

**Synthesis and Application of Iron/Copper Nanoparticles and Biosurfactants for
Remediation of Oil-contaminated Soil**

Anh Kien Vu

A Thesis
In the Department
of
Building, Civil and Environmental Engineering

Presented in Partial Fulfillment of the Requirements
For the Degree of
Doctor of Philosophy (Civil Engineering) at
Concordia University
Montreal, Quebec, Canada

September 2022
© Anh Kien Vu, 2022

**CONCORDIA UNIVERSITY
SCHOOL OF GRADUATE STUDIES**

This is to certify that the thesis prepared

By: Anh Kien Vu

Entitled: Synthesis and Application of Iron/Copper Nanoparticles and
Biosurfactants for Remediation of Oil-contaminated Soil

and submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy (Civil Engineering)

complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

Signed by the final examining committee:

_____	Chair
Dr. Zhibin Ye	
_____	External Examiner
Dr. Bing Chen	
_____	External to Program
Dr. Deniz Erol	
_____	Examiner
Dr. Chunjiang An	
_____	Examiner
Dr. Zhi Chen	
_____	Thesis Supervisor
Dr. Catherine Mulligan	

Approved by _____

Dr. Michelle Nokken, Graduate Program Director

07 September, 2022

Dr. Mourad Debbabi, Dean

ABSTRACT

Synthesis and Application of Iron/Copper Nanoparticles and Biosurfactants for Remediation of Oil-contaminated Soil

Anh Kien Vu, Ph.D.

Concordia University, 2022

Oil (or petroleum), consisting of a mixture of hydrocarbons, can leak from oil exploration, production, and use. Due to their complex mixture and interaction with the subsurface soil and water, they are hard to treat and can become a significant environmental concern. Rhamnolipid and sophorolipid biosurfactants, biologically produced surfactants, can be used to remove petroleum hydrocarbons. Nanoparticles have gained attention as promising materials for soil remediation. In many studies, nanoparticles have shown their effective degradation of oil pollutants in the soil, both at bench and field scales. However, the combination of biosurfactants and nanoparticles to treat oil-contaminated soil has not been thoroughly researched. In this study, suspension of iron/copper (Fe/Cu) nanoparticle and biosurfactant and mixture of biosurfactant foam and Fe/Cu nanoparticle were investigated for remediation of oil-contaminated soil. The results showed that Fe/Cu bimetallic nanoparticles were successfully produced with an average diameter of less than 20 nm, while Fe content was higher than Cu. The appearance of iron oxide and copper oxide was confirmed by X-ray diffraction (XRD) analysis.

The biosurfactant/nanoparticle suspension displayed a high oil removal rate from contaminated soil, followed the first-order reaction. For batch experiments, the oil remediation efficiency was

up to 84%, based on the experimental conditions. Optimum conditions to achieve the highest oil remediation performance included a rhamnolipid biosurfactant: nanoparticle ratio of 10:1 (wt%: wt%), pH 7, room temperature, and shaking speed of 60 rpm for 60 minutes. The remediation rate was improved by higher temperature and lower ionic strength. In the presence and absence of nanoparticles, rhamnolipid biosurfactant demonstrated a higher remediation efficiency than sophorolipid biosurfactant and ultraplex surfactant. The presence of other surfactants decreased the treatment productivity by 9-14% compared to using only rhamnolipid biosurfactant. After three cycles, nanoparticles were reused with a remediation efficiency of 59% by rhamnolipid biosurfactant.

In column experiments, biosurfactant foam/nanoparticle and biosurfactant/nanoparticle mixtures were effectively used to remediate the actual oil-contaminated soil (fine sandy soil with the original oil content of 3722 mg/kg), whereas the highest treatment efficiency was 67%, 59%, and 52% for rhamnolipid biosurfactant foam/nanoparticle, rhamnolipid biosurfactant/nanoparticle, and only rhamnolipid biosurfactant, respectively. The oil removal productivity decreased with the increase of flowrate due to the shorter contact time between the foam mixture and oil droplets. The breakthrough curves of oil pollutants in the soil column also suggested that the foam mixture's maximum oil treatment efficiency was higher than biosurfactant/nanoparticle suspension and only biosurfactant.

These results suggested that biosurfactant/nanoparticle and biosurfactant foam/nanoparticle suspension can be effectively used to remediate oil from contaminated soil. This work will significantly benefit the soil remediation field by providing an environmentally friendly and economical method for the remediation of oil-contaminated soil. Future studies will evaluate the effect of other factors, such as biosurfactant concentration, nanoparticle dosage, pH, on column

experiments. In addition, oil remediation effectiveness by suspension of biosurfactant or biosurfactant foam with other nanoparticles, such as Fe/Ni or Fe/Pd, in batch and column experiments should be evaluated.

ACKNOWLEDGMENTS

First and foremost, I would like to express the deepest gratitude to my advisor, Dr. Catherine Mulligan. Thank you for your endless support, encouragement, and invaluable advice for my dissertation. I would like to say thank you to my committee members, Dr. Zhibin Ye, Dr. Chunjiang An, Dr. Zhi Chen, Dr. Bing Chen, and Dr. Deniz Erol for their time and useful comments for my dissertation. My special thanks to Dr. An for his advice and support with my experiments and sample analysis. I would also like to acknowledge the funding assistance of the Natural Sciences and Engineering Research Council (NSERC) of Canada, NSERC PURE Create programme, and Concordia University. My research would not be possible without their support.

I would like to say thank you to all labmates for their help in setting up the experiment and analyzing the samples. Thanks Hong for the lab training and maintenance, thanks Dileep for the ICP-MS analysis, thanks Antonio for the endless conversation regarding the daily lab stuffs.

Finally, I would like to sincerely thank my family and friends for their endless support during my Ph.D. journey. Thanks my beautiful wife Thu Nguyen for your constant support and encouragement. Thanks for your patience with my boring stories regarding the lab experiment and job interview. Thank you for being there and continuing to support me. Thanks my little angel James “Còi” for your funny stories and quotes every day. You make us become a true family and we love you so much. To my parents, parents-in-law, siblings-in-law, and friends, thank you for your help for taking care of James when I was often too busy with my experiment and research.

Some parts of this dissertation were published in different journals, such as Environmental Technology, Environmental Technology Reviews, Environmental Science and Pollution Research. I would like to acknowledge these journals for their review and acceptance.

TABLE OF CONTENTS

LIST OF FIGURES	x
LIST OF TABLES	xii
LIST OF ABBREVIATIONS.....	xiii
CHAPTER 1: INTRODUCTION.....	1
1.1. General background.....	1
1.2. Research objectives.....	3
CHAPTER 2: LITERATURE REVIEW	5
2.1. Oil pollutant chemistry	5
2.1.1. <i>Composition of oil pollutants</i>	5
2.1.2. <i>Fate and transport of oil pollutants in the soil</i>	8
2.1.3. <i>Toxicity of oil contamination</i>	9
2.1.4. <i>Treatment methods for oil pollutants in soil</i>	11
2.2. Surfactants	37
2.2.1. <i>Synthetic surfactants</i>	38
2.2.2. <i>Biosurfactants</i>	39
2.2.3. <i>Use of surfactants for remediation of contaminated soil</i>	45
2.3. Fe-based nanoparticles.....	48
2.3.1. <i>Use of Fe-based nanoparticles for remediation of oil-contaminated soil</i>	49
2.3.2. <i>Use of bimetallic nanoparticles for removal of oil pollutants in soil</i>	60
2.4. Use of surfactant-stabilized nZVI for remediation of oil pollutants in soil.....	63
2.4.1. <i>Mechanisms of nanoparticle agglomeration and stabilization</i>	63

2.4.2.	<i>Mechanisms of surfactant-stabilized nZVI</i>	64
2.4.3.	<i>Remediation of organic contaminants in soil using surfactant-stabilized nZVI</i> ...	69
CHAPTER 3:	MATERIALS AND METHODS	72
3.1.	Materials	72
3.2.	Soil source and characterization	72
3.3.	Measurement of total petroleum hydrocarbon content in the soil	74
3.4.	Measurement of total metal concentration in suspension.....	75
3.5.	Measurement of surface tension and interfacial tension of biosurfactants	75
3.6.	Synthesis of Fe/Cu bimetallic nanoparticles.....	75
3.7.	Characterization of Fe/Cu nanoparticles.....	77
3.8.	Properties of biosurfactant/nanoparticle suspension.....	77
3.9.	Batch experiments.....	78
3.10.	Determination of total petroleum hydrocarbons in the soil	79
3.11.	Column experiments	80
CHAPTER 4:	RESULTS AND DISCUSSION.....	88
4.1.	Soil characterization	88
4.2.	Characterization of Fe/Cu particles	89
4.2.1.	<i>Scanning electron microscopy of Fe/Cu particles</i>	89
4.2.2.	<i>Transmission electron microscope of Fe/Cu particles</i>	90
4.2.3.	<i>X-ray diffraction of Fe/Cu particles</i>	91
4.3.	Critical micelle concentration value of surfactants.....	92
4.4.	Change of surfactant CMC with the addition of nanoparticles and soil	94
4.5.	Batch experiments.....	95

4.5.1.	<i>Effect of shaking speed</i>	96
4.5.2.	<i>Effect of shaking time</i>	97
4.5.3.	<i>Effect of surfactant concentration</i>	98
4.5.4.	<i>Effect of nanoparticle dosage</i>	100
4.5.5.	<i>Effect of soil amount</i>	101
4.5.6.	<i>Effect of pH</i>	106
4.5.7.	<i>Effect of temperature</i>	107
4.5.8.	<i>Effect of order of chemical addition</i>	109
4.5.9.	<i>Effect of particle size</i>	111
4.5.10.	<i>Effect of ionic strength</i>	112
4.5.11.	<i>Effect of surfactant combinations</i>	114
4.5.12.	<i>Reuse of nanoparticles</i>	116
4.6.	Column experiments	117
4.6.1.	<i>Foam quality and stability</i>	117
4.6.2.	<i>Evaluation of pressure gradient in the soil column</i>	120
4.6.3.	<i>Effect of flowrate</i>	122
4.6.4.	<i>Change in oil concentration in the soil column</i>	125
4.6.5.	<i>Mechanisms of surfactant-nanoparticle oil removal</i>	128
4.7.	Limitations	131
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS		133
5.1.	Conclusions	133
5.2.	Future research	135
REFERENCES		138

LIST OF FIGURES

Figure 1. Surfactant structure.....	37
Figure 2. Relationship between surfactant concentration, surface tension, micelle formation	41
Figure 3. Structure of four different rhamnolipid biosurfactants produced by <i>P. aeruginosa</i>	43
Figure 4. Structure of sophorolipid produced from <i>Candida bombicola</i>	44
Figure 5. Use of surfactants to remove oil pollutants from soil.....	47
Figure 6. Remediation of oil pollutants by nZVI.....	50
Figure 7. Use of nZVI for the in-situ remediation process	54
Figure 8. Interaction of nZVI and biosurfactant (in micelle form).....	68
Figure 9. Remediation of organic contaminants in soil by surfactant and nZVI.....	70
Figure 10. Calibration curve of oil pollutants in n-hexane	74
Figure 11. Fe/Cu bimetallic nanoparticle synthesis system.....	76
Figure 12. Column experiment for remediation of oil-contaminated soil	81
Figure 13. Foam column experiment for surfactant/nanoparticle mixture	83
Figure 14. SEM images of Fe/Cu particles.....	89
Figure 15. TEM images of Fe/Cu particles.....	90
Figure 16. Elemental distribution of Fe/Cu nanoparticles	91
Figure 17. XRD analysis of Fe/Cu nanoparticles	92
Figure 18. Surface tension of four surfactants at various concentrations	93
Figure 19. Increase of surfactant CMC in the presence of nanoparticles and soil.....	94
Figure 20. Effect of shaking speed on the oil treatment efficiency	96
Figure 21. Effect of shaking time on the oil treatment efficiency	97
Figure 22. Kinetics of oil treatment over time	98

Figure 23. Effect of surfactant concentration on oil treatment efficiency	99
Figure 24. Effect of nanoparticle dosage on the oil treatment efficiency	101
Figure 25. Effect of soil amount on the oil treatment efficiency	102
Figure 26. FTIR analysis of soil before and after adding biosurfactant/nanoparticle	103
Figure 27. Effect of pH on the oil treatment efficiency	107
Figure 28. Effect of temperature on the oil treatment efficiency.....	108
Figure 29. Effect of chemical order on the oil treatment efficiency	110
Figure 30. Effect of particle size on the oil treatment efficiency.....	111
Figure 31. Effect of ionic strength on the oil treatment efficiency.....	113
Figure 32. Effect of surfactant mixtures on the oil treatment efficiency	115
Figure 33. Reuse of nanoparticles for soil remediation	116
Figure 34. Effect of foam quality and biosurfactant concentration on foam stability	119
Figure 35. Effect of flowrate, foam quality, biosurfactant concentration on pressure gradient .	121
Figure 36. Effect of flowrate on the oil treatment efficiency by column	123
Figure 37. Breakthrough curves of oil pollutants in the soil column.....	126
Figure 38. GC analysis for oil compounds before and after treatment process	129
Figure 39. Proposed mechanism of oil removal by surfactant-nanoparticle	130

LIST OF TABLES

Table 1. Characteristics of some oil components	6
Table 2. Pros and cons of some common soil treatment methods	34
Table 3. Potential toxicity of some nanoparticles	57
Table 4. Summary of different stabilizers for nZVI particles.....	65
Table 5. Operation conditions for GC-FID analysis.....	86
Table 6. Characteristics of tested soil	88
Table 7. Change in absolute zeta potential value after adding surfactant.....	95
Table 8. Comparison of the oil treatment efficiency with other methods	104
Table 9. Correlation coefficient of flowrate and treatment efficiency.....	123
Table 10. Mass balance for oil pollutants after column experiment.....	131

LIST OF ABBREVIATIONS

ABS	Alkylbenzene sulfonate
BTEX	Benzene, toluene, ethylbenzene, and xylene
CMC	Critical micelle concentration
CMP	4-chloro-3-methyl phenol
CVOCs	Chlorinated volatile organic compounds
DOM	Dissolved organic matter
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
HDPE	High density polyethylene
HOCS	Halogenated organic compounds
LNAPLs	Light nonaqueous phase liquids
NOM	Natural organic matter
nZVI	Nanoscale zero valent iron
NTA	Nitrilotriacetic acid
PAA	Polyacrylic acid
PAC	Powdered activated carbon
PAHs	Polycyclic aromatic hydrocarbons
PAM	Polyacrylamide
PAP	Polyaspartate
PCB	Polychlorinated biphenyl
pCBA	4-chlorobenzoic acid
PCE	Perchloroethylene

PCP	Pentachlorophenol
PFOA	Perfluorooctanoic acid
POMs	Polyoxometalates
POPs	Persistent organic pollutants
PSS	Polystyrene sulfonate
ROS	Reactive oxygen species
SDBS	Sodium dodecylbenzene-sulfonic acid
SEM	Scanning Electron Microscopy
SVOCs	Semi volatile organic compounds
TCB	Trichlorobenzene
TCE	Trichloroethylene
TEM	Transmission electron microscope
USEPA	United States Environmental Protection Agency
VOCs	Volatile organic compounds
XRD	X-ray diffraction

CHAPTER 1: INTRODUCTION

1.1. General background

Oil pollutants (or petroleum hydrocarbons) may leak from improper production, use, and disposal and become soil contamination sources. Oil pollutants can represent a variety of organic compounds and by-product contaminants in the environment, such as persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs). Due to the adverse effects on humans, animals, and the environment, these contaminated sources are considered a significant environmental issue (Ramirez et al., 2017). After adsorbing into the soil particles, the oil pollutants may stay stably in the soil for an extended time (Gennadiev et al., 2015). Due to the limited solubility in the soil of these compounds, the low mass transfer rate for biodegradation, and the complex composition of some oil mixtures, it is difficult to treat this type of contamination. In addition, leaching from the soil makes them a continuous source of soil contamination which can cause adverse impacts to the surrounding communities. For example, petroleum hydrocarbons-contaminated soil may change the soil's physical and chemical properties or inhibit the growth of microbes and plants due to increased moisture content (Vázquez-Luna, 2014).

Oil pollutants can be identified by their toxicity, classified in the "priority pollutants" list of the United States Environmental Protection Agency (USEPA). According to the USEPA Toxic Release Inventory report (2005), the crude oil industry is considered one of the primary sources that discharge oil pollutants into the environment. The liquid organic contaminants existing as a separate phase in aqueous media are named nonaqueous phase liquids (NAPLs). NAPLs can be

classified as dense nonaqueous phase liquids (DNAPLs) (e.g., carbon tetrachloride, chlorophenols, PCBs) and light nonaqueous phase liquids (LNAPLs) (e.g., gasoline, heating oil, jet fuel), which are denser and lighter than water, respectively. Because of the interfacial forces, part of the LNAPLs will be retained as the immobile ganglia or globules within the soil pores when moving through the subsurface (Pennell et al., 1993).

Oil pollutants may be derived from different sources. Some significant sources are industrial, municipal, and medical wastes. Notably, a few potential origins are leaks and spills from industrial activities or gas stations, oil discharges or chemical storage tanks, inappropriate disposal of cleaners, oil, household wastes in the municipality, and leakage from landfills and garbage dumps. For example, petroleum hydrocarbons may leak from underground storage or during transportation. Otherwise, PAHs are employed in coal storage sites, o-dichlorobenzene and p-dichlorobenzene are discharged from industrial chemical factories, ethylbenzene and toluene are discharged from petroleum refineries and factories (Canada Environmental Protection Service, 1984).

Due to the weathering effect, the soil is mainly composed of minerals and organic matter. Soil may interact with contaminants by sorption, complexation, and precipitation. Adsorption is caused by the attachment or chemical bonding of oil pollutants on soil surfaces. The potential physical forms of oil pollutants in soil are solid particles, liquid films, sorbed onto and into the soil, in soil macropores, and soil micropores (Wild, 1993).

Therefore, it is critical to promote an environmentally friendly and more effective method for remediation of oil from contaminated soil. The results from this study can be used to evaluate and predict the fate and transport, physical and chemical properties, removal mechanism, and the interaction of oil pollutants with soil particles and microorganisms in the short and long term on

the contaminated sites. From that, the scope and best soil remediation alternative can be determined, which will help to reduce the adverse effects of oil pollutants to humans, animals, and the environment (Artiola et al., 2004; Valentin et al., 2013).

1.2. Research objectives

This study aims to provide an evaluation of the application of surfactants and nanoparticles (mostly nZVI) for soil remediation, examine the fate and transport of surfactant-stabilized nZVI in soil, evaluate the factors affecting the reactivity and features of surfactant-stabilized nZVI, and determine the knowledge gaps and future research needs for resolving significant challenges. The specific objectives of this work are to:

- Prepare and characterize Fe/Cu nanoparticles
- Investigate the interaction of Fe/Cu nanoparticles with biosurfactants and contaminated soil
- Determine the effect of various conditions on soil remediation experiments
- Evaluate the mechanisms of interaction between surfactant and nanoparticle and the removal of oil pollutants by the surfactant/nanoparticle mixture

This thesis consists of five chapters, which are the introduction, literature review, materials and methods, results and discussion, conclusions and recommendations.

Chapter 1 presents the introduction of the problem and the objectives of this study

Chapter 2 describes the literature reviews regarding the oil pollutants in soil. In particular, the composition, fate and transport, toxicity of oil pollutants in the soil were introduced. The existing treatment methods for oil pollutants in soil, such as physicochemical, chemical, thermal, phytoremediation, biological treatment methods were also presented. In addition, it reviews the definition, types, properties of biosurfactants and Fe/Cu nanoparticles, and their application in soil remediation.

Chapter 3 gives the materials and methods utilized to synthesize and characterize the soil source, Fe/Cu nanoparticles, and biosurfactants. Oil pollutants were extracted by sonication in n-hexane and were measured by UV-Vis spectrophotometer. The total concentration of Fe/Cu nanoparticles in the surfactant-particle suspension and supernatant was measured by ICP-MS. The surface tension and interfacial tension of surfactants were determined by force tensiometer. The Fe/Cu nanoparticles were synthesized by a simple method and were characterized by SEM, TEM, XRD. The properties of biosurfactant/nanoparticle suspension were determined by the zeta potential, FTIR, and pCBA formation. The column experiments were conducted to investigate the performance of biosurfactant/nanoparticle suspension to stimulate in-situ remediation of oil-contaminated soil.

Chapter 4 includes all the results and discussion regarding the soil, Fe/Cu nanoparticles, and biosurfactants mentioned in Chapter 3. Moreover, the effect of some factors, such as shaking speed, shaking time, surfactant concentration, nanoparticle dosage, soil amount, pH, temperature, order of chemical addition, particle size, ionic strength, reuse of nanoparticles, column experiments, were provided. The limitations of this study were also discussed.

Chapter 5 summarizes all key points from the research project including some contributions to soil remediation field. In addition, some suggestions for future research are recommended.

CHAPTER 2: LITERATURE REVIEW

2.1. Oil pollutant chemistry

2.1.1. *Composition of oil pollutants*

Oil compounds are the yellowish-black liquid found naturally in deposits, underground pools and reservoirs, within sedimentary rocks or subterranean. They may occur in the gas (e.g., natural gas), semisolid (e.g., bitumen), solid (e.g., wax), or liquid forms (Ossai et al., 2020). They comprise a mixture of hydrocarbons formed by the decomposition of dead plants and animals millions of years ago (US Energy Information Administration, 2021). They have been used as the energy source for thousands of years. Oil compounds are mostly found below the Earth's surface and can be extracted through drilling. Oil compounds may leak and be released into the environment during the production and storage process, whereas they will be degraded due to the physical, chemical, and biological changes (or weathering) (Devold, 2013).

Oil pollutants are mainly composed of two groups: aliphatics and aromatics. Aliphatics include alkanes, alkenes, and cycloalkanes, while aromatics comprise at least one benzene ring in their structure, such as PAHs (e.g., naphthalene) or BTEX (Williams et al., 2006). In addition, a small component of oil compound includes the non-hydrocarbon parts, such as sulfur compounds (e.g., sulfides, cyclic sulfides), oxygen compounds (e.g., alcohols, carboxylic acids, esters, ethers, ketones), nitrogen compounds (e.g., pyridine, nitriles, pyrrole), and metals (Costa et al., 2012; Speight, 2006). The properties of some aromatic hydrocarbons in oil are presented in Table 1. Crude oil mainly contains aliphatic hydrocarbons.

Table 1. Characteristics of some oil components (Williams et al., 2006)

Name	Typical amount in crude oil (%wt)	Physical and chemical properties				Regulatory and human health information	
		Molecular weight, g	K_{oc} , L/kg	Solubility in water at 25°C, mg/L	Henry's law constant at 25°C	MCL, mg/L	HBL, mg/L
Benzene	0.16	78	59.0	1800	0.228	0.005	---
Toluene	0.67	92	182	530	0.272	1	---
Ethylbenzene	0.17	106	363	170	0.323	0.7	---
Total xylenes	---	---	---	---	---	10	---
m-xylene	0.66	106	407	160	0.301	---	---
o-xylene	0.26	106	363	180	0.213	---	---
p-xylene	0.26	106	389	190	0.314	---	---
Naphthalene	0.069	128	2000	31	0.0198	---	1
Acenaphthene	0.0057	154	7080	4.2	0.00636	---	2
Fluorene	0.020	166	13800	2.0	0.00261	---	1
Anthracene	0.0011	178	29500	0.043	0.00267	---	10
Fluoranthene	0.0004	202	107000	0.21	0.00066	---	1
Pyrene	0.0008	202	105000	0.14	0.00045	---	---
Benz (a) anthracene	0.0003	228	398000	0.009	0.00014	---	0.0001
Chrysene	0.0013	228	398000	0.0016	0.00388	---	0.01

Benzo (a) pyrene	0.0002	252	1020000	0.0016	0.00005	0.0002	---
Benzo (b) fluoranthene	0.0004	252	1230000	0.0015	0.00455	---	0.0001
Benzo (k) fluoranthene	0.0016	252	1230000	0.0008	0.00003	---	0.001
Indeno (1,2,3- c,d) pyrene	0.0007	276	3470000	0.000022	0.00007	---	0.0001

K_{oc} = organic carbon-water partition coefficient

MCL = drinking water maximum contaminant level

HBL = water health based limits

Many aromatic hydrocarbons in Table 1 are in the “priority pollutants” list by USEPA and can cause cancer for humans. The BTEX and PAHs are also classified in The Clean Water Act Priority Pollutant list and Comprehensive Environmental Response, Compensation, and Liability Act Priority List of Hazardous Substances. In other words, they are considered toxic substances that should be treated with priority. From Table 1, the K_{oc} of BTEX compounds is lowest, reflecting that BTEX compounds are mobile in soil. In addition, PAHs are likely to partition into sediments and soils due to their low volatility, low solubility, and high K_{oc} . Petroleum hydrocarbons may be biodegraded by bacteria and organisms in soils and sediments, such as *Pseudomonas*. Due to the high-energy electrons in their composition, petroleum hydrocarbons are considered food sources (or electron donors) for microbial populations. The biodegradation rates for different types of petroleum hydrocarbons are dependent on the occurrence of their terminal electron acceptor processes (TEAP), such as dissolved oxygen (DO), nitrate (NO_3^-), insoluble manganese (Mn^{4+}),

ferric iron (Fe^{3+}), sulfate (SO_4^{2-}), and carbon dioxide (CO_2). The biodegradation rates are generally low for high molecular weight hydrocarbons due to their excellent biodegradation-resistant properties (Williams et al., 2006).

