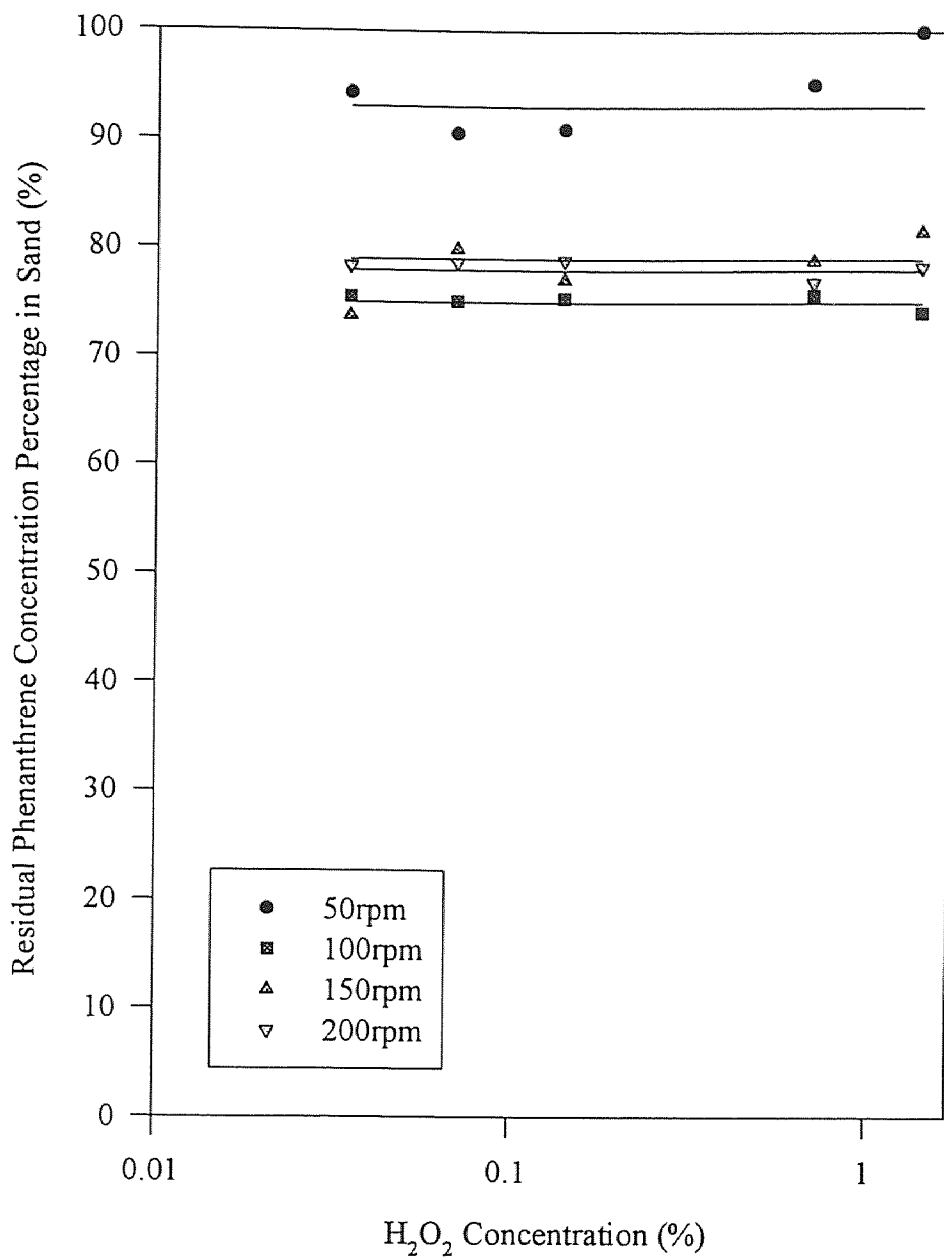
* 2.0g spiked sand (100mg/Kg) + 1.0 mL reagents (0.5 mL Fe⁺² + 0.5 mL H₂O₂), [H₂O₂]= 0.7%, at 150 rpm, for 30 minutes.

Figure 24 The Fenton's reagent concentration effects at 150rpm



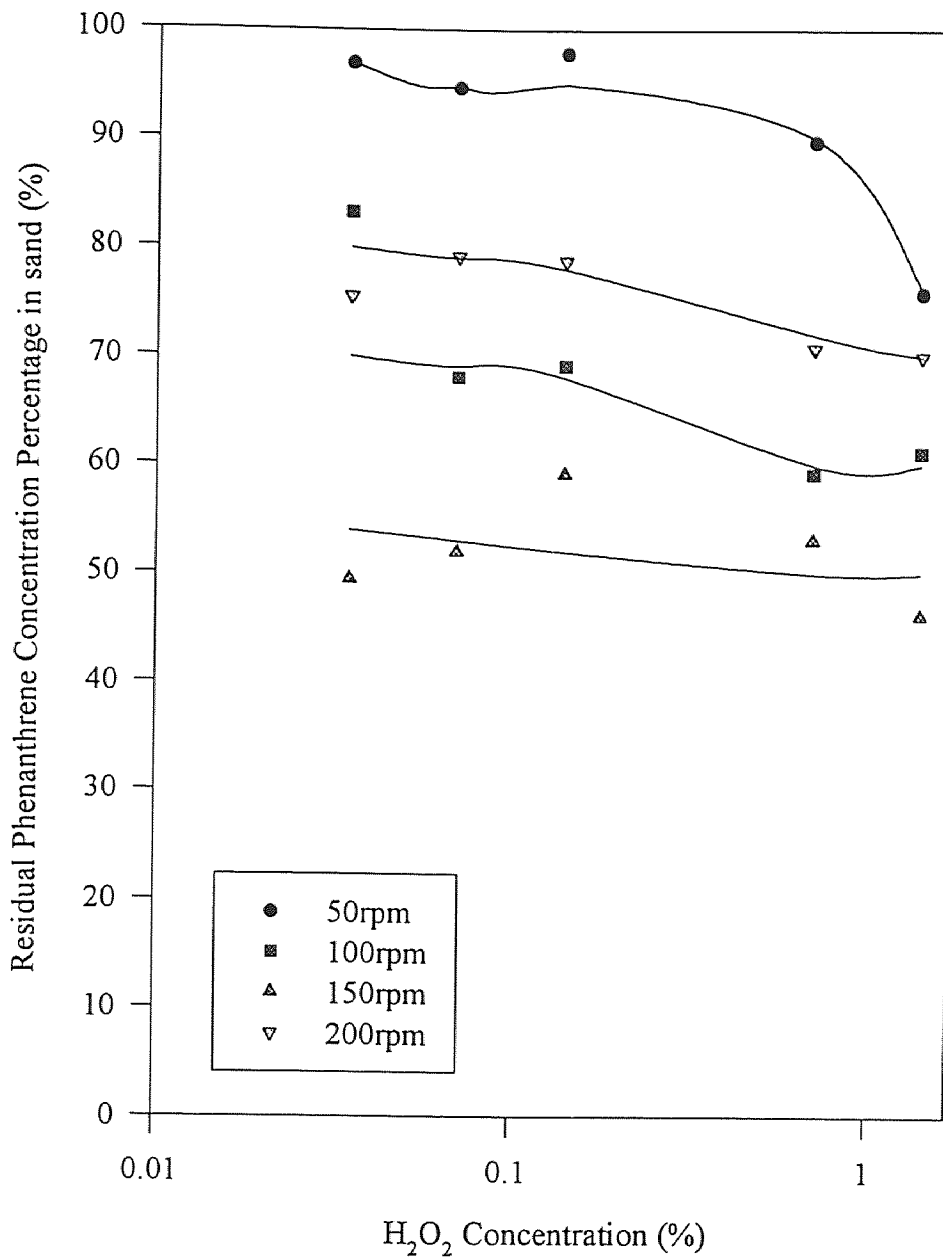
* 2.0g spiked sand (100mg/Kg) + 1.0 mL reagents (0.5 mL Fe⁺² + 0.5 mL H₂O₂), [H₂O₂]= 0.7%, at 200 rpm, for 30 minutes.