2.1.2. Fate and transport of oil pollutants in the soil

When oil pollutants are released into the soil, their physical, chemical and biological characteristics can be changed due to the interaction with soil particles, microorganisms, and metabolic pathways (or weathering) (Abdel-Shafy and Mansour, 2016). In the meanwhile, oil pollutants can influence the soil characteristics, such as physical features (e.g., soil compaction, texture hydraulic conductivity) or chemical properties (e.g., mineral, heavy metal, or organic matter content) (Liu et al., 2020; Hreniuc et al., 2015).

The transport of oil pollutants in the environment includes three main processes: desorption from soil particles, volatilization into the air, or dissolution in the soil moisture (Souza et al., 2014). In particular, oil pollutants can survive in soil pore space as the residual saturation in the liquid form, evaporate into the atmosphere through soil pores, or dissolve in the soil pore water. Their transport in the soil is strongly dependent on their composition, physical, and chemical properties (Elijah, 2022; Esbaugh et al., 2016). Due to the difference in molecular structure and lower molecular weight, the evaporation of aliphatic hydrocarbons is higher than aromatic hydrocarbons. Hence, at contaminated sites where volatilization is the predominant process, it is easier for the aliphatic hydrocarbons to volatilize and become the primary air pollutants.

In nature, oil deposits are mainly discharged into the environment from deep onshore (or inland) and offshore explorations (Varjani, 2017). When oil pollutants enter the soil, due to their

hydrophobicity features and affinity for organic matter, they may attach to soil particles or adsorb to organic materials and stay in the soil for an extended period, contaminating the soils and sediments. The transport of oil pollutants in contaminated soil may cause adverse effects to the aquatic communities downstream of the contaminated sites (Priyadarshane et al., 2022). Their permeability through the unsaturated soil layers also plays a crucial role in their widespread inside the soil (Banerji et al., 1995).

Oil is released to the soil by two general pathways: flow infiltration of bulk oil as a result of gravity forces and capillary action, and separation of individual compounds from bulk oil mixture and dissolution in air or water, which contribute significantly to the soil contamination. During regular operation at the oil fields, the oil-contaminated soil is caused by the leakage and spillage of crude oil from oil wells, sumps and pits, tank batteries, gathering lines, and pump stations. The oil pollutant levels in the soil depend on the site location, soil moisture content, terrain, climate, rate of release, and oil viscosity. The waste crude oil is typically collected to a waste pit. After that, the upper layer of oil in the waste pit is transferred to stations, the combustible portion is discarded and burnt at an isolated location, and the remaining contaminated soil in the waste pit is left to be degraded by natural processes. During the rainy season, flooding or accidents, the crude oil from the waste pit may spread to surrounding areas and cause pollution to the soil.

2.1.3. Toxicity of oil contamination

The toxicological effect of oil pollutants is caused by a small fraction of oil pollutants (Parish, 2013). Due to the wide range of molecular mass and boiling points of various oil compounds, their toxicity level to the environment is also different. Oil pollutants' chemical composition and

physical state also play a key role in their toxicity and bioavailability to substrates (Van der Heul, 2011). In particular, their harmfulness and lethality strongly depend on the chemical composition and characteristics of compound fractions, exposure mode, level, and time. Some examples of toxicity of oil pollutants on human health and animals are haemotoxicity, carcinogenicity, genotoxicity, mutagenicity, teratogenicity, cytotoxicity, neurotoxicity, immunotoxicity, nephrotoxicity, hepatotoxicity, cardiotoxicity, ocular toxicity, which may damage red blood cells, cause cancer, break non-transmissible DNA, activate transmissible genetic mutations, create embryo or foetus malformation, harm cells, destruct brain and nervous system, stop immune system function, injure kidney, damage liver, weaken heart muscles, or cause eye disorders, respectively (Azeez et al., 2015; Elijah, 2022; Gutzkow, 2015; Lawal, 2017; Ogunneye et al., 2014; Priyadarshanee et al., 2022; Zheng et al., 2014).

The influence of oil contamination on soil comprises short-term and long-term effects due to the bioaccumulation, leaching, and extension of oil into the soil. The presence of oil may change the physical and chemical properties of soil. In particular, it may change the pH, organic matter, phosphorus (P) and potassium (K), and cation exchange capacity of the soil, which inhibits the microbial growth, reduces the microbial populations or decreases the soil capacity in retaining P and K (Vázquez-Luna, 2014). Besides, it may change the water retention capacity in soil due to an increase in moisture content. In addition, the formation of macroaggregates and macropores in oil-contaminated soil can improve water flow and kill plants due to water pressure.

Furthermore, the existence of oil in soil may inhibit the growth of plants. In particular, it can form a coarse layer outside and around the plants, which protects them from water and mineral salt. As a result, the biomass formation of plants in soils is limited, the biomass production in leaves and stems is decreased, and the transport of water to plants is diminished. Therefore, plants'

height and root length are reduced, seed germination is inhibited, and plant metabolic processes are broken, leading to a decrease in the resistance to pests and diseases, and stunted growth (Vázquez-Luna, 2014). Hence, the development of plants is negatively influenced, causing some plant diseases, such as roots deformation, chlorosis and necroses in leaves and flowers (Mendez-Natera et al., 2004; Rusin et al., 2015; Shan et al., 2014).

The attendance of oil in soil may affect the soil microorganisms. It can change soil's physical and chemical properties, which stops the gas exchange of soil and atmosphere that significantly reduces microbial populations. Moreover, it is harder for aerobic bacteria to degrade the oil-adsorbed soil, which negatively impacts their growth. However, some microorganisms may adsorb and use hydrocarbons in oil as the food source to improve their growth significantly. These microorganisms, such as *L. leucocephala*, can be used to remove PAHs from polluted soils in contaminated sites (Vázquez-Luna, 2014).

Otherwise, the oil-contaminated sediments may toxify the aquatic environment, killing the creatures like fish. It was proven that the presence of crude-oil-contaminated sediments in the aquatic environment might kill the young fish *Carassius auratus* due to the ingestion of oil-contaminated sediment, invasion of toxic substances, and environmental stress (Yuanyuan et al., 2009).

2.1.4. Treatment methods for oil pollutants in soil

Various methods have been widely used to remediate soil contaminated with oil pollutants. According to the USEPA, some common approaches are chemical, physical, and biological methods (US Environmental Protection Agency, 2007). They are classified as in-situ or ex-situ

treatment methods, in which contaminants are treated at the same site (onsite) or in another place from the original site (offsite), respectively. Choosing the suitable remediation method depends on the site characteristics, composition, and properties of contaminant, component of microbial community present, as well as physical, chemical, and biological conditions of the contaminated surrounding. Furthermore, the remediation mechanisms, regulatory concerns, total cost and time, and treatment system alternation should also be considered (Ossai et al., 2020).

2.1.4.1. Physicochemical treatment methods

The in-situ or ex-situ physicochemical methods involve remediation, recovery, and containment approaches that use physical, chemical, and mechanical barriers to separate or recover oil pollutants from the contaminated soil. Common physicochemical methods include soil isolation and containment, soil washing, soil vapor extraction, and soil extraction.

2.1.4.1.1. Soil isolation and containment

This technique involves the utilization of physical and mechanical barriers to reduce and prevent the oil pollutants from horizontal and vertical migration, seepage, permeability, and leaching in the soil (Jankaite and Vasarevičius, 2005). In this technique, contaminated soil is isolated and contained by barriers made of various materials, such as steel, bentonite, cement, asphalt, or concrete. For soil remediation, this technique includes mainly surface capping and pump and treat.

2.1.4.1.1.1. Surface capping

This in-situ technique involves using a thick and impermeable cap to cover and separate the contaminated media and surface at the polluted site. Through this technique, the impacted soil is isolated from potential receptors. The infiltration of rainfall is limited, reducing the movement and migration of oil pollutants to the surface and protecting humans and animals from direct contact with the contaminated materials. A good cap, such as HDPE liner, geomembrane, asphalt, cement, or clay, can minimize oil pollutants' potential leaching or migration from the contaminated site by restricting or avoiding the leachate infiltration to the surrounding areas (Ossai et al., 2020). Surface caps can prevent the formation of contaminated dust and the volatilization of oil pollutants, limiting the upward movement of vapor. However, it cannot restrict the horizontal movement and migration of oil pollutants due to the groundwater flow. Hence, combining the surface cap with vertical barriers is suggested to create a land encapsulation around the polluted site (USEPA, 2007). A layer of vegetative cover is usually included on top of a typical surface capping to minimize runoff, soil erosion, and precipitation. Cornelissen et al. (2016) showed a flux decrease of 80% to 90% for polychlorinated dibenzodioxin and dibenzofuran by PAC surface capping after five years at a large scale field. This value is much higher than the non-active caps with a 20% to 60% flux reduction.

2.1.4.1.1.2. Pump and treat

In this in-situ technique, contaminated soil is pumped to the ground and treated by other remediation methods, such as biodegradation, air stripping, or activated carbon (Zhang, 2019). The

pump and treat technique is suitable for remediation of different soil contaminants, for example, VOCs, SVOCs, or fuel oil. It will help prevent and control the release, migration, and spread of oil pollutants from the contaminated site. The treatment efficiency of the pump and treat method depends on the characteristics of the contaminated site (e.g., hydrogeological), remediation objectives, and features of oil pollutants (e.g., sorption, solubility) (Ossai et al., 2020). For example, the pump and treat method effectively removed a large amount of oil pollutants from 15 polluted sites (Zhang, 2019).

2.1.4.1.2. Soil washing

In this technique, contaminated soil is washed and scrubbed with a liquid, such as surfactants or additives, to obtain clean soil, which is then separated from the polluted soil and flush water (Mulligan, 2021; Fabbicino et al., 2018). In particular, soil washing can breakdown the bond between oil pollutants and soil particles and disconnect them from contaminated soil. The water after the treatment process can be discharged or recirculated for a new washing process by a mechanical pump. Depending on the contaminant characteristics and remediation objectives, soil washing can be used as a separate treatment technique or a pretreatment step for other remediation methods (Sharma and Reddy, 2004). The limitation of this technique involves the potential formation of soluble complexes between flush water and contaminants. This technique has been effectively used for the remediation of oil-contaminated soil. The soil washing system removed 97% total petroleum hydrocarbon and 73% benzo(a)pyrene from contaminated soil in an old railroad (Kang et al., 2012). In another paper, up to 80% of petroleum hydrocarbons were eluted

by soil washing with a surfactant mixture (Tween 80 and sodium dodecyl sulfate) (Zhang et al., 2022).

2.1.4.1.3. Soil vapor extraction

In this technique, the oil pollutants are volatilized by a pressure gradient caused by adequate gas or airflow from vacuum pumps or extraction wells. The oil pollutant vapors will transport through the extraction wells to the aboveground, where they will be collected and treated (Ma et al., 2016; Dadrasnia et al., 2013). Due to the dependence on the contaminant volatility, this technique is suitable for removing the highly volatile VOCs and some SVOCs from contaminated soil, especially soil in the active industrial sites. In a pilot-scale study, soil vapor extraction removed up to 89% of SVOCs in contaminated soil (Zhang et al., 2015).

2.1.4.1.4. Soil extraction

In this technique, a single or mixture of solvents, such as hexane, dichloromethane, or chemical surfactants, is used to extract, remove, or separate the oil pollutants from contaminated soil. After that, the solvent-oil mixture may be separated by the filtration method, while solvent can be recovered by the distillation process (Al-Zubaidi and Al-Tamimi, 2018). In particular, the soil extraction method includes the desorption and elution of contaminants from the soil matrix to the extracting fluid. This technique is ideal for removing hydrophobic oil pollutants in soil (USEPA, 2001). The treatment efficiency of soil extraction is strongly dependent on the contact between contaminated soil and solvent mixture (Silva et al., 2005). Solvent extraction by a mixture of

hexane and acetone removed up to 97% oil contaminants from the contaminated soil (Li et al., 2012).

2.1.4.2. Chemical remediation methods

These treatment methods involve using chemicals to remove, precipitate, or separate oil pollutants from the soil or contain the contaminants. Some common chemical remediation methods are stabilization, chemical oxidation-reduction, adsorption by activated carbon, supercritical fluid extraction and oxidation, and encapsulation.

2.1.4.2.1. Stabilization

In this technique, soil contaminants are locked into a durable matrix or converted to chemically stable form by the formation of immobilizing mass, monolithic block, clay-like material, or non-leachable granular particular due to the addition of cementitious binding materials into the contaminated medium (Ba-Naimoon and Hamid, 2016; Bates and Hills, 2015). As a result, the migration and movement of contaminants in the soil will be restricted and prevented. Through the stabilization, soil contaminants are transformed into less toxic and soluble forms, which will decrease their harmful risk. This approach can be obtained by different methods, such as pozzolanic, thermoplastic, cement-based, organic polymer, and encapsulation approaches (Banaszkiewicz and Marcinkowski, 2017; Bikoko and Okonta, 2016; Bates and Hills, 2015). The solidification performance is dependent on the properties of binding materials and target contaminants, such as structural integrity, compressibility, and permeability (Anderson and

Mitchell, 2003). The contaminant mobility, solubility, and chemical reactivity are decreased due to different processes (e.g., precipitation, complexation, adsorption) caused by solidifying or stabilizing materials (e.g., portland cement, gypsum, silicates, carbon, phosphates) (USEPA, 2006). The stabilization technique showed a high solidification efficiency of petroleum-contaminated soil using asphalt emulsions (Meegoda, 1999) or biochar-cement (Fang et al., 2016).

2.1.4.2.2. Chemical oxidation-reduction

This in-situ technique involves the transformation and conversion of oil pollutants into the less toxic or nontoxic compounds due to the addition of chemical oxidants or catalysts, for example, permanganate (MnO_4^-), sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), hydrogen peroxide (H_2O_2), hydroxyl radical ($\bullet\text{HO}^-$), or sulfate radical ($\bullet\text{SO}_4^-$), to the contaminated soil (Asgari et al., 2017; Kluck and Achari, 2004). Other treatment processes can be required for the converted organic compounds (Besha et al., 2018). After being injected into the subsurface of contaminated soil, oxidants and catalysts can react with oil pollutants to form innocuous compounds, such as carbon dioxide and water. The treatment efficiency by chemical oxidation depends on contact time between contaminants and the oxidants. In addition, site characteristics and soil properties, such as pH, natural organic matter, soil hydraulic conductivity, soil permeability, or contaminant amount, also contribute critical roles to the degradation performance (Ossai et al., 2020). Chen et al. (2016) showed a remediation efficiency for diesel contaminated soil of 48% to 93% after 120 days by in-situ chemical oxidation using permanganate, persulfate, and hydrogen peroxide. Meanwhile, the removal performance decreased in the order of persulfate, permanganate, hydrogen peroxide. There was a positive correlation between removal efficiency and oxidant persistence.

2.1.4.2.3. Adsorption by activated carbon

In this in-situ technique, oil pollutants are adsorbed on the surface of an activated carbon filter. The adsorption efficiency is dependent on the properties of the activated carbon filter, such as sorption capacity, hydrophobicity, specific surface area, and pore structure (Zahed et al., 2021). The adsorption mechanism is controlled by the van der Waals force through a reversible process (Karanfil and Kilduff, 1999). Kalmykova et al. (2014) showed a removal performance of 50% and 99% for petroleum hydrocarbons and PAHs, respectively, from landfill leachate by granulated activated carbon filters.

2.1.4.2.4. Supercritical fluid extraction and oxidation

This in-situ technique involves the use of solvents, for instance, carbon dioxide, methane, or water at high temperature and pressure (above the critical point of water 374.3°C and 22.12 MPa) to extract oil pollutants from contaminated soil matrix or convert oil pollutants into less toxic or nontoxic compounds (e.g., carbon dioxide, water, and nitrogen) (Meskar, 2018). Compared with solvent extraction, supercritical fluid extraction is more effective with less extraction time and energy consumption, while no residue formation due to the transport of supercritical fluid (Sankula et al., 2014). The extraction fluid is pumped and heated to supercritical conditions through the treatment process, then injected into the contaminated soil matrix, where the contaminants are adsorbed to the fluid (Ossai et al., 2020). The treatment efficiency of this technique is dependent on the fluid characteristics (e.g., density, permeability, viscosity), temperature and pressure

extraction, contaminant properties, and soil features. The supercritical fluid extraction removed 70%-100% petroleum hydrocarbons from a clay-sand soil at 80°C and 227 atm (Morselli et al., 1999). Furthermore, adding a modifier like acetone may alter the selectivity for the extraction process and the solvent properties, resulting in lower removal efficiency.

2.1.4.2.5. Encapsulation

This in-situ technique involves the compaction of contaminated soil in an inert material coating with low permeability surface caps, slurry walls, grout curtains to avoid contaminant migration or leaching to the surrounding soil (Camenzuli and Gore, 2013; Khan et al., 2004). A suitable encapsulation cell must limit direct contact with the contaminated soil, avoid leachate formation and migration, and obtain long-term treatment efficiency without extensive maintenance requirements (Ossai et al., 2020). The encapsulation performance strongly depends on the characteristics and depth of contaminants in the polluted site (Khan et al., 2004). A micro-encapsulation using reactive silicate and emulsifier reduced 85% to 99.97% of total petroleum hydrocarbons from contaminated soil while not interfering with the soil porosity and permeability in the existing site (Wami et al., 2015).

2.1.4.3. *Thermal treatment methods*

Oil pollutants are volatilized, desorbed, and removed from contaminated media under high temperatures (>300°C) in these remediation methods. Standard thermal techniques are thermal desorption, smoldering combustion, incineration, pyrolysis, and vitrification.

2.1.4.3.1. Thermal desorption

In this technique, contaminants are volatilized, desorbed, and separated by the direct or indirect use of heat under vacuum or in a carrier gas (Ivshina et al., 2015; Kastanek et al., 2016). The main mechanisms of this method are oxidation, incineration, thermal cracking, and pyrolytic reactions. This approach is practical to remove VOCs and SVOCs, such as PAHs or petroleum hydrocarbons (Zhao et al., 2019). The treatment efficiency is dependent on temperature and oxygen amount (Vidonish et al., 2016a). In particular, hydrocarbons with low oxygen content and high oxygen content will be heated at thermal desorption temperatures of 300°C-550°C and 100°C-300°C, respectively. The actual temperature of soil under the thermal desorption condition may reach 800°C-900°C, at which the hydrocarbons undertake thermal cracking. If the soil moisture is low and the treated soil can be re-moisturized, less dust will be formed, and fuel and heat can be recovered (Zhao et al., 2019). The ex-situ thermal desorption removed 94% of PCBs at 600°C using 1% calcium hydroxide in a rotary kiln (Liu et al., 2019).

2.1.4.3.2. Incineration

In this technique, oil pollutants are completely destroyed by burning or combustion at a high temperature of 870°C-1200°C in rotary kilns, circulating bed combustors, liquid injection incinerators, or infrared combustor heaters (Vidonish et al., 2016b; Ivshina et al., 2015). During the incineration process, the suitable ratio of oxygen level and soil loading must be maintained for safe incineration. The exhaust fumes and gaseous products (e.g., nitrous oxide, carbon monoxide,

sulfur dioxide) will turn into less toxic gases (e.g., carbon dioxide, water vapor, nitrogen) through the filtration and conversion process in the electrostatic precipitators and catalytic converters, respectively (Morselli et al., 2008). Meanwhile, the fly ash can be landfilled (Vidonish et al., 2016b). Soils are re-moisturized after the treatment process to reduce the dust amount before reusing for other purposes. This technique offers a high treatment efficiency of different contaminants but is expensive due to high-temperature requirements.

2.1.4.3.3. Pyrolysis

In this technique, contaminated soil is thermally heated or cracked in an anoxic condition at a high temperature of 400°C-1200°C (Moldoveanu, 2019; Vidonish et al., 2016a). Contaminants are transformed into by-products like chars, bio-oil, and non-condensable gas during this process, contributing extra heat for the pyrolytic reaction. In particular, at a temperature of 300°C-500°C, the carbonaceous materials (e.g., chars) are formed due to the breakdown of chemical bonds in petroleum hydrocarbon compounds through different processes, such as cracking, dehydrogenation, condensation, or dimerization (Vidonish et al., 2016a). The pyrolytic process is similar to *ex-situ* incineration and thermal desorption but under anoxic conditions through the indirect electric heating source. This technique is effective for remediation of soil contaminated with high molecular weight petroleum hydrocarbons, such as PAHs, fuel oil, and refined oil (Vidonish et al., 2016a). The pyrolysis transformed 48.5% and 95% chlorobenzene after 2s at 900°C and 1000°C using a fused silica jet-stirred reactor and an aluminum tubular reactor, respectively (Vin et al., 2019). In addition, the main products are methane, acetylene, and char.

2.1.4.3.4. Vitrification

In this technique, soil contaminants are heated at a high temperature of 1600-2000°C and converted into glass-like and crystalline products, such as bulk glass or crystals (Vidonish et al., 2016a). After the vitrification, the molten contaminated soil is quickly cooled to form a much stronger material than concrete and maintains similar characteristics with obsidian or basalt rock. Vitrification technique includes three main processes, electrical heating (1400-2000°C), thermal (>5000°C), and plasma arc process. The cons of this method are the high cost of energy consumption and specialized training and skill requirements. However, it can treat contaminants not removed by other remediation methods. For example, vitrification effectively treated a highly toxic hexavalent chromium in contaminated soil. After the treatment process, the lixiviation of the toxic vitrified and glassy products is smaller than 0.5 mg/L that meets the environmental regulatory standards (Ballesteros et al., 2017).

2.1.4.4. *Phytoremediation method*

Oil pollutants are removed or extracted from soil using green plants in this process. This method is based on the synergistic relationship between plants, microbes residing in soil and on plant roots. Plants may act as filters or traps that break down, stabilize, degrade, or bioaccumulate the oil compounds. In particular, plants can produce enzymatic reactions and uptake processes, provide nutrients and habitat for microbes on their root and shoots, and act as the symbiotic host for aerobic and anaerobic microbes (Ecobiol, 2006). Oil pollutants can be converted into less toxic or persistent compounds through different mechanisms like phytoaccumulation, phytodegradation,

phytostabilization, and phytotransformation (Cristaldi et al., 2017). The remediation efficiency of the phytoremediation method is strongly dependent on the bioaccumulation capacity of the contaminant into the plant's cell wall structure (Kvesitadze et al., 2009). Besides, the characteristics of oil pollutants and soil bioavailability also play a vital role in the phytoremediation performance (Gouda et al., 2016). The phytoremediation technique has been effectively used to adsorb or degrade petroleum hydrocarbons from contaminated soil (Cook and Hesterberg, 2013; Cartmill et al., 2014; Agamuthu et al., 2010).

2.1.4.4.1. Phytostabilization

In this technique, oil pollutants are immobilized in the contaminated soil using plants. In particular, oil pollutants are stabilized to reduce their mobility and limit their leakage, erosion, or transformation into less bioavailable forms by rhizospheric precipitation (Lim et al., 2016; Pilon-Smits, 2005). The main stabilization mechanisms include humification (incorporation of oil pollutants into the soil), lignification (trap of pollutants in plant cell walls), and binding (binding of pollutants into the soil matrix) (Adam, 2001). The phytostabilization of oil pollutants can occur in the rhizospheric zone, in the root cells, or on the root membrane of plants (Byström and Hirtz, 2002). Plants with large or broad root systems, which can easily absorb or accumulate the oil pollutants in the rhizosphere, are suitable for the phytostabilization method. For example, petroleum hydrocarbons in the rhizosphere region were immobilized into shrub plant *Salix viminalis* (or *Osier willow*) from 584 mg/kg to 1018 mg/kg after ten days (Byström and Hirtz, 2002).

2.1.4.4.2. Phytovolatilization

In this method, oil pollutants are absorbed and assimilated through the plant root, metabolized into volatile form, and transpired with water vapor from the surface of the plant's stem and leaf to the atmosphere (McCutcheon and Schnoor, 2004). In other words, oil pollutants are diffused from the plant's stem and leaves to the atmosphere via plant metabolism and transpiration. Through these processes, oil pollutants are transformed into less toxic compounds. However, oil pollutants are not removed permanently, and oil pollutants or metabolites released into the atmosphere can accumulate in vegetation and plant fruits and cause danger for humans or animals (Rock, 1997).

2.1.4.4.3. Phytotransformation

In this technique, oil pollutants are absorbed into plant systems and transformed by enzyme actions (e.g., dehalogenase, laccase, nitroreductase) within the plant tissues. The transformation efficiency of oil pollutants depends on properties of oil pollutants (e.g., solubility, polarity, hydrophobicity), plant (e.g., type, age), and soil (e.g., texture, structure, porosity) (Hellstrom, 2004). In particular, hydrophobic oil components are likely absorbed on the plant roots and transformed within the plant tissues (Schnoor et al., 1995). Through this process, oil pollutants can be degraded by plant enzymes under different environmental conditions, such as high contaminant concentration or microorganisms' absence. Meanwhile, the formation of toxic intermediates or products and the difficulty in detecting metabolite status are disadvantages of this technique (Ossai et al., 2020). The roots of herbaceous plants, such as Scots Pine (*Pinus sylvestris*) and Poplar

(*Populus deltoides* x *Wettsteinii*), showed a high removal of diesel fuel pollutants from contaminated subarctic soil, legumes, and grasses (Palmroth et al., 2002).

2.1.4.5. Biological treatment methods

The biological treatment methods have been effectively used to degrade oil pollutants to less or nontoxic substances in both in-situ and ex-situ techniques while do not cause harmful effects on the environment (Lim et al., 2016). Their treatment efficiency is strongly dependent on the site characteristics and contaminated soil properties. Biological treatment methods require a longer treatment time (months or years) than other treatment approaches. In addition, the highly polluted soil can reduce microbial activity, resulting in low remediation efficiency (Margesin et al., 2003). Different types of biological remediation approaches are available. Choosing the best biological treatment method will depend on the limiting factors and contaminated site characteristics (Ossai et al., 2020).

2.1.4.5.1. Bioremediation

The bioremediation method has been widely used to clean up oil pollutants since 1980 after the Exxon Valdez spill (Ossai et al., 2020). This approach is simple, environmentally friendly, sustainable, and effective in cleaning contaminated soil. It includes the natural degradation or oxidation of oil pollutants by hydrocarbon-degrading microorganisms (e.g., bacteria, yeast, fungi) or aerobic microbes, respectively (Yuniati, 2018). Some examples of oil pollutants degrading microorganisms are *Pseudomonas* bacteria (Wang et al., 2011b), *Penicillium*, *Fusarium*, *Rhizopus*

fungi species (Mancera-Lopez et al., 2008). Through the bioremediation method, oil pollutants in the soil will be removed and neutralized into less or nontoxic compounds, such as water or carbon dioxide (Wu et al., 2017). This technique effectively degrades the aliphatic hydrocarbons (e.g., alkanes, alkenes), whereas the hydrocarbon-degrading microbes use carbon compounds as the energy source for their growth and reproduction. Meanwhile, removing the long-chain or cyclic chain hydrocarbons is difficult due to their high resistance to bioremediation (Maletic et al., 2013).

2.1.4.5.2. Bioattenuation

The bioattenuation method utilizes physical, chemical, and biochemical processes in nature to transform or decrease the mass, volume, concentration, or toxicity of oil pollutants in soil. In particular, the indigenous microbial communities can degrade the oil pollutants through their metabolic procedure. Some significant processes are aerobic and anaerobic biodegradation, advection, dispersion, sorption, dissolution, volatilization, stabilization, chemical and biological transformation (Abatenh et al., 2017; Agarry and Latinwo, 2015). This method is suitable for contaminated sites where low oil pollutant concentration and no other remediation techniques are available (Vásquez-Murrieta et al., 2016).

2.1.4.5.3. Biostimulation

This method involves adding stimulatory materials, such as nutrients, biosurfactants, and biopolymers, to a contaminated site to support the growth of chemical-degrading microorganisms for remediation activities (Wu et al., 2016; Agarry and Latinwo, 2015). The presence of inorganic

macronutrients (e.g., N, P, K), micronutrients (e.g., Mg, S, Fe, Cl, Zn, Mn, Cu, Na), organic nutrients (e.g., sewage sludge, compost, manure) plays a key role in recovering contaminated soils. This approach is more effective than other in-situ remediation methods for removing oil pollutants from oil-simulated soil (Simpanen et al., 2016). The remediation efficiency of oil pollutants strongly depends on the type, concentration, and characteristics of nutrients and microorganisms. For example, the biostimulation of oil pollutants in soil using consortia of bacterial strains and a mixture of nutrients was up to 99.9% after 18 months (Singh et al., 2012). The removal of phenanthrene from contaminated soil was optimal with the addition of a high amount of macronutrient (67-87%) or a low amount of micronutrient (12-32%) (Kalantary et al., 2014). The presence of polyacrylamide, an inorganic nutrient, improved the removal of phenanthrene and anthracene in contaminated soil (Fernandez-Luqueno et al., 2009). In other studies, the bioremediation of oil-contaminated soil was greatly enhanced with compost (Sayara et al., 2011), manure, or vermicompost (Alvarez-Bernal et al., 2006).

2.1.4.5.4. Bioaugmentation

This technique relies on adding specific competent strains of microorganisms, such as exogenous microbial cultures, autochthonous microbial populations, to the contaminated site to improve the biodegradation process (Kastner and Miltner, 2016; Nwankwegu and Onwosi, 2017; Poi et al., 2017). With the introduction of a fungal strain *Scopulariopsis brevicaulis*PZ-4 in a PAH-contaminated soil, the removal rate of total PAHs, phenanthrene, and benzo[a]pyrene was 77%, 89%, and 75%, respectively, after 28 incubation days (Mao and Guan, 2016). The degradation rate of oil pollutants was 83.7% after 75 days with the addition of six bacterial isolates to the in-situ

bioaugmentation process in an oil-contaminated site (Varjani et al., 2015). In another paper, adding autochthonous filamentous fungi to an oil-contaminated soil improved the bioaugmentation performance up to 79.7% after 60 days (Covino et al., 2015).

2.1.4.5.5. Bioventing

In this in-situ method, air (oxygen) is injected into the contaminated soil to enhance the degradation efficiency of volatile oil pollutants, which will decrease their release into the atmosphere (Trulli et al., 2016; Camenzuli and Freidman, 2015). The presence of air increases the aerobic condition inside the soil, which will improve the biological activities of indigenous soil microorganisms, resulting in a higher biodegradation performance of oil pollutants. The bioventing and combination of bioventing method with brewery waste effluents amendment removed diesel oil from contaminated soil after 28 days up to 61.7% and 91.5%, respectively (Agarry et al., 2015). In another study, the removal performance of a blend of biodiesel and diesel oil from contaminated soil by bioventing was 85% over 60 days (Thome et al., 2014).

2.1.4.5.6. Biosparging

In this technique, air (oxygen) and nutrient are injected into the saturated zone of contaminated soil. This injection increases the oxygen level inside the soil and improves the growth of indigenous microorganisms, leading to a higher degradation rate of oil pollutants (Azubuiké et al., 2016). The treatment efficiency of biosparging is dependent on soil permeability and oil pollutant

properties (Atlas and Philp, 2005). Kao et al. (2008) showed a removal performance of 70% for BTEX at an oil spill site after ten months.

2.1.4.5.7. Bioslurry

In this ex-situ technique, contaminated soil is treated in a bioreactor, for example, feed batch, sequencing batch, continuous, or multistage bioreactor (Megharaj and Naidu, 2017; Azubuike et al., 2016). The treatment process involves the addition of nutrients to the bioreactor to increase microbial activities for removing the contaminants. The bioreactor has many advantages, such as easy to control and monitor treatment conditions (e.g., temperature, mixing speed and time, nutrient amount) and emissions, fast reaction kinetics, small space requirement to obtain the highest removal performance (Ossai et al., 2020). On the contrary, some limitations are long treatment time, cost and time consuming for soil excavation and transportation from a contaminated site to treatment facility, possible pretreatment, and volatile emission control requirement (Banerji, 1995). The removal efficiency of naphthalene in oil pollutants using a slurry bioreactor with the addition of microbial consortia of *Bacillus cereus* and *Pseudomonas putida* was between 79.4%-99.7% after 49 days (Tuhuloula et al., 2018).

2.1.4.5.8. Biopiling

In this ex-situ method, oil pollutants are biodegraded by landfarming and composting in an engineered cell. In particular, three main mechanisms are soil excavation and piling, nutrients, air and moisture supply, and biostimulation. During the treatment process, the optimal condition for

microbial activities are maintained by blowers and vacuum pumps, irrigation and nutrient system, and leachate collection system inside the cell (Kim et al., 2018; Benyahia and Embaby, 2016). It may reduce the volatilization of low molecular weight oil pollutants (Dias et al., 2015). This technique can be effectively used to remediate a large volume of contaminated soil in a limited space or extreme environments (Whelan et al., 2015). Gomez and Sartaj (2014) demonstrated a removal performance of 90.7% for oil pollutants in contaminated soil on a field-scale by biopiling treatment using a consortium of microbes at low temperature after 94 days.

2.1.4.5.9. Biotransformation

This method involves the transformation of oil pollutants to another form that is less toxic and persistent using microorganisms or enzyme systems (Jiang et al., 2016; Størdal et al., 2015). The biotransformation approach includes natural and microbial biotransformation, whereas the latter is faster and more effective. In the presence of bacteria, yeast, fungi, biotransformation has effectively been used to remediate the soil contaminated with petroleum hydrocarbons (Atlas, 1981). For example, the biotransformation efficiency of 50 ppm naphthalene from oil-contaminated soil slurry was approximate 90% after 50 days under denitrifying conditions, whereas the highest remediation rate was 1.3 ppm per day (Al-Bashir et al., 1990).

2.1.4.5.10. Landfarming

In this approach, oil-contaminated soil is tilled, plowed, spread, and treated in a thin layer on the land surface through the activities of aerobic microorganisms. This method has been effectively

used for remediation of low molecular weight oil pollutants, VOCs, or different types of organic compounds (Guarino et al., 2017; Brown et al., 2017; Wang et al., 2016). The biodegradation performance is strongly dependent on oxygen, moisture, and nutrient. Brown et al. (2017) removed 53% of oil pollutants from contaminated soil by landfarming after six weeks with nutrient addition. In another study, Guarino et al. (2017) showed a performance reduction of 86%, 70%, and 57% for the oil pollutants from contaminated soil after 90 days by bioaugmentation-assisted landfarming, landfarming, and natural attenuation, respectively.

2.1.4.5.11. Composting

This method involves the degradation of oil pollutants into less toxic or harmless substances or compounds by the aerobic microorganisms in the soil (Ren et al., 2018). The treatment efficiency by composting method depends on the nutrient amount, tilling, watering, microbial consortia addition, and presence of bulking material (or organic waste) (Prakash et al., 2015). In addition, the composting process is strongly dependent on the temperature, whereas a temperature of 50-65°C is the optimal condition for removing oil pollutants from contaminated soil (Saum et al., 2018). During the composting process, the temperature increases due to the heat generation from microbial activities to break down the oil compounds. The removal efficiency of 380,000 mg/kg oil pollutants in soil by sewage sludge compost was 99% after 19 months (Atagana, 2008).

2.1.4.5.12. Windrows

This ex-situ approach involves the biodegradation of oil pollutants by aerobic microbial activities through the periodic tillage and turning piled contaminated soil. In particular, the microbial activities are improved by the autochthonous and transient hydrocarbonoclastic microorganisms in the soil through the biotransformation, assimilation, and mineralization, resulting in a higher biodegradation performance (Azubuike et al., 2016; Jiang et al., 2016). However, the oil pollutant treatment efficiency is not high due to the release of volatile compounds during the periodic tillage and turning. Hobson et al. (2005) observed the emission of CH₄ from the mechanically turned windrow systems due to the development of an anaerobic zone. In another study, the biodegradation efficiency of total petroleum hydrocarbons in soil by windrow system after eight months was 60% (Al-Daher et al., 1998). In addition, aeration condition and moisture content play a vital role in the removal efficiency.

2.1.4.5.13. Vermicomposting

This method involves the bioremediation of oil pollutants in soil using earthworms (Njoku et al., 2017; Chachina et al., 2016; Ekperusi and Aigbodion, 2015). The addition of earthworms to the soil can enhance the biological, physical, and chemical characteristics of soil and establish the optimal conditions for the presence of soil microorganisms (Dabke, 2013). As a result, the microbial availability and activity will be improved, resulting in higher removal efficiency of oil pollutants by microbes (Schaefer and Juliane, 2007). The development of earthworms in the soil is strongly dependent on pH, moisture, and organic matter content. Azizi et al. (2013) showed a vermicomposting efficiency of 99.9% for PAHs in contaminated soil by *Lumbricus rubellus*

earthworms after 60 days. In another study, 80% of PAHs were removed from PAHs-contaminated soils in a gas station site using earthworms (Sinha et al., 2008).

2.1.4.5.14. Trichoremediation

This method removes oil pollutants from the contaminated soil by keratinolytic microbes and pollutant degrading microbes. The microbial activities are enhanced adding hairs and feather materials, resulting in higher removal productivity. In particular, the enzymatic actions of keratinolytic and keratinophilic microbes, such as actinomycetes or fungi found on hairs and feathers, can effectively degrade oil pollutants in contaminated soil (Ossai et al., 2020). For example, keratinolytic fungi from human or animal hairs and feathers showed a high removal efficiency of petroleum hydrocarbons from contaminated soil (Ulfig et al., 2006).

2.1.4.5.15. Mycoremediation

This method includes the utilization of fungi to degrade oil pollutants in contaminated soil to less toxic or nontoxic compounds (Kumar et al., 2018; Amjad et al., 2017; Anderson and Juday, 2016). In particular, extracellular enzymes (e.g., peroxidases), chelators, or oxidative enzymes produced by fungi may break down or degrade different recalcitrant pollutants like oil pollutants (Jang et al., 2009). A variety of fungi types, such as white rot fungi *Polyporus sp.*, *Phanaerochaete chrysosporium*, *Penicillium sp.*, have degraded toxic organic pollutants (Bhatnagar and Kumari, 2013; Yamada-Onodera et al., 2001). Ulfig et al. (2003) showed a high degradation of hexadecane and pristane from crude oil by keratinolytic fungi *Trichophyton ajelloi*. In another study, fungi

Pleurotos pulmonarius removed up to 68.34% of total petroleum hydrocarbons from contaminated soil after 62 days (Njoku et al., 2016). The advantages and disadvantages of some standard soil treatment methods are shown in Table 2.

Table 2. Pros and cons of some common soil treatment methods (oilandgas portal, 2022)

Name	Mechanism	Advantages	Disadvantages
Soil washing	Washes soil by a mixture of water with a primary leaching agent, surfactant, or chelating agent	<ul style="list-style-type: none"> - Cheaper and eco-friendlier than stabilization and landfilling - Effective for a wide range of organic soil pollutants 	<ul style="list-style-type: none"> - Not effective for complex waste mixture, such as metals with organics - Require pretreatment for soil with high humic concentration - May need further treatment for washing solvent remaining in the treated residuals - Not practical for the removal of organics adsorbed on clay-size particles.
Soil vapor extraction	Applies a vacuum to the soil to collect contaminated vapor	<ul style="list-style-type: none"> - Effective for upper soil layer or unsaturated soil zone 	<ul style="list-style-type: none"> - Expensive for soil with a high amount of fines or high saturation degree - Low removal rate of soil with high organic content or dry - Require further treatment for exhaust air and off-gas from the SVE system

Chemical oxidation-reduction	Uses chemicals (e.g., peroxide, ozone, chlorine dioxide, permanganate) to destroy contaminated soil	<ul style="list-style-type: none"> - Effective for various organic compounds - No further liability - May reuse soil 	<ul style="list-style-type: none"> - Some concerns with chemicals and temperatures required to catalyze reactions - Requires a large amount of soil, which leads to high cost and technical difficulties - May form by-products - Needs more success validation
Thermal desorption	Uses heat to excavate soils and volatilize the oil from the soil. The resulting gases are treated in a vapor treatment system	<ul style="list-style-type: none"> - Produces less gases - Decreases the size of the off-gas handling system 	<ul style="list-style-type: none"> - Expensive - Requires dewatering to obtain acceptable soil moisture content levels - Needs further treatment for solid residue by heavy metals
Incineration	Combusts the organic constituents in the soil at high temperature (>1200°C) with the presence of oxygen	<ul style="list-style-type: none"> - Effective for oil pollutants - Decrease the toxicity and volume of substances at contaminated sites 	<ul style="list-style-type: none"> - Requires treatment for off-gases and combustion residuals - Toxicity of radioactive contaminants - Needs further treatment for bottom ash produced by heavy metals
Phytoremediation	Uses trees and other deep-rooted plants	<ul style="list-style-type: none"> - Low cost 	<ul style="list-style-type: none"> - Needs more research for the remediation efficiency

	absorb contaminants in soil	- Plants prevent soil erosion	- Difficult to access deep contamination - Requires a long time
Biodegradation	Uses living microorganisms to breakdown the organic compounds	- No need for excavation and transport of soil for the treatment process - Low cost for removal of petroleum hydrocarbons - Safe for the environment - May be combined with other treatment methods	- Limited to biodegradable compounds - Degradation products may be more toxic - Potential of hydrocarbon biodegradation is dependent on the availability of desired microorganisms. - Not effective for clay soils, compact, which have limited oxygen and nutrients
Biosparging	Injects air into the soil to enhance biodegradation	- Effective for removal of BTEX from the saturated soil zone	- Potentially dangerous vapors may flow through the saturated zone - Must design air injection wells for specific conditions - Must consider the depth of contaminants and geology of specific site

In summary, these existing treatment methods have many disadvantages for soil remediation. As a result, it is crucial to research and to develop new oil-contaminated soil remediation techniques.

2.2. Surfactants

Surface-active agents or surfactants are heterogeneous, long-chain organic molecules containing hydrophilic and hydrophobic portions (Figure 1). Due to the hydrophobic and hydrophilic groups in their composition, they may formulate micelles in a solution that gives surfactants their detergency and solubilization properties. Hence, they can be used to wash or flush the soil. Due to the capacity to decrease surface tension, improve solubility, detergency strength, wetting and foaming performance, surfactants are generally used as additives in cleaning agents, household detergents, adhesives, flocculating, and wetting or foaming agents (Mulligan, 2005).

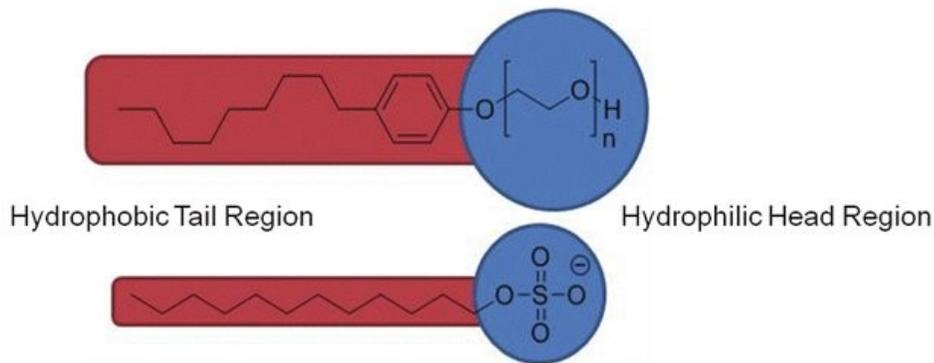


Figure 1. Surfactant structure with hydrophobic tail (red) and hydrophilic head (blue)

(Liang, 2010)

Figure 1 clearly shows the hydrophilic head (e.g., carbohydrate, amino acid, carboxylic acid, phosphate, alcohol) the hydrophobic tail (e.g., fatty acids, hydroxy fatty acids) of surfactant molecules. Therefore, in an aqueous solution, the combination of these hydrophobic tails (micelles) may trap and dissolve more easily the hydrophobic organics, which enhances the solubility of these hydrophobic organic compounds.

Surfactants have many advantages that make them be widely used, such as saving energy, low cost, physicochemical behavior, and solubility and adsorption behavior. In addition, they can reduce the surface or interfacial tension, increase the solubility of water-insoluble compounds, detergency power, wetting ability, and foaming capacity. Therefore, biosurfactants may be applied for enhancing the oil removal by increasing the solubility of petroleum components in petroleum applications or floating minerals in pharmaceutical applications (Mulligan, 2005). They may improve the biodegradation rate of organic compounds in bioremediation techniques. They may increase the emulsification, micellization, and adhesion–de-adhesion of microorganisms to and from hydrocarbons and desorption of contaminants (Vu, 2013).

Depending on the properties of the hydrophilic group, surfactants may be distinguished as anionic, cationic, zwitterionic, and nonionic (Rosen and Kunjappu, 2012). Surfactants may be produced chemically or biologically, equivalent to synthetic surfactants or biosurfactants, respectively. Choosing the best surfactant for a specific purpose depends on production costs, energy costs, charge type, solubility, and physiochemical behavior (Mulligan, 2005).

2.2.1. Synthetic surfactants

The hydrophilic portion of synthetic surfactants is commonly a carboxylate group (anionic surfactants), quaternary ammonium group (cationic surfactants), or polypeptide (nonionic surfactants). Meanwhile, the hydrophobic part of synthetic surfactants is generally paraffin, alkylbenzene, or alcohol (Paria, 2008).

Gemini surfactants, a group of synthetic surfactants containing at least two hydrophilic heads and hydrophobic tails, have gained much attention owing to their notable features. Compared to monomeric surfactants, gemini surfactants possess lower CMC values, higher solubilization capacity, and more surface activity. The composition of gemini surfactants includes two surfactant molecules connected by a spacer group composed of 2-8 bridging atoms (Paria, 2008).

Synthetic surfactants can remediate PAHs in contaminated soils (Makkar and Rockne, 2003). The effectiveness of synthetic surfactants is dependent on the chemical structure of the surfactant. The addition of synthetic surfactants was found to limit the bioremediation of PAHs, which was due to the toxicity of the surfactant to PAH-degrading bacteria and the low bioavailability of PAHs inside the surfactant micelles (Makkar and Rockne, 2003).

2.2.2. Biosurfactants

Biosurfactants are biologically produced from the microbial population, such as yeasts, bacteria, or fungi. The main groups of biosurfactants are glycolipids, phospholipids, and lipoproteins (Paria, 2008). In particular, their hydrophilic part is usually a carboxylic acid, cyclic peptide, or phosphate. At the same time, their hydrophobic portion is regularly a long-chain fatty acid or hydroxyl fatty acid. Various microorganisms may create biosurfactants. For example, rhamnolipids, glycolipids, surfactin are produced by *Pseudomonas aeruginosa*, *Arthrobacter sp.*,

Bacillus subtilis, respectively. Biosurfactants are mostly anionic or nonionic, while a limited number are cationic (Mulligan, 2005).

Biosurfactants have been widely utilized in various fields, such as petroleum, environmental, food, pharmaceutical, agriculture, and cosmetics industries. In particular, they were used for enhanced oil recovery and de-emulsification in petroleum, bioremediation and soil washing in the environment, emulsification and de-emulsification in food, antibacterial and antiviral agents in pharmaceutical, biocontrol of parasites and microorganisms in agriculture, and health and beauty agents in cosmetics. Some notable biosurfactants are rhamnolipids, sophorolipids, glycolipids, or lipopeptides as they are highly surface-active and degradable, of low toxicity, and stable in emulsions with hydrocarbons (Mulligan et al., 2019).

Due to the higher biodegradability, biosurfactants are more environmentally friendly than synthetic surfactants ([Vu and Mulligan, 2022e](#); Mulligan, 202105). For instance, the toxicity of glycolipid biosurfactant was 50% less than Tween 80 synthetic surfactant in the tests for solubilization of naphthalene from crude oil (Kanga et al., 1997). Kuyukina et al. (2005) investigated the remediation performance of crude oil in the soil by biosurfactant (from *Rhodococcus ruber*) was more significant than Tween 60 synthetic surfactant. Likewise, biosurfactants may be generated by a cheaper and more sustainable process, in which clean, renewable, and low-cost raw materials are used (Mulligan et al., 2019).

2.2.2.1. Critical micelle concentration value of surfactants

The effectiveness of a biosurfactant is determined by its ability to lower the surface tension, which correlates to a critical value called critical micelle concentration (CMC). If the surfactant

concentration is higher than CMC in an aqueous solution, the monomer molecules may aggregate and form micelles. In other words, CMC is the minimum concentration of surfactant to form a micelle (Figure 2).