Figure 25 The Fenton's reagent concentration effects at 200rpm



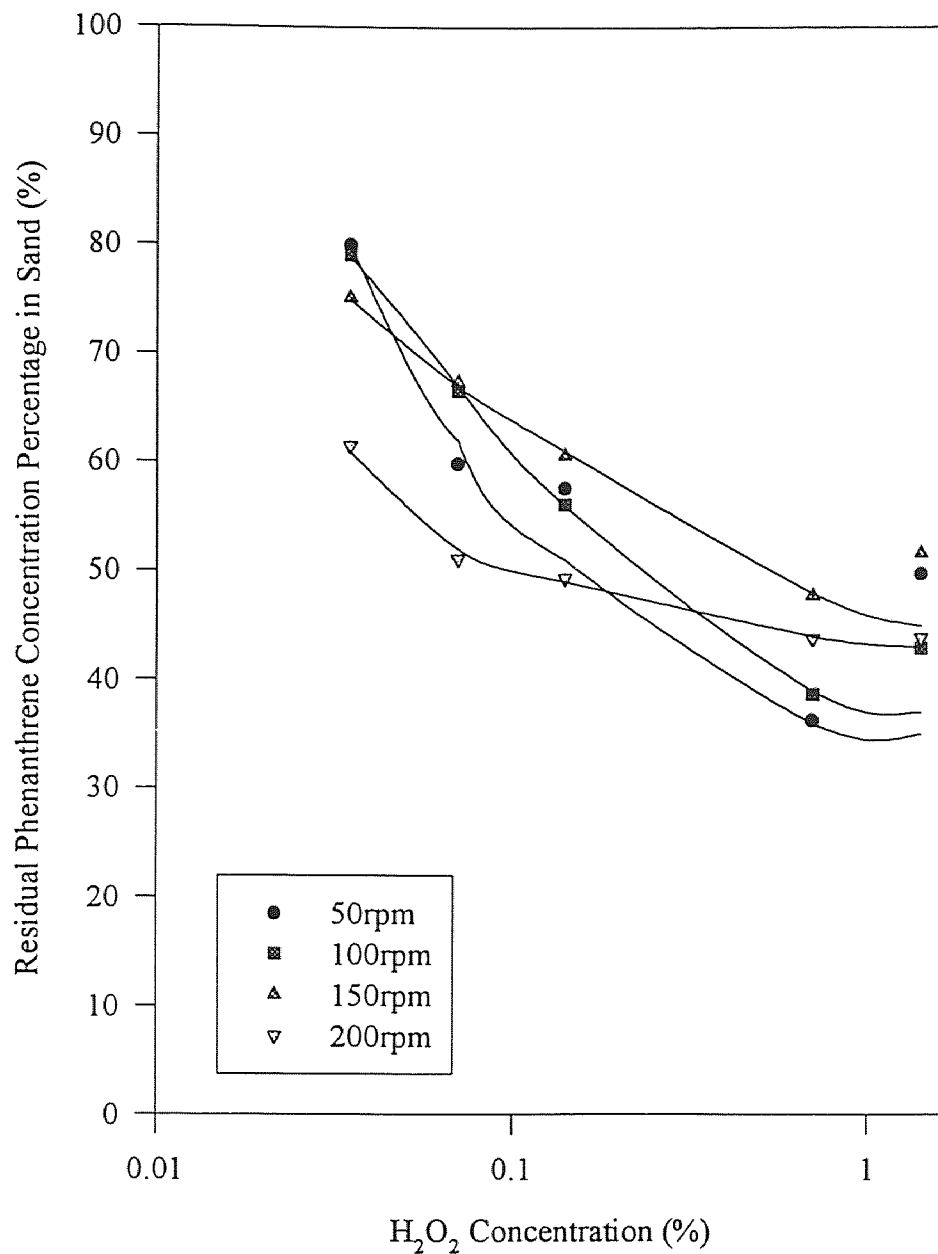
* 2.0g spiked sand (100mg/Kg) + 1.0 mL reagents (0.5 mL Fe⁺² + 0.5 mL H₂O₂), [Fe⁺²]= 0 g/L, for 30 minutes.