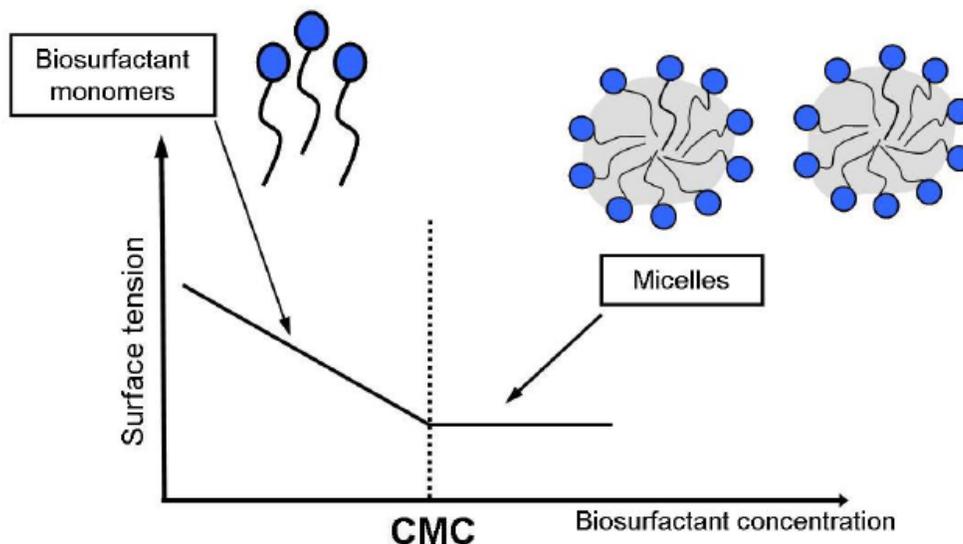


Figure 2. Relationship between biosurfactant concentration, surface tension, and micelle formation (Pacwa-Płociniczak et al., 2011)

The activities of biosurfactants are dependent on the concentration of the surface-active compounds until obtaining the CMC. If the biosurfactant concentration is more than CMC, their molecules will associate together to form micelles and bilayers. The CMC is also used to estimate the surfactant efficiency. The lower CMC, the higher the surfactant efficiency. The reason is that the low CMC means less biosurfactant is required to decrease the surface tension.

2.2.2.2. *Rhamnolipid biosurfactant*

Rhamnolipid biosurfactants are the biosurfactants produced from *Pseudomonas aeruginosa*. There are four different types of rhamnolipid produced by *P. aeruginosa* (Figure 3), depending on the length of the carbon chain and the total of monosaccharide rings. In particular, type 1 (R1) is L-rhamnosyl- β -hydroxydecanoyl- β -hydroxydecanoate, type 2 (R2) is L-rhamnosyl- β -L-rhamnosyl- β -hydroxydecanoyl- β -hydroxydecanoyl- β -hydroxydecanoate, type 3 (R3) is one rhamnose connected to β -hydroxydecanoic acid, and type 4 (R4) is two rhamnoses connected to β -hydroxydecanoic acid. They may decrease the water surface tensions to 29 mN/m, and their CMC ranges from 10 to 230 mg/L with different structures (Mulligan, 2007).

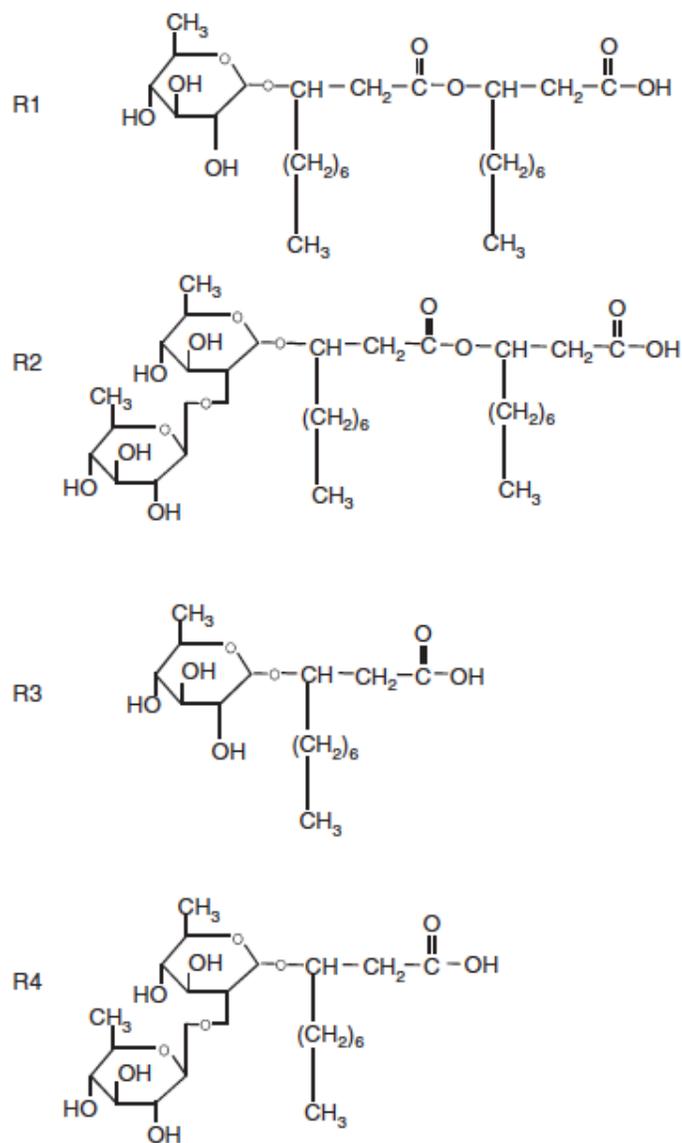


Figure 3. Structure of four different rhamnolipid biosurfactants produced by *P. aeruginosa*

(Mulligan, 2007)

The rhamnolipid biosurfactants may biodegrade different compounds in liquid systems (e.g., hexadecane, octadecane) or soils (e.g., hexadecane, pristane, hydrocarbon mixtures). Their bioremediation relies on the increase of substrate solubility for the microbial cells and the

interaction and improvement of the hydrophobicity of cell surface that make them trap the hydrophobic organic compounds (Mulligan, 2021). Accordingly, they can be used for oil biodegradation in soil.

2.2.2.3. Sophorolipid biosurfactant

Sophorolipid biosurfactants are produced from *Candida* yeasts (Figure 4). They can lower the water surface tension to 33 mN/m. Moreover, 10 mg/l of sophorolipid biosurfactant may reduce the interfacial tensions of n-hexadecane and water from 40 mN/m to 5 mN/m. Their CMC changes from 35 mg/l to 130 mg/l, depending on the structure (Pacwa-Płociniczak et al., 2011).

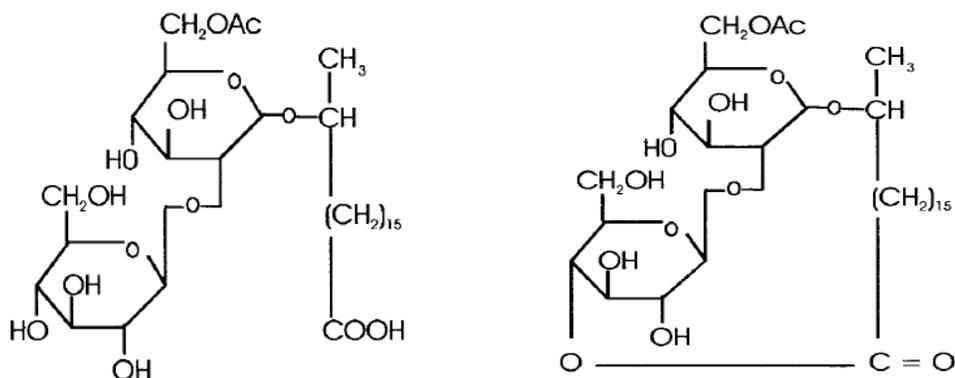


Figure 4. Structure of sophorolipid produced from *Candida bombicola*

(Mulligan and Gibbs, 2004)

Sophorolipid biosurfactants can be used as protective substances, humectants, or skin moisturizers in the cosmetic industry. Moreover, they can improve the removal efficiency of

hydrocarbon and heavy metals in contaminated soils and sediments, and enhance oil recovery and recover hydrocarbons from dregs and muds (Mulligan and Gibbs, 2004).

2.2.3. Use of surfactants for remediation of contaminated soil

2.2.3.1. Interaction of surfactants and contaminated soil

When surfactants enter the water-soil system, part of them will be adsorbed on the soil particle surface. These adsorbed surfactants may improve the soil hydrophobicity, which leads to an increase in the re-adsorption rate of removed solubilized organic compounds on the soil surface (Paria, 2008). In addition, surfactants can increase the bioavailability of contaminants through mobilization and solubilization, which will break the bonds between contaminants and soil. based on that, the contaminants will be separated from the soil, leading to the removal of soil contaminants by surfactants. Hence, the adsorption properties of surfactant, which relates to their molecular structure and soil characteristics (Zhang et al., 2013), play a crucial role in choosing the suitable surfactants for the remediation processes. Together with improving the solubilization and desorption of soil pollutants, surfactants may support microbial development, which will enhance the contaminant decomposition efficiency (Mao et al., 2015).

For soil washing, surfactants should have high solubilization potentials and low adsorption on soil particles. The sorption of surfactants in soils may cause some surface reactions, altering the soil's physicochemical and biological features (Jia et al., 2005). The residue of toxic surfactants, such as PFOA, may cause adverse effects on the soil ecosystems and the environment after the soil washing (Paustenbach et al., 2006). Also, surfactants in the soil/water systems may negatively affect the environment due to their biological activities, for example, inhibiting the growth of

different bacteria and soil microorganisms (Elsgaard et al., 2001), which relates to the interaction of bacteria and porous media (Vu et al., 2015a; Vu et al., 2015b; Yang et al., 2015). However, highly biodegradable biosurfactants may avoid this concern. They may also increase the bioavailability of pollutants, leading to the biodegradation of soil pollutants (Moldes et al., 2011). Moreover, biosurfactants can be used as a carbon source for bacteria (Bailey et al., 2012) or can modify the permeability of root cell membranes that promote the water and nutrient uptake of plants' advantages surfactant-enhanced bioremediation. Therefore, biosurfactants are considered promising agents for soil remediation.

2.2.3.2. Use of surfactants for remediation of oil pollutants in soil

One of the most typical ways to promote the bioavailability of oil pollutants in the soil is to use surfactants. In particular, surfactants can increase the desorption and solubilization of petroleum hydrocarbons, allowing microorganisms to assimilate them favorably (Kuyukina et al., 2005). Compared with other surfactant types, such as synthetic surfactants, biosurfactants showed higher surface activity and biodegradability at extreme conditions (e.g., temperature, pH, salinity), better environmental compatibility, lower toxicity, and easier production from renewable resources (Pekdemir et al., 2005). Moreover, using biosurfactants for oil pollutants in the soil will not form toxic by-products during the remediation processes, which is good for the environment. Hence, biosurfactants can be favorably used in the bioremediation of contaminated soil (Silva et al., 2021). Biosurfactants have shown higher removal of crude oil from the soil than synthetic surfactants (Kuyukina et al., 2005; Befkadu and Quanyuan, 2018; Wang et al., 2019).

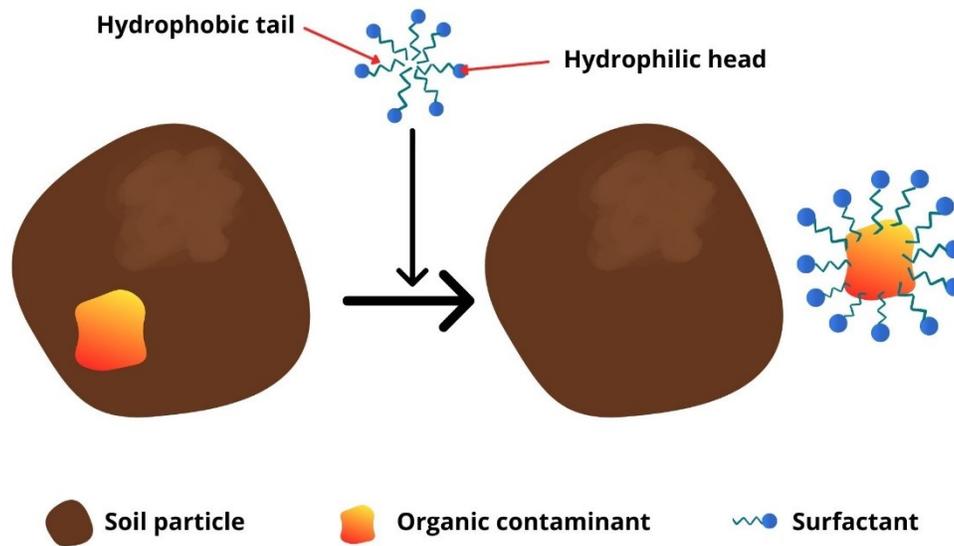


Figure 5. Use of surfactants to remove oil pollutants from soil

The removal of oil pollutants by biosurfactants may occur at biosurfactant concentrations below or above the CMC value, equivalent to the mobilization mechanism and solubilization mechanisms, respectively (Vu and Mulligan, 2020; Vu and Mulligan 2022a). If the biosurfactant concentration is below CMC, the surface and interfacial tension between air/water, organic compounds/water, and soil/water systems will be lower, causing the decrease of the capillary force that holds organic compounds and soil together, which leads to the mobilization of organic compounds from contaminated soil (Urum et al., 2004). Besides, the accumulation of biosurfactant monomers at the soil/contaminant and soil/water interfaces may increase the contact angle between the soil and hydrophobic oil pollutants, leading to the system's alternation wettability (Mao et al., 2015). Furthermore, the adsorption of biosurfactant molecules on the contaminant surface may create a repulsion force between the hydrophilic groups of biosurfactant and the soil particles, enhancing the detachment of the contaminants from the soil particles (Deshpande et al., 1999; Vu and Mulligan, 2022a). The mobilization mechanism is strongly dependent on the biosurfactant

ionic charge. The concentration of biosurfactants tends to decrease due to their adsorption on the soil. Thus, the mobilization mechanism is ineffective in soil remediation. If the biosurfactant concentration is above CMC, the aggregation of biosurfactant monomer molecules may form micelles, leading to an increase in organic compounds solubility. Inside the micelle, the hydrophobic portion may aggregate together, while the hydrophilic portion may contact the aqueous phase of exterior compounds. As a result, the hydrophobic organic molecules will be entrapped in a micelle called solubilization (Urum et al., 2004).

Biosurfactants have shown their effective removal of crude oil from contaminated soil (Urum et al., 2003; Urum and Pekdemir, 2004), hydrophobic organic compounds (Kanga et al., 1997; Whang et al., 2008), low solubility oil pollutants in soil (Maier and Soberon-Chavez, 2000), PAHs and naphthalene (Straube et al., 2003), gasoline-contaminated soil (Rahman et al., 2002), and NAPL-dissolved phenanthrene (García-Junco et al., 2001). The remediation efficiency of oil pollutants by biosurfactants may be influenced by alkane growing microorganisms, process temperature, and biosurfactant type and concentration (Kuyukina et al., 2005).

2.3. Fe-based nanoparticles

Nanoparticles are particles with at least one dimension is less than 100 nm. Due to their small size, nanoparticles have various physical and chemical characteristics that can be used for environmental applications, such as remediation techniques. In particular, nanoparticles can be applied to remove different contaminants, such as PAHs, pentachlorophenol (PCPs), polychlorinated biphenyl (PCBs), and trace elements, with higher treatment efficiencies and less

generation of toxic intermediates. For soil remediation, they have been utilized to remove various oil pollutants (Li et al., 2016; Yan et al., 2013; Zhang et al., 2009; Xu and Zhao, 2007).

Nanosized iron particles were observed to wholly and quickly transform halogenated organic compounds (HOCs), particularly trichloroethylene (TCE) and PCBs, in soil and other contaminants for field remediation (Yan et al., 2013). Most studies may be classified based on the type and properties of contaminants treated and material modifications. Nanoparticles have been employed to effectively treat some contaminants, including pesticides, dyes, or antibiotics. With broader field applications of nanoparticles in soil remediation, investigations about nanoparticles' stability, mobility, and eco-toxicity have gained more attention.

Nanoscale zero-valent iron particle (nZVI) is one of the most widely used materials among different nanoparticle types due to the large specific (or more chemically reactive) surface area and potential for broader application. The soil remediation techniques using nZVI are more effective, faster, and cheaper than conventional remediation methods. The reaction rate and sorption capacity of nZVI are much higher than granular iron (Karn et al., 2009). Many pilot or full-scale systems using nZVI have been operated globally for in-situ soil remediation, whereas most were in the United States and Europe (Zhao et al., 2016; Mueller et al., 2012; Schrick et al., 2002). nZVI-based technology is typically used for in-situ soil remediation due to its ability to reach contaminants in areas not accessible by other methods, low toxicity and cost, and short treatment times (Karn et al., 2009).

2.3.1. Use of Fe-based nanoparticles for remediation of oil-contaminated soil

In recent years, nanoparticles have unique properties owing to their small size and large surface area per unit of mass. Therefore, it is easier for them to interact with other particles in the mixture (e.g., nanocomposite, nanofilm), which will improve the mixture's material strength and heat resistance (Singh et al., 2010). Moreover, low cost and high reactivity are other advantages of nanoparticles over conventional methods (Murgueitio et al., 2018).

2.3.1.1. Removal mechanisms

The main remediation mechanisms of oil pollutants by nZVI are adsorption and redox reactions, where petroleum hydrocarbons are reduced to less toxic compounds (Figure 6).

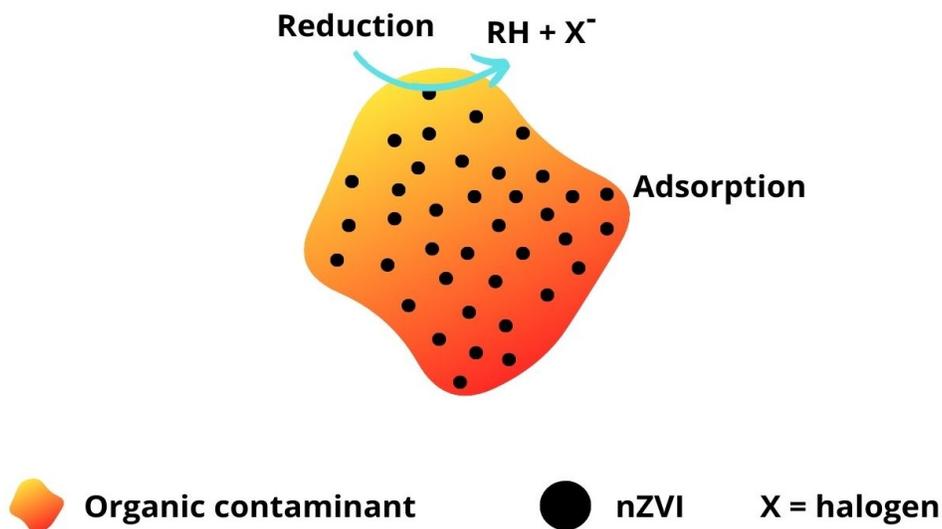
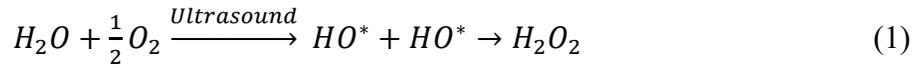
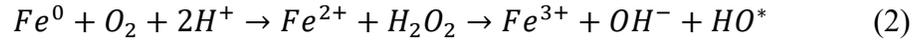


Figure 6. Remediation of oil pollutants by nZVI

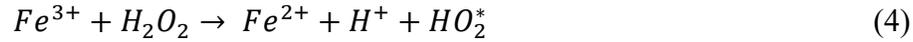
In particular, oil pollutants can be removed through the Fenton reaction with the sonication of the nZVI solution (Murgueitio et al., 2018). During this process, hydrogen peroxide may be formed following the equation (1):



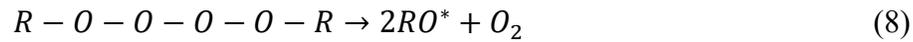
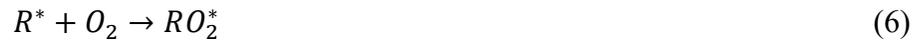
In the meanwhile, Fe^{3+} is formed by the oxidation of Fe^0 nanoparticles as follows:



Fe^{3+} will react with H_2O_2 in the solution to form HO_2^*



These reactive oxygen species (ROS), HO^* and HO_2^* , may oxidize the petroleum hydrocarbons as follows:



where: R is a group of carbon or hydrogen atoms

RH is the oil pollutant.

RO* and RO₂* are the reactive oxygen species

TPH and TPH* are a fraction of stable hydrocarbon and hydrocarbon radicals, respectively.

Based on the larger surface area and reactive oxide layer, nZVI generates more ROS than the bulk iron. Hence, nZVI has been used for oxidative transformations of oil pollutants. For example, the Fenton-like redox reactions with nZVI have been effectively used to remove atrazine and lindane under aerobic and anaerobic conditions (Joo and Zhao, 2008), halogenated organics (He and Zhao, 2005), herbicide molinate (Feitz et al., 2005), biocide CMP (Xu and Wang, 2011). The oxidizing capacity of nZVI is dependent on pH, reaction time, amount of nZVI, presence of a ligand, and nature of the nZVI oxide shell (oxalate, NTA, EDTA) (Xie et al., 2014; Lee et al., 2008). The primary oxidants under low and neutral pH are HO* and O₂*, respectively (Yan et al., 2013). The oxidative activity of nZVI can be increased by adding chelating agents (e.g., EDTA) or electron shuttles (e.g., NOM, POMs) (Lee et al., 2008; Kang and Choi, 2009). In a single treatment system, the reducing and oxidizing activities of nZVI may be concurrently or sequentially used in the redox processes to obtain a higher treatment efficiency (Xu and Wang, 2011). When nZVI is used for treating polluted soil, it requires less disruption at the contaminated site, worker exposure, and waste emission than ex-situ methods. The optimal conditions include an anaerobic state and neutral or acidic pH (Bardos et al., 2011).

In field applications, nanoparticles can be applied as direct injection. In this method, nZVI will be mixed to form a suspended slurry and pumped into the topsoil (Mueller and Nowack, 2010),

whereas the oil pollutants will be adsorbed or degraded into less toxic compounds (Figure 7). Direct injection can be blended directly into a contaminated source or a treatment zone with a specific amount of contaminant. For example, the direct injection of iron nanoparticles was used to remove up to 96% TCE (after four weeks) at a manufacturing site (Elliott and Zhang, 2001). nZVI has shown high treatment efficiency for halogenated solvents such as chlorinated methanes, chlorinated benzenes, polychlorinated hydrocarbons (Mueller and Nowack, 2010; Song and Carraway, 2005), and halogenated organics (Yan et al., 2013). The main mechanisms of the dechlorination process by nZVI include the adsorption of contaminants on the nZVI surface, followed by the breakage of carbon-halogen bonds (Mueller and Nowack, 2010). Their removal of PAHs from contaminated soil at room temperature was high (Chang et al., 2007), while their degradation performance of PCBs was low due to the strong adsorption of PCBs to soil particles (Varanasi et al., 2007). Wang and Zhang. (1997) claimed that the rapid and complete dechlorination of TCE and PCBs by nZVI was much higher than the commercial Fe powders.

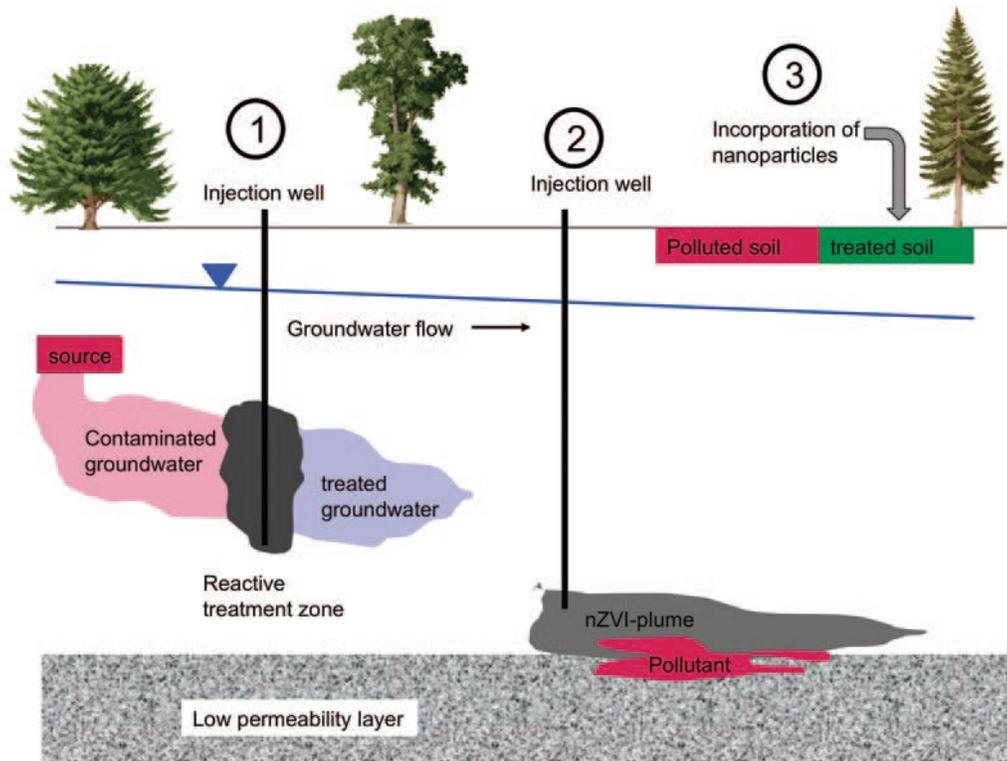


Figure 7. Use of nZVI for the in-situ remediation process. (1) Injection of nZVI to form a reactive barrier, (2) Injection of mobile nZVI to form an nZVI plume, (3) Incorporation of nZVI into the topsoil to adsorb or degrade soil pollutants (Mueller and Nowack, 2010)

The combination of ZVI with other transition metals, such as Pd or Ni, may form a bimetal which accelerates the reaction of nZVI and oil pollutants (Zhao et al., 2016). In particular, the presence of transition metals will cause a galvanic effect that improves the transfer of electrons and the production of reactive hydrogen species and increases the formation of reactive atomic hydrogen (He and Zhao, 2008). As a result, the reaction rates will be faster, leading to higher treatment efficiency.