Figure 26 Mixing effects of the Fenton's reactions in [Fe(II)]=0g/L



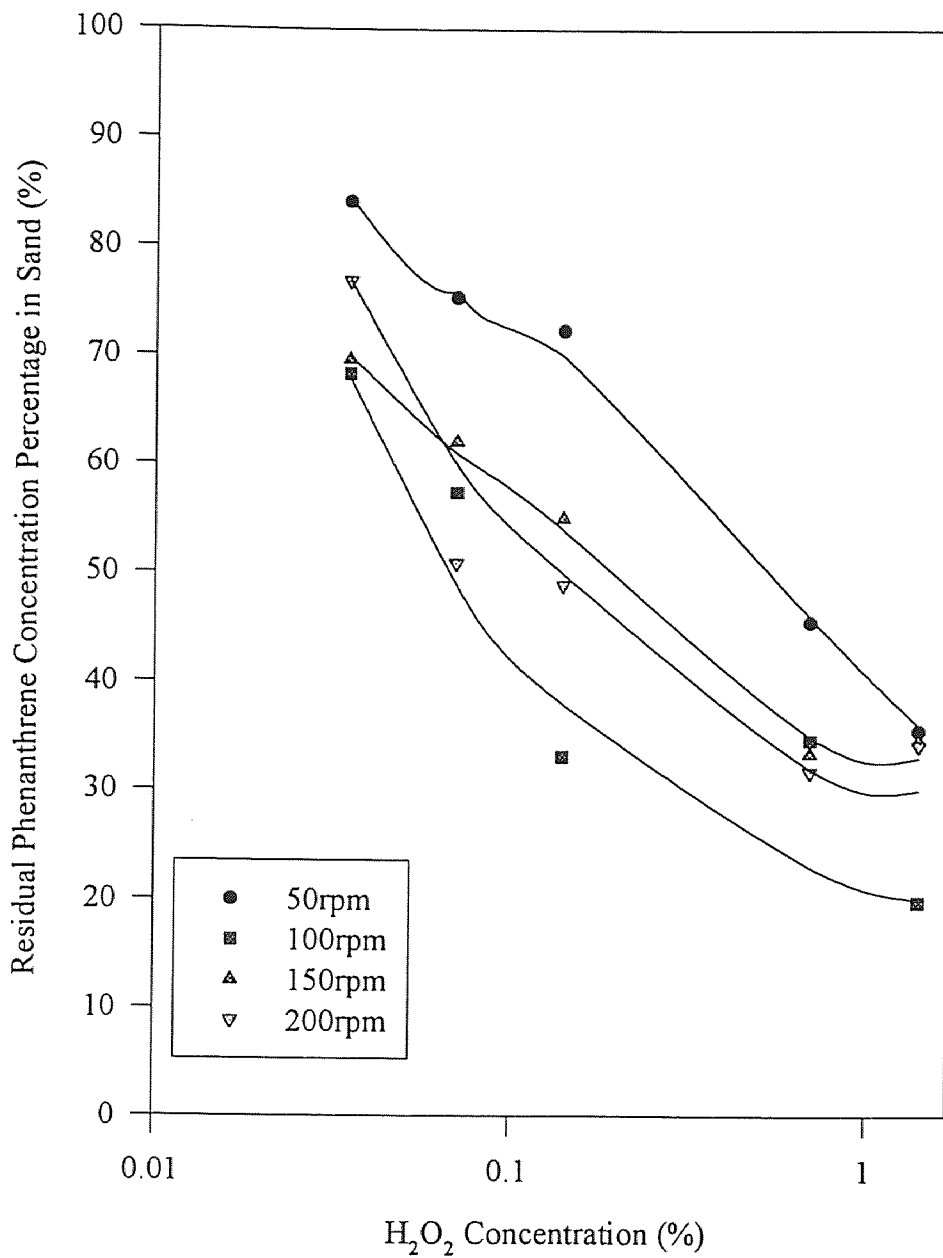
* 2.0g spiked sand (100mg/Kg) + 1.0 mL reagents (0.5 mL Fe⁺² + 0.5 mL H₂O₂), [Fe⁺²]= 0.4 g/L, for 30 minutes.

Figure 27 Mixing effects of the Fenton's reactions in [Fe(II)]=0.4g/L



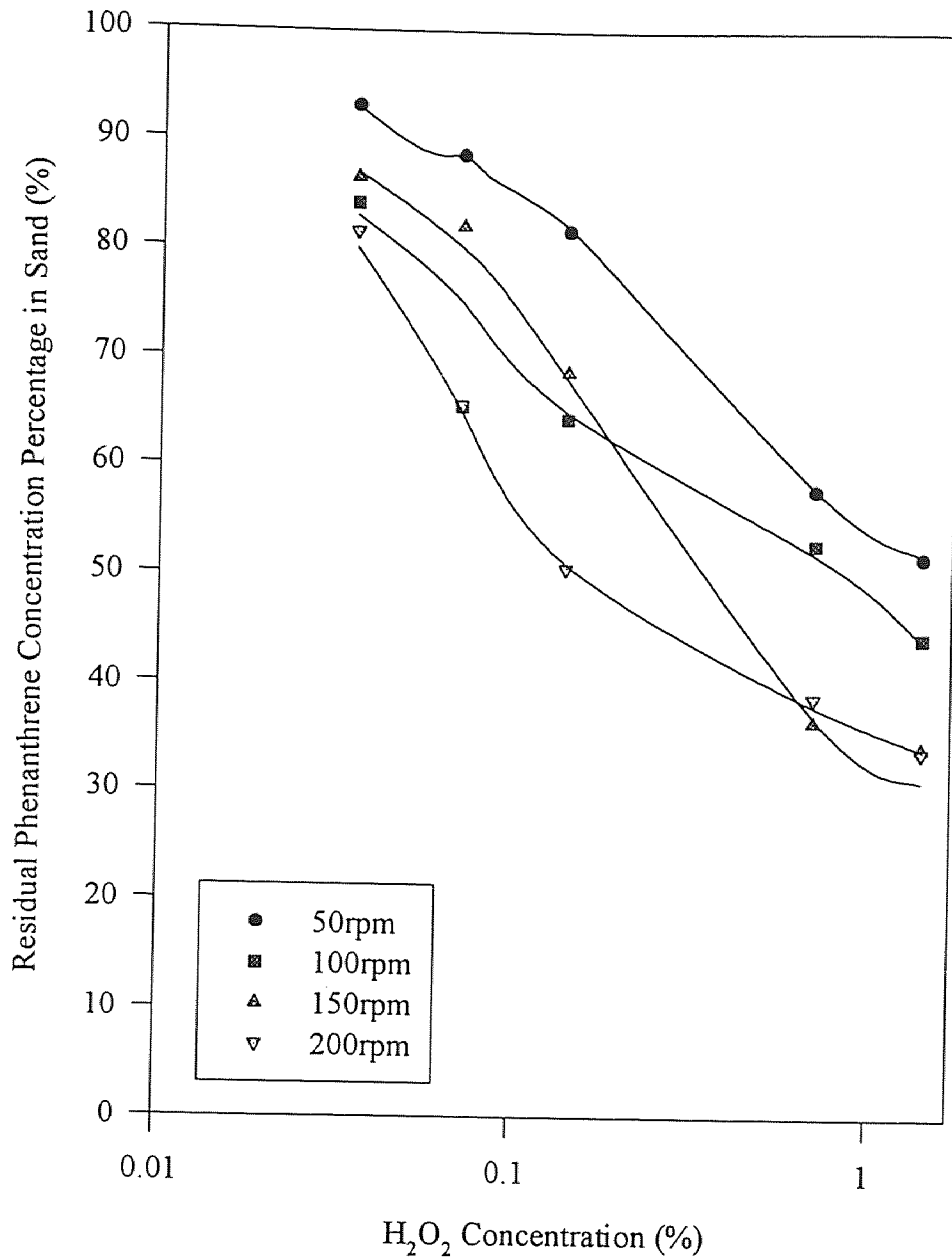
* 2.0g spiked sand (100mg/Kg) + 1.0 mL reagents (0.5 mL Fe⁺² + 0.5 mL H₂O₂), [Fe⁺²]= 2.0 g/L, for 30 minutes.