2.3.1.2. Interaction between soil and nZVI

The presence of nZVI may significantly change the physicochemical (Liu et al., 2018) or geotechnical properties of soil (Nasehi et al., 2016). In particular, the soil characteristics, such as particle size, electrical conductivity, surface area, and buffering capacity, were changed with the addition of nZVI. In other studies, adding nZVI increased the pH of soil due to the change in soil buffering capacity, decreased the electrical conductivity due to the alternation of metal availability in soil, and changed the soil surface due to the generation of agglomerates (Mar Gil-Díaz et al., 2014; Baragaño et al., 2020). The impact of nZVI on the soil characteristics strongly depended on their dose (Gil-Díaz et al., 2020). However, the use of nZVI doses (up to 20%) did not cause any adverse effects on the physicochemical and biological features of the soil for a short-term time (Mar Gil-Díaz et al., 2014). Due to the interaction between nZVI and soil microorganisms, the cell membrane of soil microbial communities was damaged, which would change the soil ecosystem in the short term (Chaithawiwat et al., 2016).

Meanwhile, the soil properties may influence the reaction of nZVI and oil pollutants. The mobility of nZVI in soil was significantly inhibited due to the high electrostatic interactions between nZVI and organic matter and inorganic minerals in the soil, limiting the reaction of nZVI and oil pollutants (Kim et al., 2014; Su et al., 2020). Due to the corrosion of nZVI, the dechlorination of tetrachloroethane decreased 70% after 15 days (Vogel et al., 2019). Organic matter content may affect the desorption kinetics of oil pollutants, which reduces the remediation efficiency. Zhang et al. (2011) showed sorption of TCE in the Smith Farm soil (organic matter content of 8.2%) and the potting soil (organic matter content of 0.7%) was 82% and 44%, respectively, after 30 hours under the identical conditions.

The pH value of 4.9 was found as the optimal pH to remove TCE (Chen et al., 2001) and 2,4,4'-trichlorobiphenyl (Wang et al., 2012) from the soil by nZVI. The high pH value, or lower amounts of H⁺, will inhibit the degradation of oil pollutants in soil. At pH values from 9 to 10, nZVI did not remove TCE from soil (Chen et al., 2001). Temperature plays a vital role in the removal capacity of nZVI. The increase in temperature may inhibit the activity of soil microbes, leading to a lower removal percentage. With the temperature increased from 30°C to 35°C, a decrease in treatment efficiency of 1,2,3,4,5,6-hexachlorocyclohexane (γ -HCH) from 99% to 78% by nZVI was observed (Singh et al., 2013). Therefore, 30°C was indicated as the optimal temperature for the degradation of γ -HCH in contaminated soil.

2.3.1.3. Limitations

When working with nanoparticles, transportation, handling, and injection of a nanoparticle slurry are typical limitations. Due to the high reactivity, the nZVI surface is readily oxidized by the atmosphere, which reduces the properties. In addition, it possesses the potential risk of ignition and dust explosion. Hence, it is necessary to have appropriate transportation, handling, and storage procedures for nanoparticles at the remediation sites. The Material Safety Data Sheets (MSDS) is able to be used as guidance for nanoparticle handling procedures and contain information about coatings for modified nanoparticles (Bardos et al., 2014).

The potential toxicity of nZVI particles is one of the biggest concerns for their broad application (Table 3). Their bactericidal activity is mainly based on ROS formation on the surface, which can cause oxidative stress on bacteria (Kim et al., 2010). Furthermore, the disruption of electron and ion transformation reactions in cell membranes due to direct contact with nZVI also

induces the antibacterial property (Kim et al., 2010). The addition of NOM or polyelectrolytes may decrease the toxicity of nZVI particles (Li et al., 2010).

Previous studies showed the relationship between toxicity and size of nanoparticles, whereas nZVI smaller than 30 nm may cause cytotoxicity (Wiesner et al., 2006; Auffan et al., 2009). In addition, nZVI particles have shown toxicity to bacterial cells (Li et al., 2010), living organisms (Nel et al., 2006), cells (Keenan et al., 2009; Xie et al., 2014), DNA (Xia et al., 2006), ecosystem (Phenrat et al., 2009b), whereas the shape and size of nanoparticles, the existence of oxygen, and presence of ionic Fe on the nanoparticle surface plays a vital role in the toxicity level (Lee et al., 2008; Xie et al., 2014; Chen et al., 2013). Auffan et al. (2009) demonstrated that the *E. coli* inactivation rate of nZVI was greater than iron oxides, such as Fe₃O₄ and Fe₂O₃. If the nZVI surface was oxidized (Lee et al., 2008) or under various environmental conditions (Li et al., 2010), this ability would be lower.

Table 3. Potential toxicity of some nanoparticles

Name	Size	Organisms or cells affected	Effects observed	References
nZVI	35 nm	<i>E. coli</i>	Oxidative stress, antibacterial	Lee et al., 2008 Ševců et al., 2009 Kim et al., 2010
nZVI	Less than 100 nm	<i>E. coli</i>	Cell adhesion and inactivation	Diao and Yao, 2009 Li et al., 2010 Xiu et al., 2010

				Xie et al., 2014
nZVI	N/A	<i>Alcaligenes eutrophus</i>	Oxidative stress	Ševců et al., 2009
nZVI	Less than 100 nm	Human bronchial epithelial Cells	Oxidative stress, cytotoxicity	Keenan et al., 2009
nZVI	Less than 100 nm	Mammalian nerve cells	Cytotoxicity and neurotoxicity	Phenrat et al., 2009b
nZVI	N/A	<i>Bacillus subtilis</i> , <i>Staphylococcus aureus</i> , <i>Pseudomonas fluorescens</i> , <i>E. coli</i>	Cell adhesion and inactivation, in vivo damage	Chen et al., 2013
nZVI	20-30 nm	<i>Bacillus subtilis</i> var. <i>niger</i> , <i>Pseudomonas fluorescens</i>	Cell adhesion and inactivation	Diao and Yao, 2009
nZVI	5-12 nm	Rat neural cell line	Cytotoxicity	Pisanic II et al., 2007
nZVI	N/A	<i>Dehalococcoides</i> spp.	Cell adhesion and inactivation	Xiu et al., 2010
TiO ₂	Less than 30 nm	<i>E. coli</i>	Cytotoxicity, oxidative DNA damage	Wiesner et al., 2006 Auffan et al., 2009
TiO ₂	20-30 nm	Phagocytic cell line	Oxidative stress	Xia et al., 2006

ZnO	N/A	Living organisms (human, pigs, rats, rabbits)	Antibacterial	Wiesner et al., 2006
-----	-----	---	---------------	----------------------

* N/A: Not available, nZVI: nanoscale zero-valent iron

Conversely, other papers demonstrated no or negligible effects on soil microorganisms by nZVI particles. Indeed, nZVI particles displayed minor effects on the growth of *E. coli* (Wang et al., 2012), *Klebsiella oxytoca* (Saccà et al., 2013), *Bacillus cereus* (Fajardo et al., 2013). Meanwhile, if the nZVI concentration was less than 10 mg/kg, adverse effects on *Bacillus nealsonii* were identified, while no toxicity was found on *Klebsiella planticola* (Fajardo et al., 2012). The influence of nZVI on the function and community structure of bacteria in soil is also small. For example, the addition of either ZVI or nZVI shows minor impacts on the microbially mediated soil processes, such as dehydrogenase, hydrolase, and ammonia oxidation potential activities (Cullen et al., 2011). Tilston et al. (2013) indicated the change in soil bacterial community structure and chloroaromatic biodegradation potential by the presence of nZVI. The nZVI toxicity level on microbial communities strongly depends on microbial species (Fajardo et al., 2012), soil texture, and organic matter amount in soil (Pawlett et al., 2013). The passivation may decrease the toxicity of nZVI. If the nZVI is oxidized, its toxicity to mammalian cell lines (Phenrat et al., 2009b) and *E. coli* (Li et al., 2010) will be less than stable metallic nZVI. Some papers demonstrated the adverse effects of nZVI on earthworms (El-Temsah and Joner, 2012a), nematode *Caenorhabditis elegans* (Saccà et al., 2014), *Typha latifolia*, and Populus plant (El-Temsah et al., 2012b). In addition, the rapid passivation also inhibits the potential bioaccumulation and biomagnification of nanoparticles in organisms and food chains, respectively (Bardos et al., 2014).

Some studies have investigated the effect of nZVI on human health. Due to the generation of ROS, nZVI and iron oxide nanoparticles might be cytotoxic to human and animal cell lines, which was found by the in vitro tests (Keenan et al., 2009). Moreover, inhalation, dermal, and ingestion may be potential exposure mechanisms for humans when using nanoparticles for remediation without personal protection (Bardos et al., 2014). The comprehension of toxicity, such as the influence of dose-response relationships (Limbach et al., 2007) or iron-containing substances (Wiesner et al., 2006), is poorly understood. However, more studies are needed to have a conclusion.

2.3.2. Use of bimetallic nanoparticles for removal of oil pollutants in soil

Due to the excellent chemical reactivity, the activity and mobility of nZVI particles in soil may be negatively affected by some physiochemical processes, such as aggregation (attachment and adherence of nanoparticles to form larger particles), passivation (inactivation of nanoparticle surfaces due to reaction of iron with non-target contaminants or other nZVI particles), or immobilization (sorption on material inside the soil). As a result, the remediation efficiency of nZVI particles will decrease. Therefore, bimetallic nanoparticles have been developed to solve these concerns. In this method, a small dosage of noble metal, such as Ni or Pd, was doped on the nZVI surface to form the bimetallic particles. Due to the catalytic behavior of this noble metal, the electron-donating capacity of iron will increase, or the reaction rates and the variety of treatable contaminants of the bimetallic particles was improved (Quinn et al., 2009; Bardos et al., 2014). In particular, the bimetallic particle created a galvanic cell, in which the noble metal and iron will work as the cathode and anode, respectively (Elliott and Zhang, 2001). Through this galvanic cell,

the redox capacity of the iron was enhanced. The electron transfer was also accelerated in the presence of noble metal, leading to the increase of dechlorination reactions or faster reaction rates (Zhu and Lim, 2007). As a result, the treatment efficiency of contaminants by the bimetallic nanoparticles was significantly improved. For example, with the addition of a noble metal catalyst, the remediation of chlorobenzenes (Zhu and Lim, 2007) and PCBs (Wang and Zhang, 1997; Xu and Bhattacharyya, 2005) was considerably higher. Nonetheless, the valuable lifetime of bimetallic particles is short, and their reactivity may be rapidly reduced (Zhu and Lim, 2007).

2.3.2.1. Fe/Ni bimetallic nanoparticles

The use of Fe/Ni bimetallic nanoparticles for environmental remediation has been previously studied (Crane and Scott, 2012; Schrick et al., 2002; Zhang et al., 2009). This combination may show a synergistic effect of both metals, which will enhance the functional and physicochemical properties of materials (Swiatkowska-Warkocka, 2021). In particular, Ni may act as cathode sites, which improve the reactivity of Fe/Ni alloys, such as degradation of contaminants or antimicrobial effect (Lozhkomoev et al., 2018).

Fe/Ni bimetallic nanoparticles are effective in the removal of oil pollutants. The presence of Ni in the bimetallic component significantly decreased the formation of by-products. For example, different toxic intermediates and chlorinated by-products, such as ethane (Zhang et al., 1998), cis-dichloroethene, vinyl chloride (Xu and Bhattacharyya, 2005), were identified after dechlorination of TCE by nZVI. However, only ethane was detected after the TCE dechlorination by Fe/Ni bimetallic nanoparticles (Xu and Bhattacharyya, 2005).

2.3.2.2. *Fe/Pd bimetallic nanoparticles*

The doping of Pd on the nZVI surface may significantly improve the reactivity of nZVI/Pd bimetallic particles. Due to forming activated hydrogen species and splitting the carbon-halogen bonds, Pd was the most effective and accepted metal (Wong et al., 2009). The bimetallic ZVI/Pd nanoparticles have shown high treatment efficiency of oil pollutants. Compared to commercial Fe particles and nZVI, the nanoscale Fe/Pd bimetallic particles displayed a higher surface-area-normalized rate constant (K_{SA}) and made them more reactive (Zhao et al., 2016). In the Fe/Pd bimetal, Pd might serve as a catalyst, which increased the dissociation rate of chlorinated hydrocarbons, resulting in higher dechlorination efficiency. The addition of Pd to the Fe surface may cause the synergistic effect, limiting the Fe oxidation and protecting the reactivity of the ZVI surface, leading to improving the dechlorination reactions (Wang and Zhang, 1997; Yan et al., 2013). Therefore, the Fe/Pd bimetal was preferred to only nZVI or only Fe particles due to the higher removal performance and little or no formation of toxic by-products (Zhao et al., 2016). However, the field results still showed the incomplete treatment of chlorinated VOCs by Fe/Pd bimetal, in which various mechanisms, such as reductive dechlorination, were recognized (Henn and Waddill, 2006). For example, Fe/Pd removal of chlorinated organics was much higher than by only nZVI (Yan et al., 2013).

The dechlorination process is based on the reduction activity of reactive hydrogen species, which were formed by the production and adsorption of H_2 on metal surfaces (Lowry and Reinhard, 1999). In the meanwhile, using ZVI particles to remove chlorinated hydrocarbons might take a long time, produce toxic intermediate by-products (Xu and Zhao, 2007), or require a very high temperature (Schrack et al., 2002).

The removal performance of Fe/Pd bimetal depends on the Pd amount and contaminant concentration. Quinn et al. (2009) showed that the degradation efficiency of chlorobenzenes by Fe/Pd bimetal reduces as the chlorine concentration increases. Meanwhile, Zhu and Lim (2007) showed a higher dechlorination efficiency of 1,2,4-TCB with a higher concentration of Pd.

2.3.2.3. Impacts from bimetallic nanoparticles

The effect of doped metals in the bimetallic nanoparticles on human health has been evaluated in some studies. Due to the small amount of these doped metals in the bimetallic nanoparticles (usually less than 1%), only a small dosage can leak into the environment, while their toxicity can be negligible (Bardos et al., 2014). The potential toxicity of doped metals on human skin, colon, and trout gills was found to be limited (Hildebrand et al., 2010). During the in-situ dechlorination process, 0.1 g/L Fe/Pd bimetal did not affect the growth and cell morphology of bacterial strain *Sphingomonas sp.* PH-07 (Murugesan et al., 2011).

2.4. Use of surfactant-stabilized nZVI for remediation of oil pollutants in soil

2.4.1. Mechanisms of nanoparticle agglomeration and stabilization

In solution, nanoparticles tend to agglomerate to form clusters, subsequently leading to pore plugging. The aggregation of nanoparticles can occur in various ways, such as Ostwald ripening, arrested precipitation, and direct inter-particle interactions (He and Zhao, 2007). In particular, the first trend involves the dissolution of small particles, which are then captured by larger particles. The second trend includes generating nucleation centers, which will catch small particles. The

third trend is caused by the van der Waals and magnetic attraction forces. The aggregation and the interaction of nanoparticles with water in solution may inhibit their movement in soil or limit their specific surface area, resulting in lower reactivity (Zhao et al., 2016). Hence, controlling the inter-particle interactions and nanoparticle agglomeration and protecting nanoparticle surfaces from rapid oxidation by the surrounding environment will improve nanoparticle stabilization.

Different methods have been studied to control nanoparticle stabilization. Surface modification and network stabilization are two of the most common techniques among these approaches. The surface modification stabilization involves the formation or improvement of repulsion forces, such as an electrostatic double layer or osmotic, due to the adherence of stabilizer molecules on the nZVI surface (Zhao et al., 2016).

Meanwhile, network stabilization includes generating a viscous matrix of hydrogen bonding and polymer capture due to the interaction of a high amount of a stabilizer and nZVI (Comba and Sethi, 2009). In particular, the nZVI can be detached by reducing collision frequency with the stabilizer matrix due to the stabilizers adsorbed on the nZVI surface through the gel structures or the stabilizer layer covered around nZVI (Tosco et al., 2014). Therefore, a stabilizer may help improve the dispersion of nanoparticles, resulting in limited agglomeration of nanoparticles.

2.4.2. Mechanisms of surfactant-stabilized nZVI

Different stabilizers have been used to inhibit the aggregation of nZVI (Table 4). Common stabilizers are surfactants (Sharma et al., 2020; Xu and Zhao, 2007; Kanel et al., 2007; Vu and Mulligan, 2020; Vu and Mulligan, 2022b; Vu and Mulligan, 2022c; Vu and Mulligan, 2022f), carboxylic acids (Zhao et al., 2016), polymers (Geng et al., 2009), long-chain alcohols (Pardoe et

al., 2001), or soluble polysaccharides (Lin et al., 2005). Surfactants have been extensively studied as surface modifiers for nanoparticle stabilization among these stabilizers. In these methods, nanoparticles will be dispersed by the surfactant to improve their stability in the mixture. They can be added either before (Cho and Choi, 2010), during (He and Zhao, 2008), or after (Phenrat et al., 2009b) the formation of nanoparticle aggregation, which is called pre-aggregation stabilization or post-aggregation stabilization, respectively. The pre-aggregation method is favored to acquire the tiny particle size, while the post-aggregation method generally needs sonication pre-treatment (Tratnyek et al., 2011). The dechlorination efficiency of TCE by nZVI prepared through the pre-aggregation stabilization method was more productive than the post-aggregation method (Cho and Choi, 2010; Phenrat et al., 2009a).

Table 4. Summary of different stabilizers for nZVI particles

Name	Type	Particle size, nm	Contaminant	Remediation efficiency, %	References
Rhamnolipid	Biosurfactant	8 - 100	TCE	>99	Basnet et al., 2013 Bhattacharjee et al., 2016 Sharma et al., 2020
Carboxymethyl cellulose (CMC)	Polysaccharide	4 - 40	TCE	>99	He et al., 2007 Phenrat et al., 2008

					Zhang et al., 2011 Bhattacharjee et al., 2016
Polyacrylic acid (PAA)	Polyelectrolyte	50 - 100	N/A	N/A	Hydutsky et al., 2011
Polyacrylamide (PAM)	Polymer	Less than 60	N/A	N/A	Cirtiu et al., 2011
Polyaspartate (PAP)	Polypeptide	5 - 40	N/A	N/A	Phenrat et al., 2008
Polystyrene sulfonate (PSS)	Polyelectrolyte	Less than 60	N/A	N/A	Cirtiu et al., 2011 Phenrat et al., 2008
Starch	Polysaccharide	9 - 14	TCE PCBs	98% TCE 80% PCBs	He and Zhao, 2005 Babaee et al., 2018
Xanthan gum	Polysaccharide	40	N/A	N/A	Comba and Sethi, 2009

Different types of surfactants have effectively shown their ability for nanoparticle stabilization, such as the anionic surfactant (e.g., SDBS), nonionic surfactant (e.g., Tween 20), carboxymethyl cellulose, or rhamnolipid biosurfactant. For example, the SDBS-stabilized commercial ZVI

through the post-aggregation method displayed smaller ZVI particle sizes and more remarkable transportability in porous media due to the improved electrostatic repulsion by the sulfonated groups of SDBS (Saleh et al., 2007). In another study, the Tween 20-stabilized nZVI through the post-aggregation approach established better transportability and arsenic remediation productivity in sandy soil (Kanel and Choi, 2007). Through the post-aggregation process, the carboxymethyl cellulose-stabilized nZVI exhibited much lower mobility in porous media but higher TCE removal effectiveness than the rhamnolipid-stabilized nZVI (Basnet et al., 2013).

Biosurfactants have been widely used as the surface modifiers of nanoparticles (Bhattacharjee et al., 2016; Basnet et al., 2013; Zhao et al., 2016; Miyazawa et al., 2021). In this method, a biosurfactant is mixed with nanoparticles to form an aqueous suspension, whereas the biosurfactant will be considered a nanoparticle surface stabilizer (or a stabilizing agent) (Basnet et al., 2013) (Figure 8).

Fe/Cu particles were used in this study due to their synergistic effect that enhanced the functional properties of both Fe and Cu in the bimetallic composition. In particular, Fe can act as the base metal and electron source while Cu can act as the catalyst additive. Therefore, Cu can delay the surface oxidation process of Fe, leading to the higher reactivity (Liao et al., 2021).

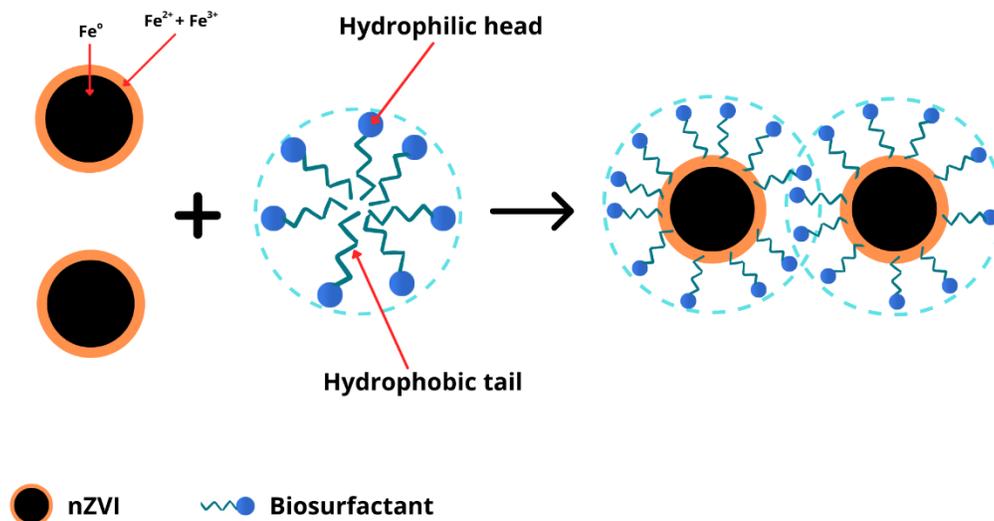


Figure 8. Interaction of nZVI and biosurfactant (in micelle form)

Via this combination, the nanoparticle surface is covered by the biosurfactant while nanoparticles are stabilized. Thus, the oxidation of nanoparticle surfaces is limited, which will improve their stability, mobility, and reactivity (Ali et al., 2020; Liao et al., 2021). Biosurfactants can inhibit nanoparticles from aggregating, which enhances their transport in a soil matrix (Mueller and Nowack, 2010; Basnet et al., 2013; Zhao et al., 2016). They can also improve the interaction of nanoparticle surface and oil pollutants by promoting the solubilization, desorption, and mobilization behavior of organic compounds in soil (Viisimaa et al., 2013). Likewise, a biosurfactant can act as the electron transport catalyst, which increases the rate of redox reactions, resulting in higher removal (Tratnyek et al., 2011). Besides, the integration of biosurfactants and nanoparticles decreases their adsorption on soil particles, improving their reactivity and ability to recycle and reuse the nanoparticles after the treatment process. Therefore, the combination of biosurfactants and nanoparticles will be a promising method for treating oil-contaminated soil.