Figure 28 Mixing effects of the Fenton's reactions in [Fe(II)]=2.0g/L



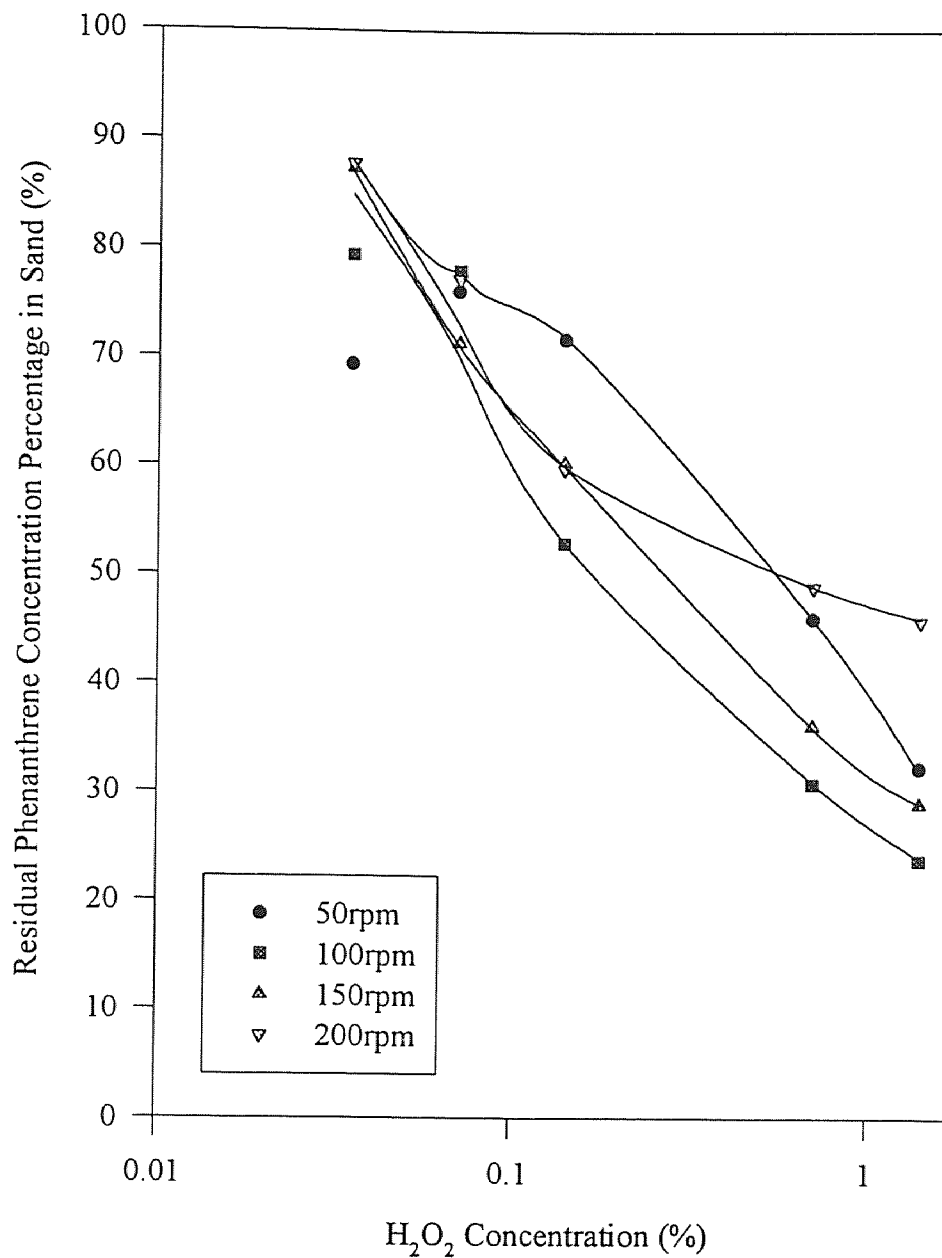
* 2.0g spiked sand (100mg/Kg) + 1.0 mL reagents (0.5 mL Fe⁺² + 0.5 mL H₂O₂), [Fe⁺²]= 4.0 g/L, for 30 minutes.

Figure 29 Mixing effects of the Fenton's reactions in [Fe(II)]=4.0g/L



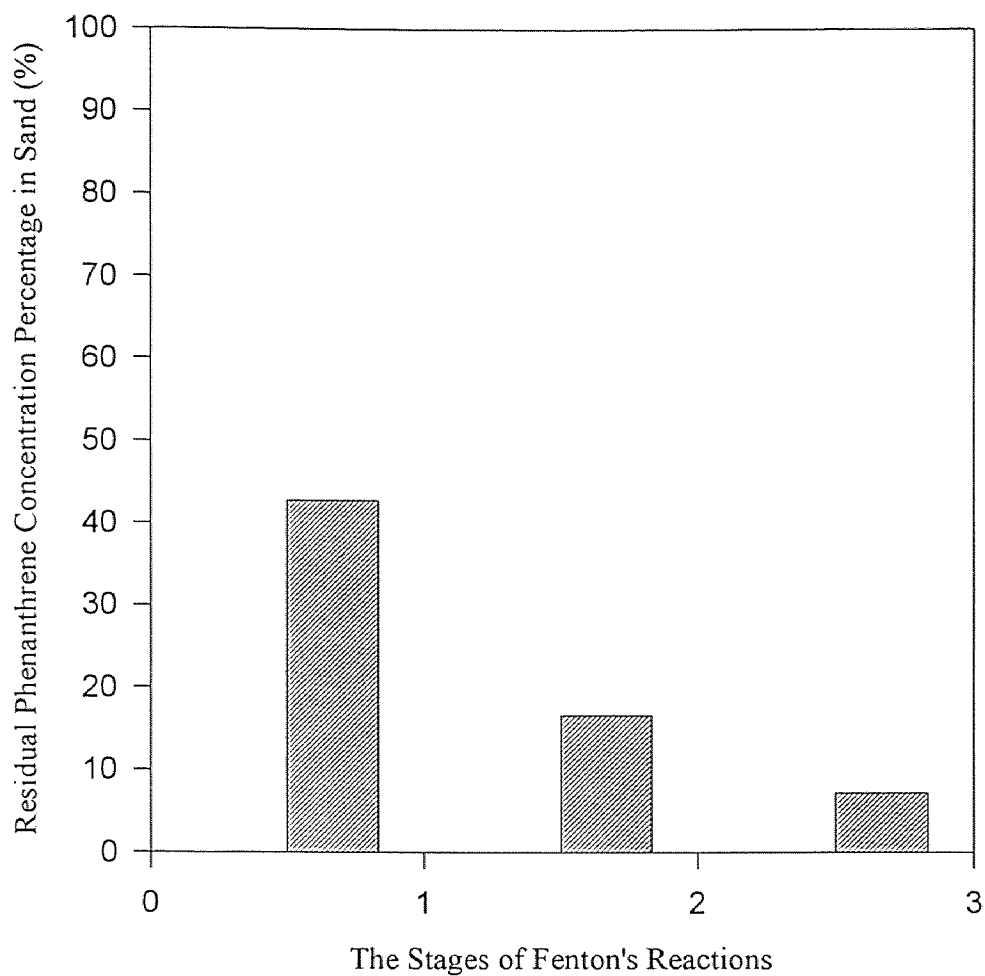
* 2.0g spiked sand (100mg/Kg) + 1.0 mL reagents (0.5 mL Fe⁺² + 0.5 mL H₂O₂), [Fe⁺²]= 6.0 g/L, for 30 minutes.