2.4.3. Remediation of organic contaminants in soil using surfactant-stabilized nZVI

2.4.3.1. Transport of surfactant-stabilized nZVI in soil

The transport of stabilized nZVI in porous media can be modeled by filtration theory (Kretzschmar et al., 1999). In particular, the main mechanisms include interaction, sedimentation, and diffusion, which were due to media, gravity, and Brownian motion, respectively. For steady flow, the classic convective-dispersive transport equation can express the stabilized nZVI transport, in which the particle deposition follows a first-order reaction (Kretzschmar et al., 1997). The transport of carboxymethyl cellulose-stabilized nZVI, PAA-stabilized ZVI in porous media has been described in previous studies (He and Zhao, 2007; He et al., 2007; Kanel et al., 2008; He et al., 2009; Zhang et al., 2017). For example, Xu and Zhao. (2007) observed the high transportability of carboxymethyl cellulose-stabilized nZVI through a sandy loam, mainly due to the interception of soil and nZVI and the oxidation of nZVI to iron oxides or iron minerals.

In field studies, the non-stabilized nZVI was less transportable in the soil. For instance, surfactant-oil emulsified ZVI particle distribution and mobility were poor (Quinn et al., 2005). Hence, pneumatic injection and direct push were suggested to obtain higher mobility. In other work, the emulsified ZVI could move up to 2.1 m and 0.89 m through pneumatic injection and direct push, respectively (Su et al., 2013). Meanwhile, the guar gum stabilized microscale ZVI slurries may travel 1.7 m via direct pressure injection (Luna et al., 2015). In addition, the transport of carboxymethyl cellulose-stabilized nZVI in the field test was greatly enhanced with the rapid increase of injection pressure or pore velocity (He et al., 2010). In another push-pull test, the mobility of carboxymethyl cellulose-stabilized nZVI particles was high over the 13-hour lag time. Furthermore, a high pore velocity was recommended to maintain the reactive nanoparticles

(Bennett et al., 2010). Another study claimed that the carboxymethyl cellulose-stabilized nZVI could travel up to 1 m through the site contaminated with PCE and TCE (Kocur et al., 2014).

2.4.3.2. Remediation of organic contaminants in soil

Surfactant-stabilized nZVI has been effectively utilized to remediate the organic contaminants in soil (Figure 9). The dechlorination process was proven to be more effective with nanoscale ZVI or the addition of stabilizers. For instance, the dechlorination reactivity of TCE and PCBs by starch-stabilized Fe/Pd nanoparticles was 37 times and six-fold higher than non-stabilized Fe/Pd nanoparticles, or the TCE dechlorination rate by carboxymethyl cellulose-stabilized Fe/Pd nanoparticles was two times faster than the starch-stabilized Fe/Pd nanoparticles due to their higher specific surface area and nanoparticle stabilization ability (He and Zhao, 2007).

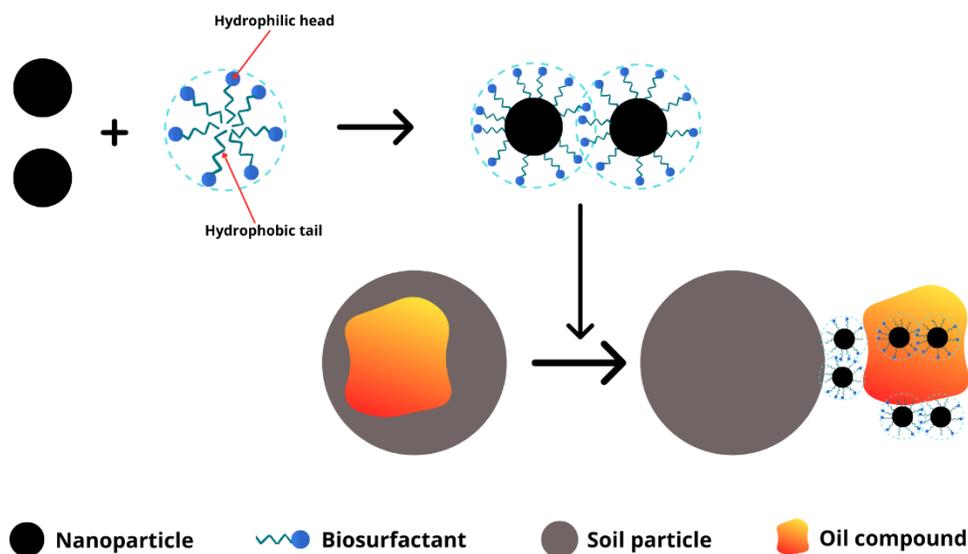


Figure 9. Remediation of organic contaminants in soil by surfactant and nZVI

Surfactant-stabilized nanoparticles have been used to remove soil pollutants in field tests. Quinn et al. (2005) indicated a significant improvement in the in-situ dehalogenation efficiency of TCE by the surfactant-oil emulsified nZVI. In particular, the removal of TCE increased about 80% and 57-100% within three months and five months, respectively, in soil sampling sites. After 2.5 years, the injection of surfactant-corn oil emulsified nZVI to field sites enhanced the remediation of total CVOCs and PCE by 86% and 93%, respectively (Zhao et al., 2016). Carboxymethyl cellulose-stabilized Fe/Pd nanoparticle suspension has been used for in-situ degradation of chlorinated solvents, such as PCE, TCE, and PCBs, in source zones in Alabama. After 596 days, up to 88% of TCE was degraded, in which the highest amount of abiotic remediation was in the first two weeks. After one month, the stabilized nanoparticles played a vital role in biotic dechlorination. In addition, the removal rate was enhanced by the performance of carboxymethyl cellulose and hydrogen (from the abiotic/biotic procedure) as the carbon source and electron donor, respectively (He et al., 2010). Another study evaluated the in-situ transport of carboxymethyl cellulose-stabilized nZVI and Fe/Pd nanoparticles in saturated sediments and their remediation of chlorinated ethenes at an existing aerospace facility (Bennett et al., 2010). After two hours, fast-abiotic degradation of chlorinated ethenes by stabilized Fe/Pd nanoparticles was detected. However, the combination of biosurfactants and nanoparticles for treating actual oil-contaminated soil has not been thoroughly researched. This study aims to evaluate biosurfactant/nanoparticle suspension to remediate oil-contaminated soil, investigate the factors affecting the treatment efficiency of biosurfactant/nanoparticle mixture, and determine the knowledge gaps and future research to resolve the challenges.

CHAPTER 3: MATERIALS AND METHODS

3.1. Materials

Iron (II) sulfate heptahydrate 99% ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), sodium borohydride 98% (NaBH_4) powders, and 4-chlorobenzoic acid 99% (pCBA) were purchased from Acros Organics, USA. Copper (II) sulfate pentahydrate 99% ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), hexane 98.5% (C_6H_{14}), n-hexane 95% (C_6H_{14}), and acetone 99.5% ($\text{C}_3\text{H}_6\text{O}$) were obtained from Fisher Scientific, USA. 8N sodium hydroxide (NaOH) and 36.5% hydrochloric acid (HCl) solutions were purchased from Fisher Scientific, USA. Deionized (DI) water was produced from the Barnstead Nanopure water purification system (Thermo Scientific).

3.2. Soil source and characterization

Contaminated soil was obtained from a contaminated site and stored at 4°C in a refrigerator in the laboratory. This soil was sieved for four days by a standard sieve of 1 mm and dried under the hood (Forma Scientific Class II A/B3 Biological Safety Cabinet). The air-dried soil was stored in a glass bottle and kept inside a desiccator (Sanplatec Dry Keeper, USA) for future use. The particle size distribution analyzer (Horiba LA-950V2, Japan) measured this soil's characteristics, such as particle size distribution, percentage of sand, clay, and silt. The organic content was determined by the ASTM D2974-14 method.

$$\text{moisture content}(\%) = \left(\frac{W_w - W_d}{W_w} \right) * 100\% \quad (10)$$

$$\text{organic content (\%)} = \left(\frac{W_d - W_b}{W_d} \right) * 100\% \quad (11)$$

where: W_w is the weight of wet soil, g

W_d is the weight of dry soil, g

W_b is the weight of ignited soil, g

The soil porosity was calculated by the following equations (ASTM 2006 method):

$$\text{soil porosity} = \frac{V_p}{V_t} * 100\% = \frac{V_p}{V_p + V_s} * 100\% \quad (12)$$

where: V_p is the pore volume or volume of water displaced, cm^3

V_s is the volume of solid (soil), cm^3

V_t is the total volume, cm^3

The hydraulic conductivity of the soil in the column was determined by Darcy's law following the ASTM D7100-11 (2020) method:

$$\text{Hydraulic conductivity} = \frac{Q * L}{A * \Delta h} \quad (13)$$

where: Q is the flowrate, $\text{cm}^3 \cdot \text{s}^{-1}$

L is the column length, cm

A is the cross-sectional area of column, cm^2

Δh is the head difference on manometers, cm

The hydraulic conductivity of this contaminated soil was calculated as $4.2 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1}$.

3.3. Measurement of total petroleum hydrocarbon content in the soil

The total petroleum hydrocarbon (TPH) content in soil was determined by the approach of Urum et al. (2003). In this method, contaminated soil was extracted four times by sonication (Branson 8510 Ultrasonic Cleaner, USA) in n-hexane for 30 min or until the extraction was colorless. The total n-hexane-oil extract was collected into the conical centrifuge tube 50 ml, centrifuged at 8000 rpm for 15 min (Heraeus multifuge 3SR+, Thermo Scientific, USA) to separate the suspended particles from the aqueous phase. Then the n-hexane-oil solution was filtered through a PTFE filter (0.45 μm nonsterile Fisher Scientific filter paper), and the oil content in the final solution was measured at 350 nm by UV-Vis spectrophotometer (Thermo Scientific Evolution 201, USA). The sonication method was more effective than the shaking or Soxhlet method for extracting total petroleum hydrocarbon from soil (Sin and Gwon, 2000). The calibration curve of oil pollutants in n-hexane was made at different oil concentrations (Figure 10).

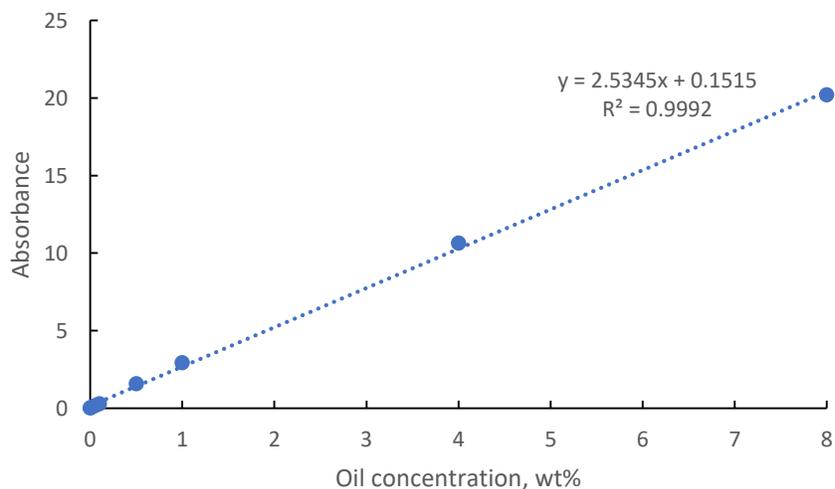


Figure 10. Calibration curve of oil pollutants in n-hexane

3.4. Measurement of total metal concentration in suspension

The total concentration of Fe and Cu (both particulate and dissolved elements) in the original surfactant-particle suspension and the final supernatant was measured by ICP-MS (Inductively Coupled Plasma Mass Spectrometer, Agilent 7700 Series). In particular, each sample was acid digested by HNO₃ (Fisher Scientific, USA), followed by the EPA method 3050B. The final digestate was filtered through a 0.45 μm filter, diluted, and analyzed by ICP-MS.

3.5. Measurement of surface tension and interfacial tension of biosurfactants

Two types of biosurfactant, rhamnolipid (10% and 25%) and sophorolipid (41%), were obtained from Jeneil Biosurfactant Company (USA) and Ecover Company (Belgium), respectively. The biosurfactant solution surface tension and interfacial tension of water-air and water-oil were measured using a Kruss K100 force tensiometer (Krüss GmbH, Germany) with a platinum plate. Each measurement was conducted in triplicate, and the average results were reported. The measurement variability was about 0.1 mN/m. The temperature was kept constant at 20°C. The CMC value of biosurfactants was determined by the change in water surface tension and interfacial tension in the presence of the surfactants at different concentrations.

3.6. Synthesis of Fe/Cu bimetallic nanoparticles

Fe/Cu particles were prepared by a simple reduction method (Morales-Luckie et al., 2008). In this approach, 500 mL of 5 mM FeSO₄·7H₂O solution and 500 mL of 5 mM CuSO₄·5H₂O were

mixed and stirred about 30 min under nitrogen at room temperature (Figure 11). The pH of the mixture was adjusted to 7.0 by 0.1M and 1M NaOH solutions. Afterward, 100 ml of 10mM NaBH₄ aqueous solution were poured quickly into the mixture under stirring.

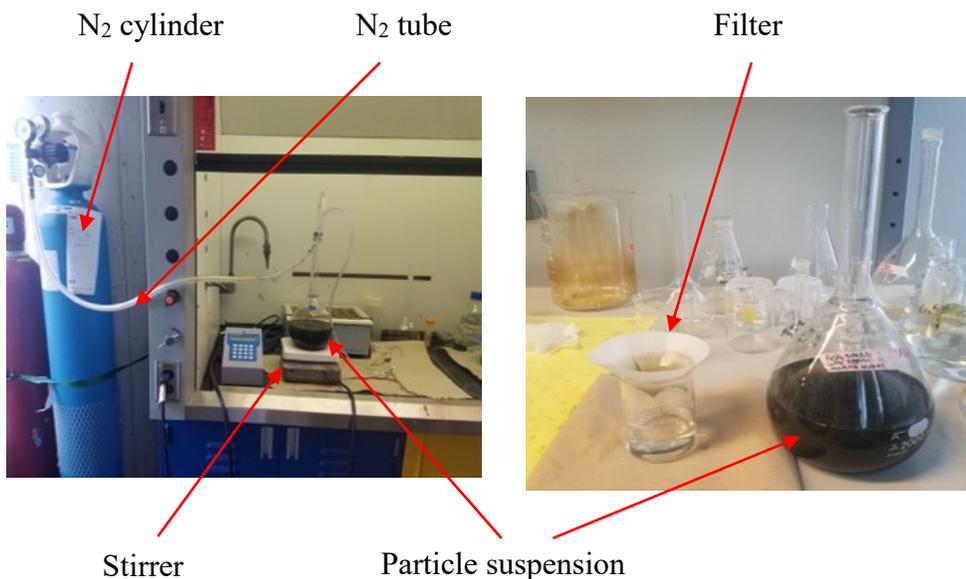
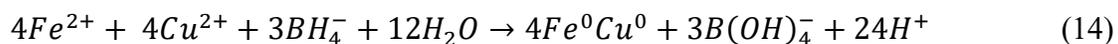


Figure 11. Fe/Cu bimetallic nanoparticle synthesis system (Vu and Mulligan, 2022d)

This process is represented in the reaction (Morales-Luckie et al., 2008):



A black precipitate (zero-valent iron, Fe⁰Cu⁰) was obtained, filtered through a 0.22 μm filter, and washed by DI water (three times), acetone (three times), and hexane (three times). Finally, the black Fe/Cu particles were attained and stored in hexane in the dark and room temperature.

3.7. Characterization of Fe/Cu nanoparticles

The Fe/Cu bimetallic particle chemical composition and crystallographic structure were obtained by an X-ray diffractometer (Philips X'Pert PRO Multipurpose, Netherlands) equipped with Cu K-alpha radiation. The air-dried Fe/Cu particle sample was ground and diffracted at 4000 positions over a 2θ range of 10° to 90° .

A scanning electron microscope (Hitachi S-3400N SEM, Japan) and a transmission electron microscope (Tecnai G2 F20 S/TEM, USA) were used to investigate the morphology of Fe/Cu particles. The high-resolution SEM and TEM images show the size, location, and morphology of synthesized Fe/Cu particles. For each technique, the air-dried Fe/Cu particle sample was put on a Cu grid with carbon support film and measured at room temperature.

3.8. Properties of biosurfactant/nanoparticle suspension

The colloidal stability of biosurfactant/nanoparticle suspension was measured through zeta potential determination. The suspension was created by mixing different amounts of nanoparticles (1-10 mg particles in hexane) with 10 mL of surfactant solutions (0.001-4 wt%), which are the optimal values from batch experiments, in the 50 mL corning centrifuge tubes. The suspension was kept inside a fume hood for 24 hours to remove all residual hexane. The zeta potential of suspension was measured by Malvern Zetasizer Nano ZS (Malvern Instruments Ltd., USA) at room temperature. The interaction of biosurfactant, nanoparticle, and soil was determined by FTIR-ATR spectrophotometer (Thermo Scientific, Nicolet 6700/Smart iTR). The formation of reactive oxygen species (ROS) by biosurfactant/nanoparticle suspension was determined by the

decrease of 4-chlorobenzoic acid (pCBA) concentration, a ROS probe compound, for seven hours of mixing. The concentration of pCBA was measured by a UV-Vis spectrophotometer (Thermo Scientific Evolution 201, USA) at the absorbance wavelength of 235 nm.

3.9. Batch experiments

A series of batch tests was carried out to investigate the effect of the Fe/Cu particles and the biosurfactant on removing petroleum hydrocarbons from contaminated soils. For each batch test, particles (1-10 mg) were mixed with biosurfactants (0.001-4 %) in the 50 mL corning centrifuge tubes. The suspension was kept inside a fume hood for 24 hours to remove all residual hexane. The tubes were sonicated for 15 minutes, and contaminated soil (1.6-10 g) was added to the mixtures. The surfactant: nanoparticle: soil ratio was chosen based on the optimal ratio in previous studies (Urum et al., 2003; Liang and Zhao, 2014; Sharma et al., 2020). The mixtures were shaken at different shaking speeds (30-250 rpm) by an orbital shaker (Wrist Action Shaker model 75, Burrell Scientific, USA) at room temperature for various time amounts (5-300 min). The tubes were left to settle for three hours until the two phases were entirely separated. The supernatant was carefully pipetted off the tubes, centrifuged at 8000 rpm for 15 min, and filtered through a filter (20 μm Whatman quantitative filter paper). The filtered supernatant surface tension and metal concentration were determined by the tensiometer and ICP-MS instrument, respectively. At the same time, oil and water in the supernatant were separated three times in a 60 mL Erlenmeyer separatory funnel. The residual water and possible emulsions formed in the water-oil extracts were removed by sodium sulfate (ACS grade, Acros Organics, New Jersey, USA) and centrifugation (8000 rpm, 15 min), respectively. Oil content in the final extract was extracted by n-hexane and

measured by UV-Vis spectrophotometer at 350 nm. All batch experiments were conducted in triplicate, and the average values were reported.

The control samples included oil-contaminated soil and DI water. The batch experiments at various temperature values were conducted in Erlenmeyer flasks (500 ml), covered by aluminum foil, and shaken inside an incubator shaker (Innova 42, Canada). After that, the oil content was extracted by n-hexane, filtered by PTFE filter (0.45 μm nonsterile Fisher Scientific filter paper), and analyzed by the UV-Vis spectrophotometer at 350 nm.

3.10. Determination of total petroleum hydrocarbons in the soil

After the soil extraction process in the batch experiment, some petroleum hydrocarbons may remain attached to treated soil particles (in the conical tube) and the interior walls of the conical tube. Therefore, an additional step was developed to determine these remaining oil amounts. In particular, DI water was added to the used soil tubes, and the supernatant was poured into a 400-mL beaker. In addition, the filter used to separate the supernatant and soil particles and DI water used to clean the Erlenmeyer separatory funnel were also collected in the beaker. Then, the beaker was shaken, and the mixture was poured into the Erlenmeyer flask for the oil separation process. The residual water and possible emulsions formed in the water-oil extracts were removed by sodium sulfate (ACS grade, Acros Organics, New Jersey, USA) and centrifugation (8000 rpm, 15 min), respectively. Oil content in the final extract was extracted by n-hexane, filtered by PTFE filter, and measured by UV-Vis at 350 nm.

3.11. Column experiments

The column experiment was conducted in a plastic column (L = 15 cm, ID = 2.6 cm) (Figure 12). The aqueous biosurfactant and nanoparticle suspensions were added at the top of the column and allowed to percolate through the column by a peristaltic pump (Masterflex L/S, USA). At the bottom of the column, a filter (0.22 μm hydrophobic fluoropore PTFE) was used to keep the soil inside while allowing water to pass during experiment time. Water was passed through the soil column for permeability tests. For each experiment, an influent was added at a certain flowrate. The effluent was collected in the centrifuge tubes, centrifuged at 8000 rpm for 15 min, and filtered (20 μm Whatman quantitative filter paper). Oil and water in the supernatant were separated three times in a 60 mL Erlenmeyer separatory funnel. The residual water and possible emulsions formed in the water-oil extracts were removed by sodium sulfate (ACS grade, Acros Organics, New Jersey, USA) and centrifugation (8000 rpm, 15 min), respectively. The oil concentration in the effluent was extracted by n-hexane, filtered by PTFE filter, and measured by a UV-Vis spectrophotometer at 350 nm. The concentration of nanoparticles in the effluent was analyzed by the ICP-MS instrument.

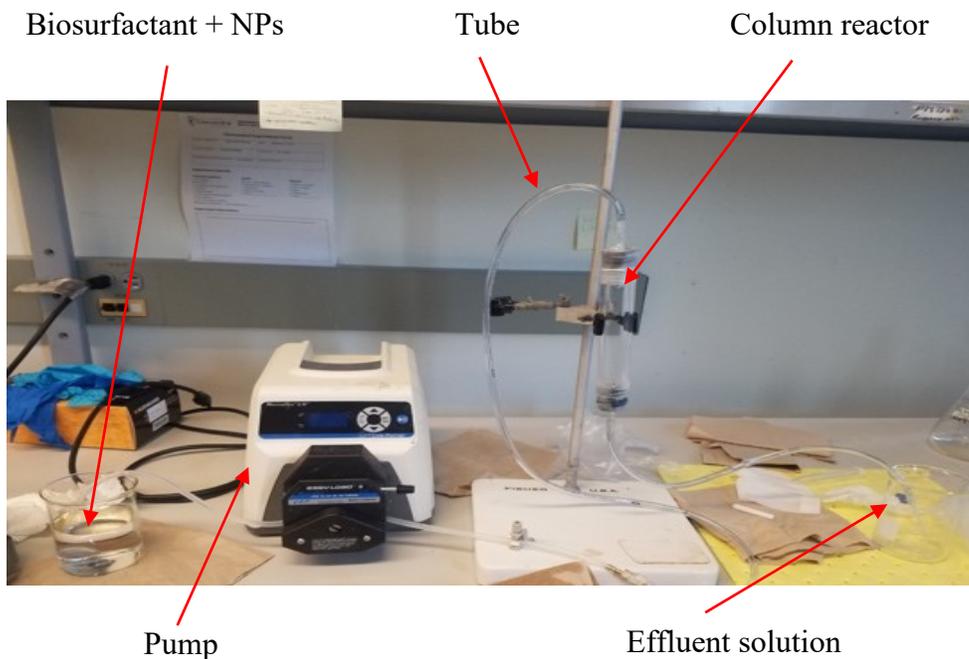


Figure 12. Column experiment for remediation of oil-contaminated soil

(Vu and Mulligan, 2020)

The change in oil concentration and the effect of flowrate on oil treatment efficiency in column experiments were determined. Control experiments were carried out by using only DI water. All column experiments were conducted in triplicate, and the average values were reported as the final results. The experiments were conducted until the amount of oil detected in the effluent was negligible.

For foam column experiments, the foam was generated in a plastic column (L=21 cm, D=2.6 cm) at room temperature and under atmospheric pressure (Figure 13). In particular, particles (1-2 wt%) were mixed with biosurfactants (0.5-2 vol%). The suspension was kept inside a fume hood for 24 h to remove all residual hexane. Before the column experiment, the biosurfactant/nanoparticle suspension was sonicated for 15 min to generate the reactive oxygen

species (ROS), which was demonstrated by the reduction of 4-chlorobenzoic acid (pCBA) concentration, a ROS probe compound. The content of pCBA was determined by a UV-Vis spectrophotometer (Thermo Scientific Evolution 201) at a wavelength of 235 nm.

In each experiment, different concentrations of aqueous biosurfactant and nanoparticle mixture and N₂ gas were simultaneously added to the bottom of the foam-generating column containing circular porous stone plates by a peristaltic pump (Masterflex L/S, USA). Two flow meters (Fisher Scientific, Oakville, Canada) were used to monitor the flow of mixture and N₂ gas passing through the foam-generating column. The varied independence of surfactant/nanoparticle mixture and N₂ gas flowrates helps control foam formation rate and quality. The foam was generated under different flowrates of surfactant/nanoparticle mixture and N₂ gas. After the bubble size and shape reached a uniform and steady-state, the foam exiting the column was sampled for quality-stability tests. For each stability-quality test, 50 mL generated foam were placed in a 100-mL beaker and left before all of the bubbles broke down. The foam stability was evaluated by the time required to break down half of the total foam, while the foam quality was decided by the total gas volume per total foam sample volume at room condition. The pH value was adjusted by 8N sodium hydroxide (NaOH) and 36.5% hydrochloric acid (HCl) solutions (Fisher Scientific, USA).

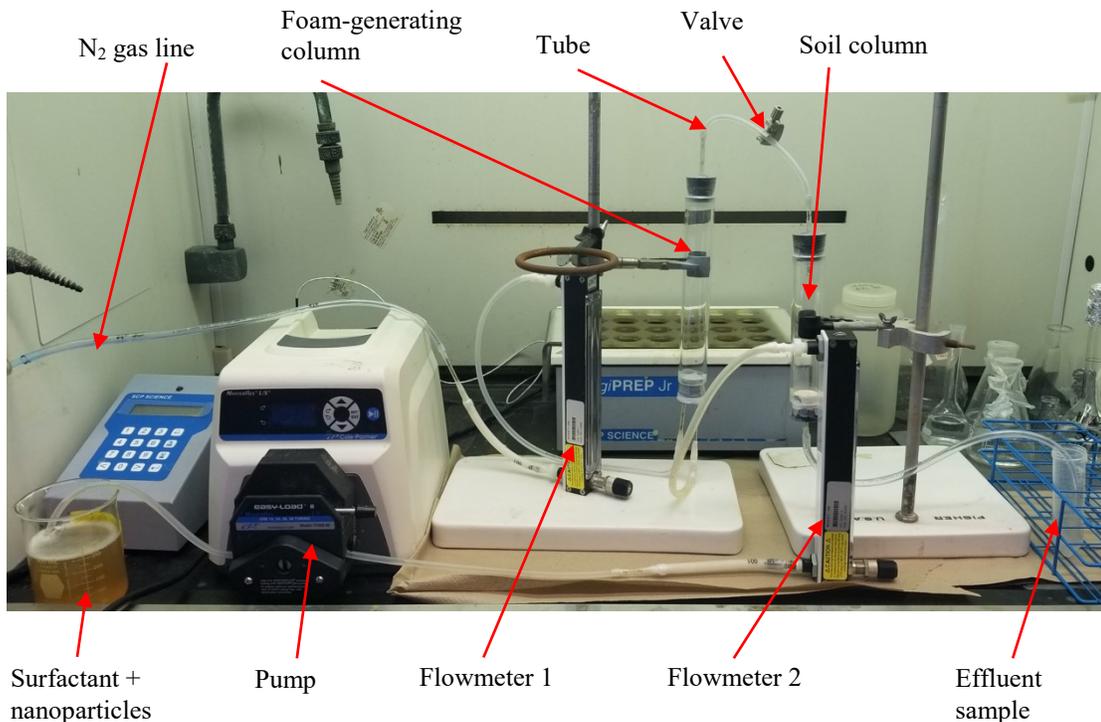


Figure 13. Foam column experiment for surfactant/nanoparticle mixture

A soil column ($L=15\text{cm}$, $D=2.6\text{cm}$) was linked with the foam-generating column through a MasterFlex silicone tubing ($D = 3\text{mm}$). A total of 320g of soil was packed uniformly in the column. At the bottom of the soil column, a filter ($0.22\ \mu\text{m}$ hydrophobic fluoropore PTFE) was attached to retain the soil and nanoparticles inside while allowing water to pass during experiment time. A pressure digital traceable manometer (Fisher Scientific, Canada) was placed on this tubing to control the input pressure of the soil column. The pressure gradient increase in the column due to the change of surfactant/nanoparticle mixture concentration, foam quality, and foam flowrate were also measured through this manometer. Before measuring the pore volume, the soil column was saturated at a minimal pressure gradient (~ 0). The pore volume is the water volume used to saturate the soil column. Prior to reaching the steady-state quality, foam injection into the soil is prevented

by a two-way valve installed before the soil column. Before injection into the soil column, foam samples were also taken through this two-way valve.

The control samples included oil-contaminated soil and DI water. The change in oil concentration and the effect of flowrate on oil treatment efficiency in column experiments were determined. The results from this foam column experiment were compared with a surfactant/nanoparticle mixture in the absence of foam. All column experiments were conducted in triplicate, and the average values are reported as the final results. The experiments were conducted until the amount of oil detected in the effluent was negligible.

Two of the most critical characteristics of surfactant foams are foamability and foam stability. Foam quality represents the surfactant capacity to generate foam (Farajzadeh et al., 2009). It is determined by the ratio of total gas volume per total liquid volume in the foam at the atmospheric pressure (Equation 15). The compression and decompression effects of pressure on foam quality are assumed to be zero for foam quality calculation. In addition, the influence of pressure and temperature on foam volume was also negligible (Mulligan and Eftekhari, 2003).

$$Foam\ quality\ (\%) = \frac{Total\ gas\ volume}{Total\ foam\ volume} * 100\% \quad (15)$$

Foam stability is the foam capacity to prevent bubble collapse. It can be calculated by the time that half of the total foam is collapsed. The foam stability is strongly dependent on the type of surfactant and gas, soil characteristics, oil pollutant properties, and static and dynamic conditions of bubble interaction behavior (Osei-Bonsu et al., 2015; Shokrollahi et al., 2014; Rohani et al., 2014). The high foam stability may decrease the gas mobility and permeability, resulting in a higher remediation efficiency (Osei-Bonsu et al., 2017; Ma et al., 2013).

A pressure gauge (Fisher Scientific, Canada) was installed after the foam-generating column and upstream of the soil column to measure the pressure inside the pipe (or inlet pressure of the

soil column) (Figure 13). The pressure gradient was controlled to be smaller than 22.6 kPa/m to prevent potential heaving and channeling (Chowdiah et al., 1998). The pressure gradient was calculated by dividing the pressure values by the column length (15cm) (Equation 16). The pressure gradient increase in the column was measured with different flowrates, biosurfactant concentrations, nanoparticle dosage, and foam quality.

$$\text{Pressure gradient} \left(\frac{\text{kPa}}{\text{cm}} \right) = \frac{\text{Pressure}}{\text{Column length}} \quad (16)$$

The hydraulic conductivity of the foams was determined by Darcy's law (Mulligan and Wang, 2006):

$$\text{Hydraulic conductivity} = \frac{\text{Foam flowrate} * \text{Pressure}}{\text{Column height} * \text{Cross-sectional area} * \text{Water density} * \text{Gravity}} \quad (17)$$

The effluent foam exiting the soil column was collected in the centrifuge tubes, centrifuged at 8000 rpm for 15 min, and filtered (20 μm Whatman quantitative filter paper). Oil and water in the supernatant were separated three times in a 60 mL Erlenmeyer separatory funnel. The residual water and possible emulsions formed in the water-oil extracts were removed by sodium sulfate (ACS grade, Acros Organics, New Jersey, USA) and centrifugation (8000 rpm, 15 min), respectively. The oil content in the final extract was extracted by n-hexane and measured by UV-Vis spectrophotometer at 350 nm. Each sample was obtained after a certain amount of pore volumes passed through the soil column and all foams were collapsed.

The oil treatment efficiency by nanoparticle-stabilized foam was investigated under controlled biosurfactant/nanoparticle mixture, flowrate, and foam quality. The concentration of nanoparticles

in the effluent was analyzed by the ICP-MS instrument (Inductively Coupled Plasma Mass Spectrometer, Agilent 7700 Series). In particular, each sample was acid digested by HNO₃ (Fisher Scientific, USA), followed by the EPA method 3050B. The final digestate was filtered through a 0.45 μm filter, diluted, and analyzed by ICP-MS. All experiments were conducted in triplicate, and the results for the effluent oil concentration did not change more than 10%. The oil treatment efficiency was calculated by the following equation:

$$\text{Oil treatment efficiency (\%)} = \frac{\text{Oil content in the effluent}}{\text{Initial oil content in soil}} * 100\% \quad (16)$$

After the column experiments, the mass balance was examined by flushing the columns with the biosurfactant/nanoparticle suspension or biosurfactant foam/nanoparticle mixture. After finishing the column experiments, residual oil concentrations in the soil samples taken from the rinsed columns were extracted by n-hexane and measured by the UV-Vis at 350 nm. The oil mass balance was validated by comparing the oil content results in the flushed column and the effluent.

Besides, a gas chromatography (GC-FID 436 SCION, DB-624 column) instrument was also used to analyze the type and fraction of oil pollutants that were degraded. The operating conditions for the GC (Table 5) were performed as suggested by Thermo Fisher Scientific.

Table 5. Operation conditions for GC-FID analysis

Parameters	Value
Carrier gas	Helium
Column flowrate, ml/min	2.0, constant flow
Oven temperature, °C	40°C (1 min), 50°C (6 min) to 300°C (12 min)

Injector temperature, °C	280
Injector mode	Splitless
Splitless time, min	0.8
Splitflow, mL/min	50
Detector temperature, °C	340
Injected volume, µL	5.0
Run time, min	24

Based on these results, the status of oil pollutants after the treatment process was specified. In particular, it investigated whether all or some oil components were removed or solubilized by surfactant/nanoparticle suspension in batch and column experiments.

CHAPTER 4: RESULTS AND DISCUSSION

4.1. Soil characterization

The composition of a soil sample is shown in Table 6. In terms of particle size distribution, this soil is classified as fine sandy soil (US Bureau of Soils 1985). The oil content in the soil was 3722 mg/kg, which was considered highly oil-contaminated soil according to the United States Environmental Protection Agency (US EPA) 510-B-94-003 guidelines. Therefore, a remediation method should be developed to treat this oil-contaminated soil.

Table 6. Characteristics of tested soil (Vu and Mulligan, 2022e)

Characteristics	Soil sample
pH	7.4
Median size, μm	91.54
Mean size, μm	99.03
D10, μm	23.46
D90, μm	185.31
Sand, %	67.49
Silt, %	30.50
Clay, %	0.00
Colloid, %	2.01
Moisture content, %	5.45

Organic content, %	1.44
Oil content, mg/kg	3722

*D10 and D90: 10% and 90% of soil particles with diameter below this value.

4.2. Characterization of Fe/Cu particles

4.2.1. Scanning electron microscopy of Fe/Cu particles

SEM analysis with high and low magnification was carried out to determine the surface morphology of Fe/Cu bimetallic particles. Figure 14 indicates the spherical shape of particles with consistent size. The particles did not distribute well in the bimetallic structure. The agglomeration of Fe/Cu bimetallic particles was displayed due to the magnetic force and surface tension (Song et al., 2017; Sang et al., 2021). The particle size was less than 1 μm in diameter.

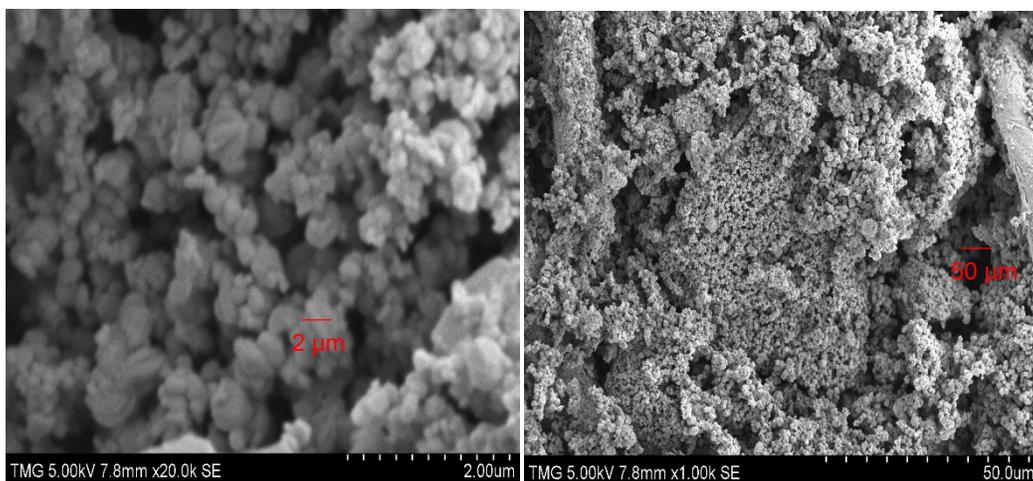


Figure 14. SEM images of Fe/Cu particles with high (left, 10k)

and low (right, 1k) magnification

Meanwhile, the surface morphology was not clearly shown by the SEM images with both magnifications. It was also challenging to see the boundaries between different particles. Therefore, more analysis techniques, such as TEM, are required for particle characterization.

4.2.2. Transmission electron microscope of Fe/Cu particles

The TEM images of nanosized Fe/Cu particles are shown in Figure 15. The average diameter of particles is about 20 nm, which is similar to previous studies (Morales-Luckie et al., 2008; Babae et al., 2018; Sang et al., 2021). Moreover, the nanoparticles are spherical and have similar sizes and shapes. The boundaries between different nanoparticles were observed. The TEM image under high magnification (right) showed the presence of nZVI in the nanoparticle structure (Babae et al., 2018). This nZVI might play a vital role in the adsorption and reduction of contaminants due to their high reactivity and specific surface area.

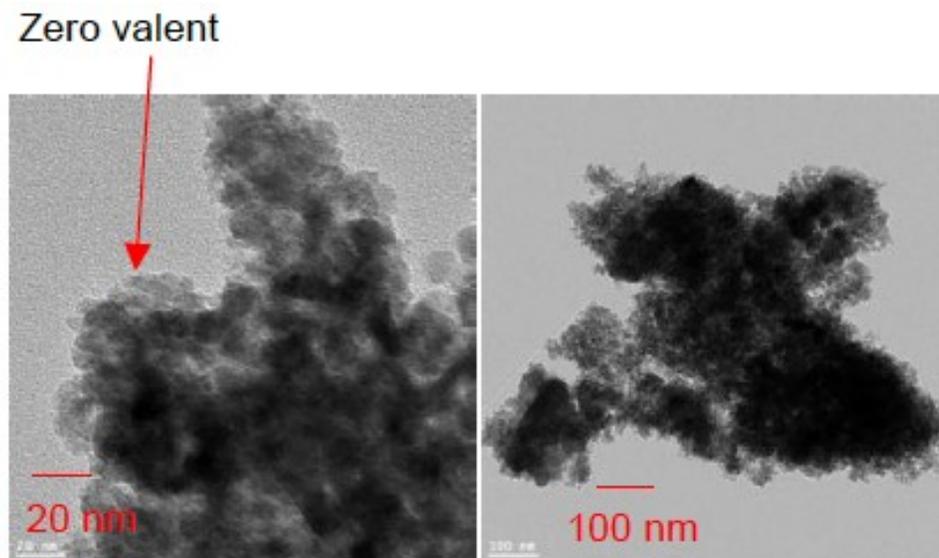


Figure 15. TEM images of Fe/Cu particles with high (left) and low (right) magnification

The elemental distribution of Fe/Cu nanoparticles (Figure 16) indicated the high content of Fe and Cu in the nanoparticle. Moreover, the distribution of Fe (~70%) was higher than Cu (~30%) in the nanoparticle composition.

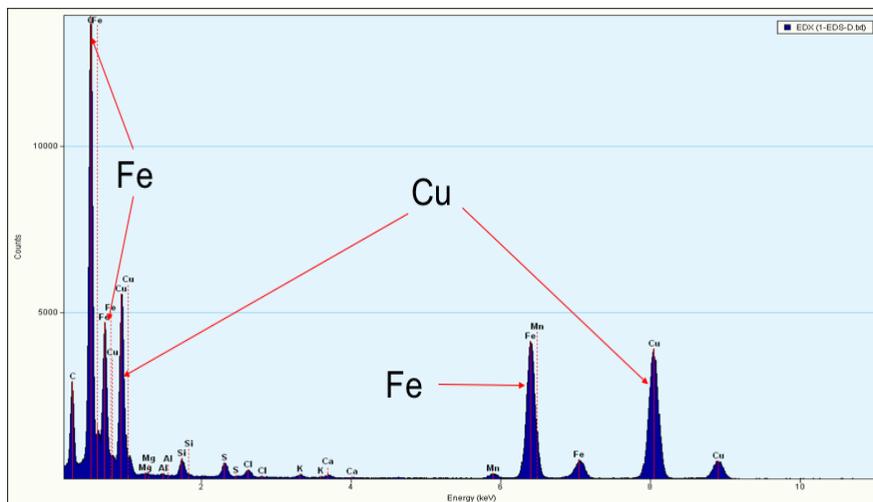


Figure 16. Elemental distribution of Fe/Cu nanoparticles

4.2.3. X-ray diffraction of Fe/Cu particles

The XRD peaks of synthesized bimetallic Fe/Cu nanoparticles are shown in Figure 17. An observation of diffraction peak observed at 44.6 of the 2θ range was equivalent to the diffraction of iron (110) and diffraction of copper (111). Moreover, iron oxide (Fe_3O_4) was confirmed by peaks at 29.2, 35.6, 43.3, 62.9 of the 2θ range (Babae et al., 2018; Sang et al., 2021). Meanwhile, copper oxide (CuO) on the grid surface was confirmed by the diffraction peaks at 34.4, 39.1, and 74.1 of the 2θ range. The presence of Fe_3O_4 and CuO was due to the oxidation of Fe and Cu, respectively.

Furthermore, the amount of Fe_3O_4 in the nanoparticle was higher than CuO , which indicated the thick layer of Fe_3O_4 and the thin layer of CuO . These XRD results suggested a Fe/Cu structure, whereas the Fe atoms were presumably embedded within the Cu matrix.

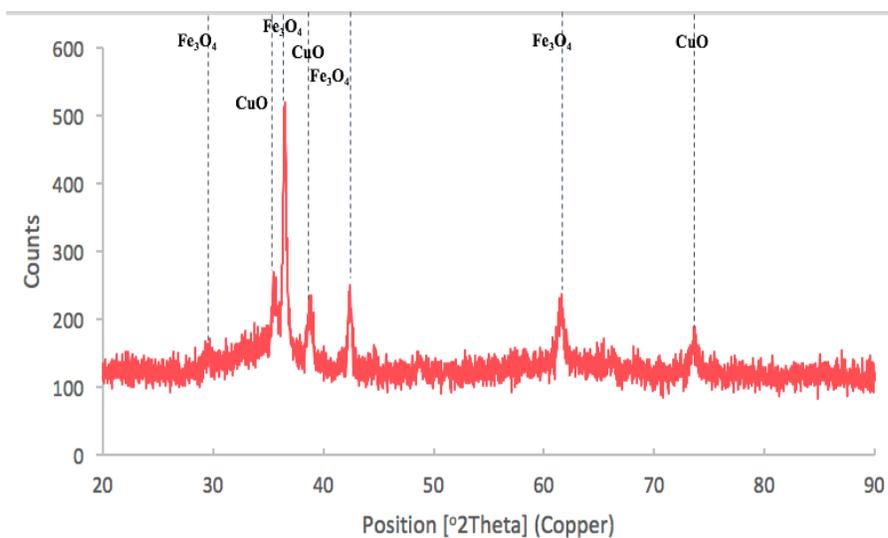


Figure 17. XRD analysis of Fe/Cu nanoparticles

This kind of structure was typical for the one-step synthesis of bimetallic nanoparticles. These results were similar to previous articles (Morales-Luckie et al., 2008; Babae et al., 2018; Tabrizian et al., 2019).

4.3. Critical micelle concentration value of surfactants

The CMC values of four surfactants were determined by the change in water surface tension and interfacial tension values in the presence of the surfactant at different concentrations. The presence of surfactants decreased the surface tension. This result was due to the accumulation of

the hydrophilic groups of the surfactant that might form a monolayer at the interface, which made water have sufficient affinity and reduced the free energy to deliver nonpolar groups into the aqueous solution. The lower the surfactant concentration, the higher surface tension (Figure 18).

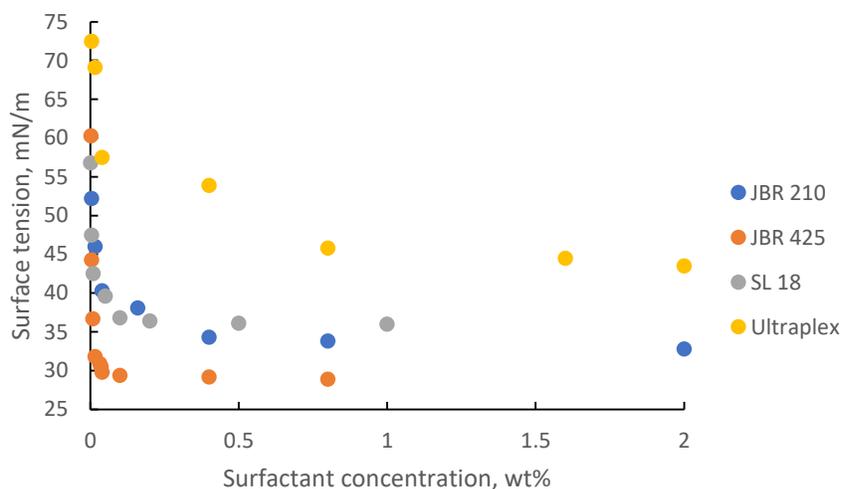


Figure 18. Surface tension of four surfactants at various concentrations

For the rhamnolipid biosurfactant JBR 210, the surface tension dropped linearly with the increase of surfactant concentration until 0.4 wt% (or 40 mg/L). Therefore, the CMC value of JBR 210 was 0.4 wt% (or 40 mg/L). Similarly, the CMC values of rhamnolipid biosurfactant JBR 425, sophorolipid biosurfactant SL 18, and nonionic surfactant Ultraplex were found to be 0.04 wt% (or 32 mg/L), 0.1 wt% (or 35 mg/L), and 0.8 wt% (or 28 mg/L), respectively. These results are similar to previous studies (Mulligan et al., 2019; Vu et al., 2015b; Nguyen and Sabatini, 2011). Therefore, the surfactant concentrations higher than these CMC values were suggested for all experiments to ensure the formation of micelles in each solution.

4.4. Change of surfactant CMC with the addition of nanoparticles and soil

After adding nanoparticles or soil to the surfactant solution, the CMC values were determined, and it was found that they increased for all surfactants, which indicates surfactant loss due to the attachment to nanoparticles or adsorption to the soil surface or the soil organic matter (Mulligan et al., 2001; Betancur et al., 2019) (Figure 19).

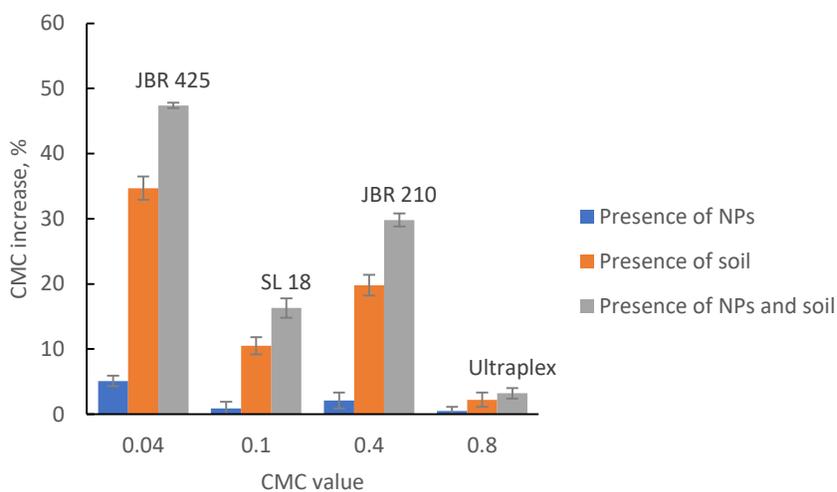


Figure 19. Increase of surfactant CMC in the presence of nanoparticles and soil

The increase in CMC value of a surfactant caused by the presence of soil was more significant than for the nanoparticles, which implied the higher sorption of surfactant to soil than attachment to the nanoparticles. In the presence of both soil and nanoparticles, the increase of CMC was higher due to the synergetic effect between free surfactant molecules in the bulk phase and soil and nanoparticles (Betancur et al., 2019). In particular, the CMC increase of JBR 425 was highest while the CMC increase of Ultraplex was lowest, which could be demonstrated by the lower adsorption

of the nonionic Ultraplex surfactant to soil (Mulligan et al., 2001; Doong and Lei, 2003; Kuyukina et al., 2005).

With the addition of biosurfactants, the absolute zeta potential values at the CMC of all surfactants increased in comparison to the zeta potentials of the control sample containing nanoparticles and DI water (Table 7).