Figure 30 Mixing effects of the Fenton's reactions in [Fe(II)]=6.0g/L



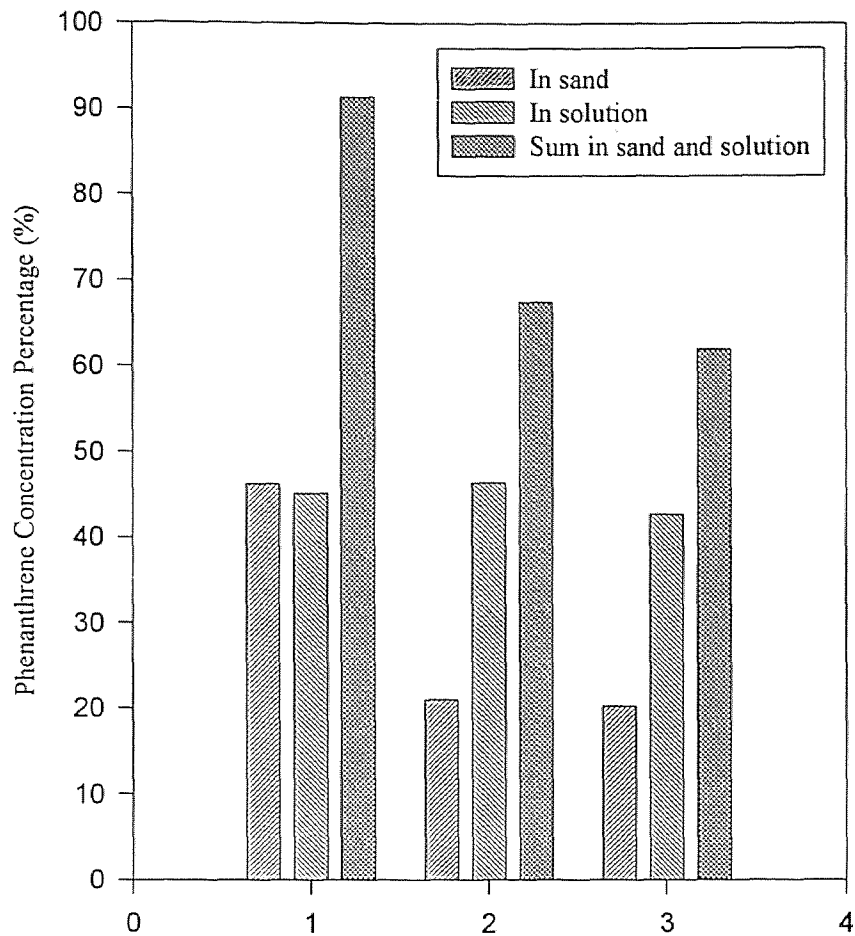
* 2.0g spiked sand (100mg/Kg) + 1.0 mL reagents (0.5 mL Fe⁺² + 0.5 mL H₂O₂), [Fe⁺²]= 8.0 g/L, for 30 minutes.

Figure 31 Mixing effects of the Fenton's reactions in [Fe(II)]=8.0g/L



* 2.0g spiked sand (100mg/Kg) + 1.0 mL reagents (0.5 mL Fe^{+2} + 0.5 mL H_2O_2),
Three times.
Each time: $[\text{Fe}^{+2}] = 4.0 \text{ g/L}$, $[\text{H}_2\text{O}_2] = 0.7\%$, at 150 rpm, for 30 minutes.

Figure 32 The effects for the series of the Fenton's reactions

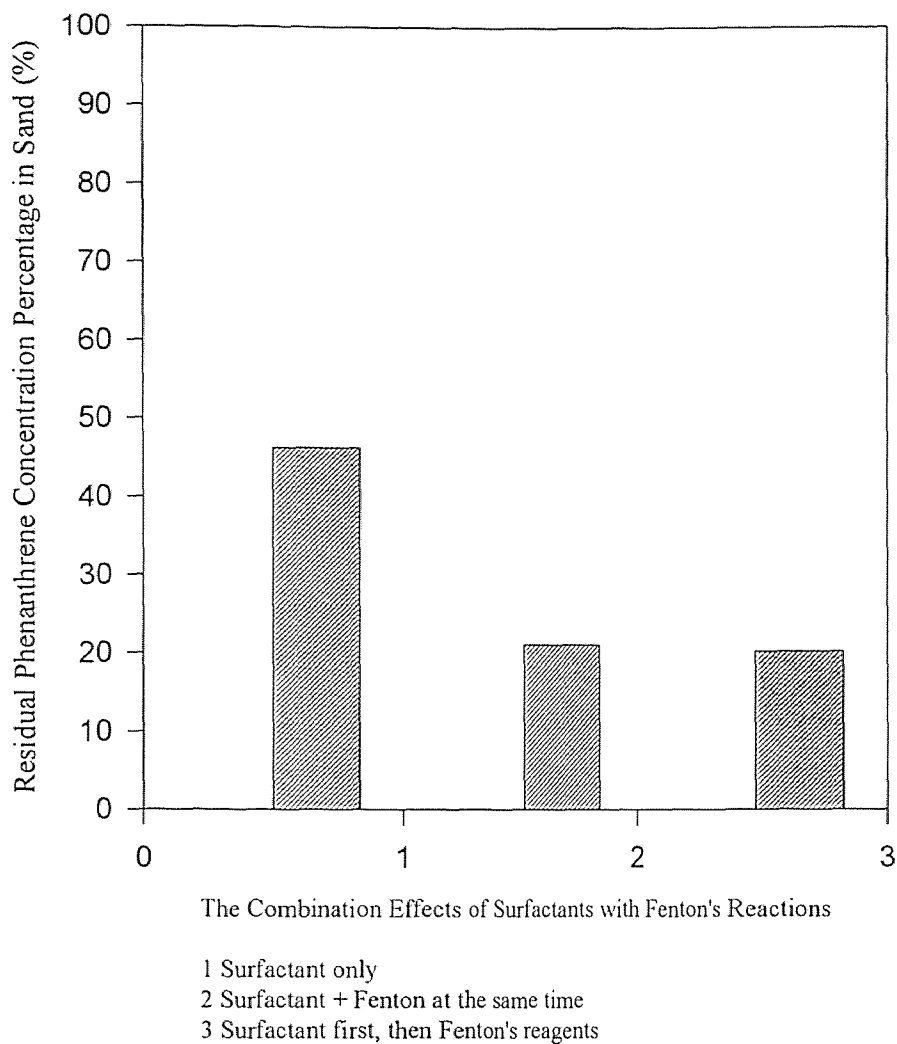


The Combination Effects of Surfactants with Fenton's Reactions

- 1 Surfactant only
- 2 Surfactant + Fenton at the same time
- 3 Surfactant first, then Fenton Rx.

* 2.0g spiked sand (100mg/Kg) + 1.0 mL TE in 4%,
 + 1.0 mL reagents (0.5 mL Fe^{+2} + 0.5 mL H_2O_2), $[\text{Fe}^{+2}] = 4.0 \text{ g/L}$, $[\text{H}_2\text{O}_2] = 0.7\%$,
 at 150 rpm, for 30 minutes.

Figure 33 The combination effects of the surfactant and Fenton's reactions



* 2.0g spiked sand (100mg/Kg) + 1.0 mL TE in 4%,
+ 1.0 mL reagents (0.5 mL Fe^{+2} + 0.5 mL H_2O_2), $[\text{Fe}^{+2}] = 4.0 \text{ g/L}$, $[\text{H}_2\text{O}_2] = 0.7\%$,
at 150 rpm, for 30 minutes.

Figure 34 The combination effects of the surfactant and Fenton's reactions for the residual phenanthrene concentration in the sand

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