Table 7. Change in absolute zeta potential value after adding surfactant

Surfactant	Absolute zeta potential of only nanoparticles, mV	Absolute zeta potential after adding 10 ml surfactant, mV
JBR 210	10.5	21.9
JBR 425	10.5	23.3
SL 18	10.5	16.7
Ultraplex	10.5	14.4

This result could be explained by the desirable aggregation of pristine nanoparticles or the establishment of Fe-O oxidation particles due to the reaction of Fe⁰ with media (Sang et al., 2021). Simultaneously, the presence of surfactants might increase the electrostatic double-layer repulsion and osmotic repulsion, which prevented the aggregation of nanoparticles in the media (Zhao et al., 2016). In summary, the results showed that the addition of biosurfactants enhanced the stability of the colloidal system, which was similar to the results in a previous study (Yekeen et al., 2020).

4.5. Batch experiments

4.5.1. Effect of shaking speed

Shaking speed may influence the contact between surfactants, nanoparticles, and soil. As shown in Figure 20, the oil treatment efficiency was higher with the increase of shaking speed. As the shaking speed increased, more surface area of the contaminated soil was exposed to the suspension, leading to higher treatment efficiency. However, a too high shaking speed might produce a high energy of flush water to the treatment process, causing more oil dispersion by the suspension that increased the oil concentration in the surrounding water (Bi et al., 2020). At 60 rpm, the oil treatment efficiency was about 51%, which did not increase substantially with a higher shaking speed. In addition, soil and suspension were mixed well at 60 rpm, and thus the impact of dynamic physical mixing on oil treatment was negligible. Therefore, 60 rpm was selected for other batch experiments to achieve good mixing and minimize electricity cost for the shaking process.

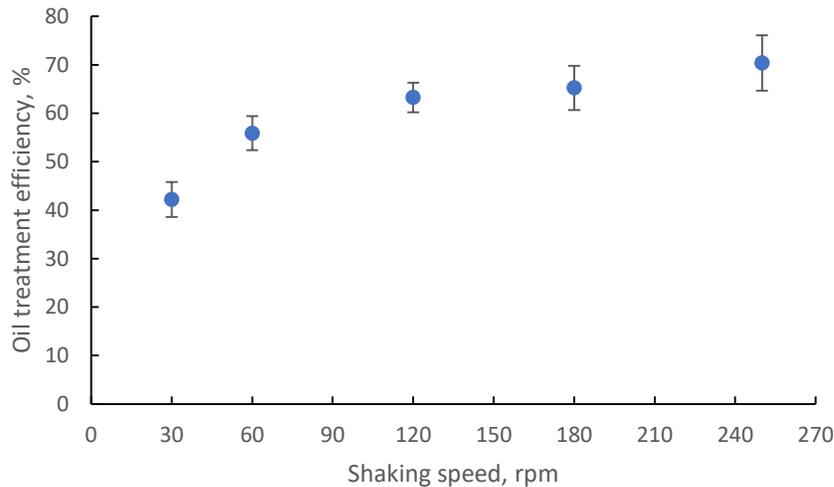


Figure 20. Effect of shaking speed on the oil treatment efficiency

4.5.2. Effect of shaking time

The influence of shaking time was conducted in the tests with the same SNR and at 60 rpm (Figure 21). The oil treatment efficiency increased with the shaking time changed from 5 min (14%) to 60 min (63%). After that, no significant change in oil treatment was observed. At longer shaking times, more energy is required, which would result in a higher operating cost. Hence, a 60-min shaking time was used for the subsequent batch experiments.

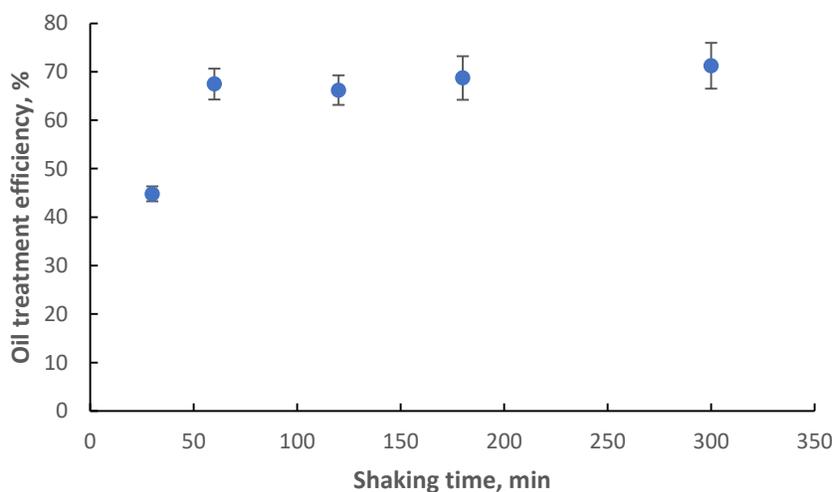


Figure 21. Effect of shaking time on the oil treatment efficiency

By observing the change in oil concentration up to 60 min shaking time, the kinetics of the treatment process were determined (Figure 22).

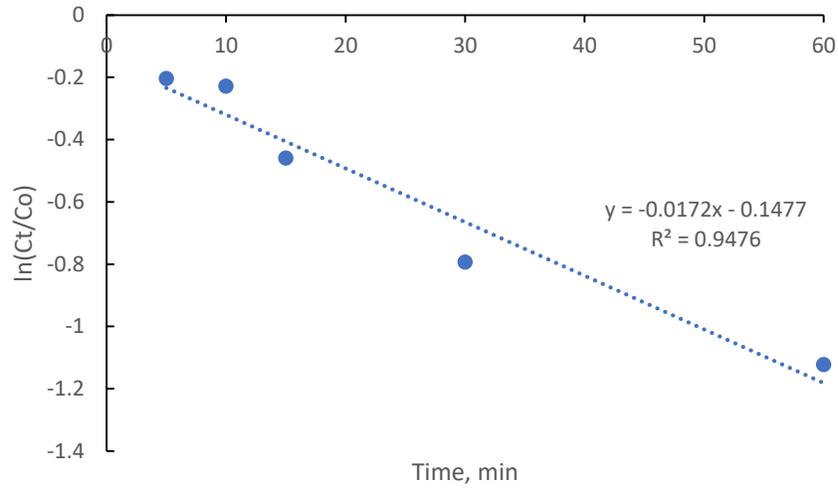


Figure 22. Kinetics of oil treatment over time

The result indicates that oil treatment followed the first-order reaction with respect to oil concentration. In other words, the reduction of oil concentration could be expressed as a pseudo-first-order reaction with respect to oil concentration as given by:

$$\frac{dC_t}{dt} = -k * C_t, \text{ or } \ln\left(\frac{C_t}{C_o}\right) = -k * t \quad (14)$$

where: C_t is the oil concentration at time t , %

C_o is the initial oil concentration, %

t is the reaction time, min

k is the observed rate constant, min^{-1}

For this specific experimental condition, k was calculated as 0.0172 min^{-1} .

4.5.3. Effect of surfactant concentration

The surfactant concentration played a vital role in the oil treatment process from the soil. To investigate the effectiveness of surfactant/nanoparticle suspension, different surfactant concentrations were used in batch experiments under the same conditions. The results showed that the higher surfactant concentration would lead to higher oil treatment efficiency (Figure 23). This result was comparable to previous studies, where high surfactant concentrations were used for soil and groundwater in-situ remediation (Crane and Scott, 2012; Zhao et al., 2016). If the surfactant concentrations were higher than these values, the oil treatment efficiency did not increase further.

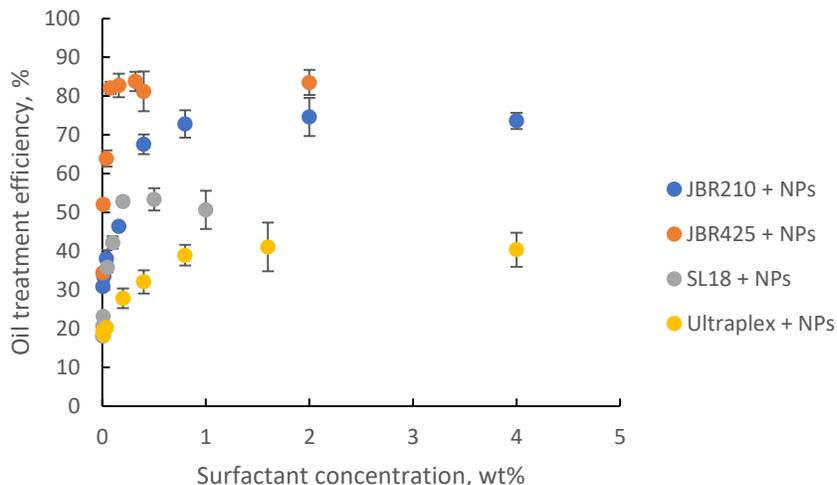


Figure 23. Effect of surfactant concentration on oil treatment efficiency

Moreover, rhamnolipid biosurfactant demonstrated a higher remediation efficiency than sophorolipid biosurfactant and nonionic Ultraplex surfactant. This result could be explained as rhamnolipid might enhance the solubilization of petroleum hydrocarbons more significantly than sophorolipid and Ultraplex, leading to a higher remediation rate (Lai et al., 2009; Mulligan, 2021). In addition, sophorolipid could increase the dispersion of oil that reduced the surface and

interfacial tension of petroleum hydrocarbons in soil (Saborimanesh and Mulligan, 2018). Among the two types of rhamnolipid biosurfactants, JBR 425 displayed a higher remediation performance than JBR 210. It was due to the higher adsorption to the soil surface or higher attachment to nanoparticles by JBR 425 (Figure 19), leading to greater treatment performance. These results suggested the potential for using rhamnolipid biosurfactants and nanoparticle suspension as a promising and effective way for remediation of oil-contaminated soils.

4.5.4. Effect of nanoparticle dosage

Nanoparticle dosage might substantially affect the oil treatment efficiency. As shown in Figure 24, the oil removal percentage of 3.2 g soil increased quickly as the biosurfactant: nanoparticle ratio increased from 30:1 to 10:1 (wt%: wt%). In particular, a higher nanoparticle amount might increase contact between oil molecules and active sites on the nanoparticle surface, whereby oil would be adsorbed on the nanoparticle surface or reduced to less toxic or nontoxic compounds, such as CO₂ and H₂O, by the ROS formed by the Fenton reaction (Murgueitio et al., 2018). The production of ROS by biosurfactant/nanoparticle suspension under sonication was confirmed via the decrease of pCBA, a ROS probe compound (Chen and Jafvert, 2010). After that, the treatment efficiency was stable with a higher nanoparticle dosage in suspension.

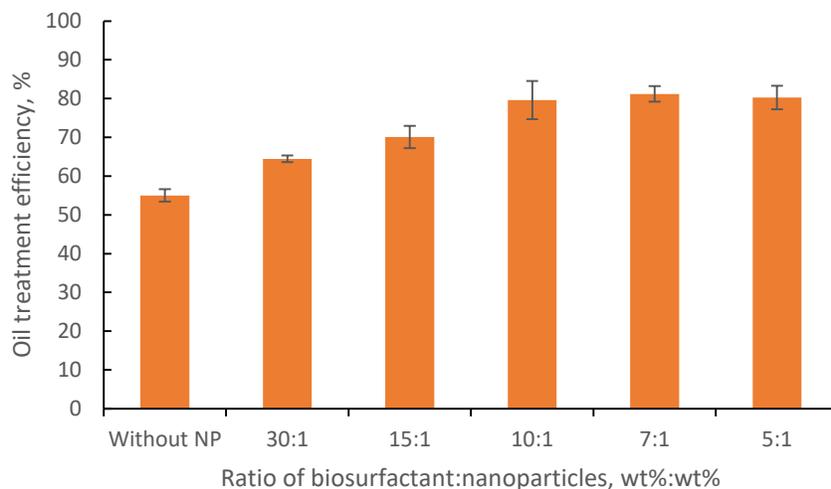


Figure 24. Effect of nanoparticle dosage on the oil treatment efficiency

If the nanoparticle dosage was too high, more nanoparticles would settle to the bottom of the tube, which would decrease the colloidal stability of biosurfactant/nanoparticle suspension, resulting in lower treatment efficiency. Therefore, the biosurfactant: nanoparticle ratio of 10:1 (wt%: wt%) was selected as the optimal dosage for the following experiments.

4.5.5. *Effect of soil amount*

The weight-to-volume ratio of soil and biosurfactant/nanoparticle suspension was explored to test the effect of soil amount on the oil treatment efficiency. Under the fixed amount of JBR 425 rhamnolipid biosurfactants and Fe/Cu nanoparticles, or biosurfactant: nanoparticle ratio of 10:1 (wt%: wt%), various amounts of contaminated soil were evaluated.

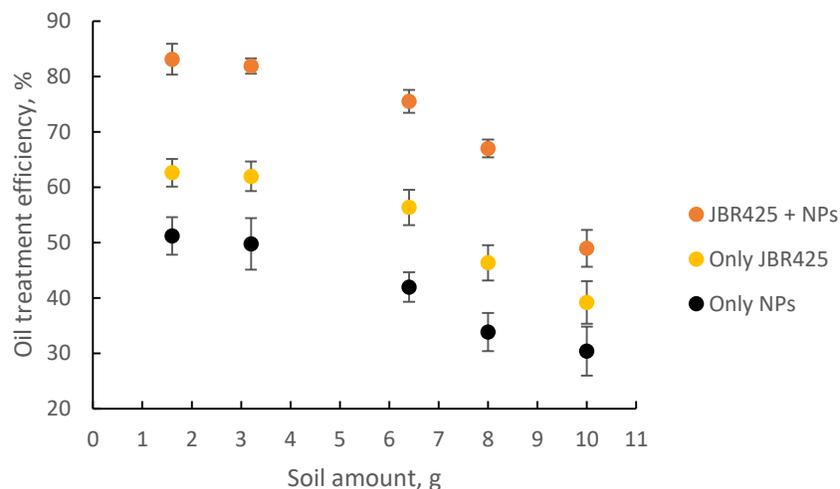


Figure 25. Effect of soil amount on the oil treatment efficiency

As shown in Figure 25, when the soil dosage increased from 1.6 g to 3.2 g, the oil treatment efficiency was nearly the same for both biosurfactants. After that, the soil remediation rate decreased with the increase in the amount of soil. The presence of soil may adsorb biosurfactants, proven by the decreased concentration of biosurfactants in the FTIR analysis of soil before and after adding biosurfactant/nanoparticle suspension. In addition, the interaction of biosurfactant, nanoparticles, and soil was also confirmed by the functional groups in the FTIR analysis (Figure 19).

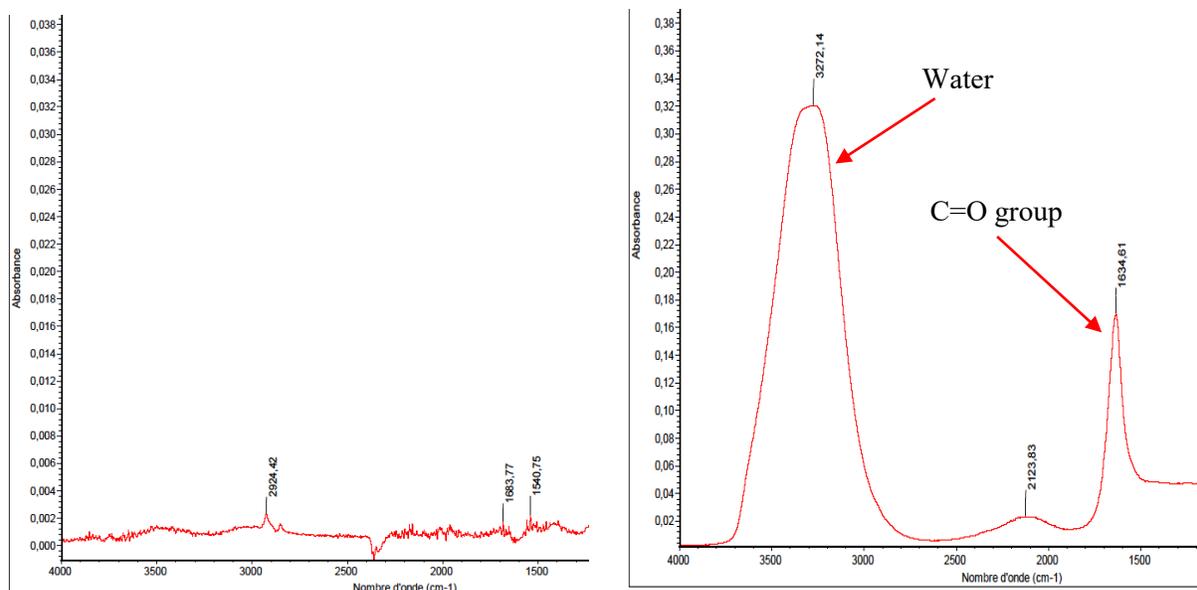


Figure 26. FTIR analysis of soil before (left) and after (right) adding biosurfactant/nanoparticle suspension

The addition of biosurfactant/nanoparticle suspension would form bonds with the functional groups of soil particles. Therefore, more biosurfactant was adsorbed or attached to the soil surface at higher soil dosages, which reduced the total of micelles in the mixture, resulting in lower oil treatment efficiency. In addition, a significant amount of soil might decrease the oil desorption and oil accumulation in the micelles (Xinhong et al., 2017), leading to a lower removal. In summary, for 10 mL biosurfactant and 2 mg nanoparticles, 3.2 g soil showed the most effective remediation percentage.

The oil treatment efficiency by biosurfactant/nanoparticle suspension in this study is compared with other nanoparticle-based or surfactant-based methods (Table 8).

Table 8. Comparison of the oil treatment efficiency with other methods

Method	Material	Initial oil concentration, mg/kg	Oil treatment efficiency, %	References
Soil washing	Pressurized water-jet	65,756	97	Kang et al., 2012
Soil washing	Surfactant (Tween 80 and SDS)	3,970-25,835	80	Zhang et al., 2022
Soil extraction	Hexane-acetone mixture	98,000	97	Li et al., 2012
Chemical oxidation	Na ₂ S ₂ O ₈ , KMnO ₄ , H ₂ O ₂	4,000	48%-93 (after 120 days)	Chen et al., 2015
Adsorption	Granular Activated Carbon (GAC)	5,400	50-99	Kalmykova et al., 2014
Supercritical fluid extraction	Acetone-CO ₂	20,000	70-100	Morselli et al., 1999
Encapsulation	Reactive silicate and emulsifier	N/A	85-99.7	Wami et al., 2015
Bioaugmentation	Autochthonous filamentous fungi	10,200	79.7 (after 60 days)	Covino et al., 2015

Bioventing	Brewery waste amendment and bioventing	~10,000	61.7-91.5 (after 28 days)	Agarry et al., 2015
Bioventing	Oxygen	40,000	85(after 60 days)	Thome et al., 2014
Biosparging	Oxygen and nutrient	~7,000 µg/L	70 (after 10 months)	Kao et al., 2008
Bioslurry	Microbial consortia of <i>Bacillus cereus</i> and <i>Pseudomonas putida</i>	~120 mg/L	79.4-99.7 (after 49 days)	Tuhuloula et al., 2018
Composting	Aerobic soil microorganisms	380,000	99 (after 19 months)	Atagana, 2008
Windrows	Aerobic microbes	15	60 (after 8 months)	Al-Daher et al., 1998
Mycoremediation	<i>Pleurotus pulmonarius</i> fungi	944-2278	68.34 (after 62 days)	Njoku et al., 2016
Bioremediation	<i>Rhodococcus</i> biosurfactant	100,000	65-82 (after 3 hours)	Kuyukina et al., 2005

Bioremediation	Organic solvent/surfactant system	167,000	97 (after 30 minutes)	Wang et al., 2019
This study	Rhamnolipid biosurfactant and Fe/Cu nanoparticle	3722	75-84 (after 60 minutes)	Vu and Mulligan, 2022a

*N/A: not available

Based on the data in Table 8, the oil treatment efficiency in this research (75-84% after 1 hour) is relatively high compared with previous studies. In addition, it takes one hour for the remediation process, which is much shorter than other studies. More studies on the effect of different factors on remediation performance will be conducted.

4.5.6. Effect of pH

The solution pH can influence the surface and interfacial behavior of surfactant solution (Özdemir et al., 2004), which could alter the CMC value and the formation of micelles (Mańko et al., 2014), resulting in an effect on the oil treatment efficiency. Besides, pH affected ROS generation via the Fenton reaction by nZVI under sonication, which changed the remediation percentage. The effect of pH on the oil treatment was studied using 10 mL surfactant, 2 mg nanoparticles, and 3.2 g soil at room temperature. The control samples included only DI water.

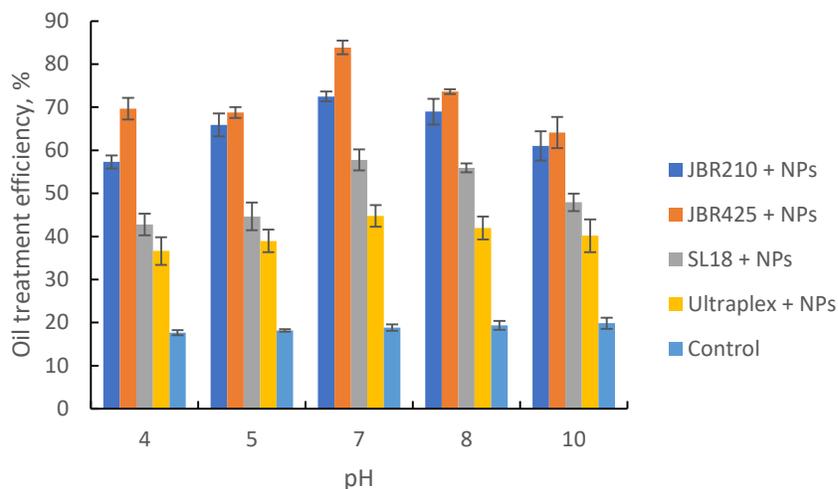


Figure 27. Effect of pH on the oil treatment efficiency

As indicated in Figure 27, the optimal pH for oil treatment was about 7, at which the oil treatment efficiency reached the highest. The reduction of Fe/Cu nanoparticles was more productive for pH near 7 (Yedra et al., 2003). In addition, the attachment of JBR 425 to Fe/Cu nanoparticles was higher than other surfactants (Figure 18), which decreased their adsorption to soil and enhanced the contact time between JBR 425/nanoparticles and oil pollutants, resulting in a greater oil removal performance. Therefore, JBR 425 biosurfactant-stabilized nanoparticles showed the highest oil treatment efficiency at pH 7.

4.5.7. Effect of temperature

Temperature contributed a vital role to the oil treatment efficiency as it might influence the oil viscosity, solubility, and transport in porous media (Das and Chandran, 2011; Bi et al., 2020). Moreover, it was one of the critical parameters representing the various environmental conditions,

which would affect the broad application of the treatment system, especially for field operation. The effect of temperature on the oil treatment performance by surfactant/nanoparticle suspension was evaluated in the range of 5-45°C and pH 7.

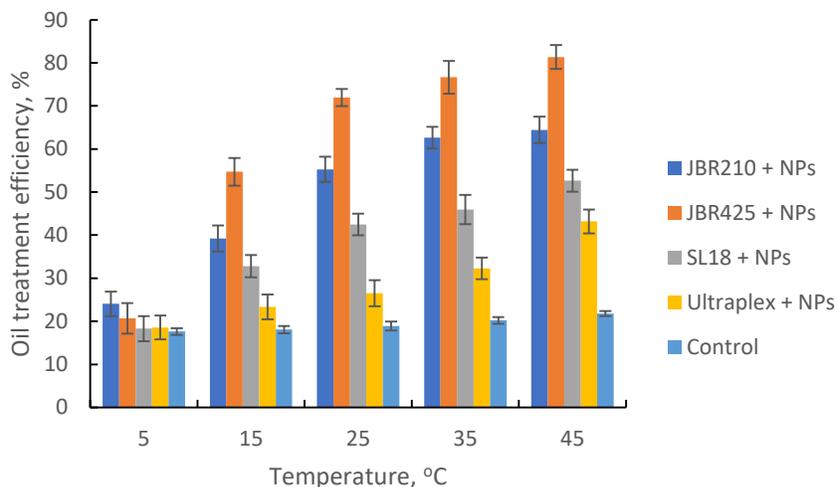


Figure 28. Effect of temperature on the oil treatment efficiency

It is evident in Figure 28 that the soil remediation efficiency was improved with the increase in temperature. In particular, the oil treatment efficiency linearly increased from 5°C to 25°C and slightly changed from 25°C to 45°C for rhamnolipid biosurfactant. In other words, the maximal oil treatment efficiency was recorded at 45°C. The high temperature might influence the oil mobilization by the biosurfactant, water saturation of dry soil, oil and surfactant penetration/activity through contaminated soil (Kuyukina et al., 2005), which could decrease the interfacial tension of oil, resulting in a higher amount of oil removal (Koran et al., 2008). In addition, the oil viscosity might be reduced while the volatility of low molecular weight petroleum hydrocarbons could be increased at high temperature (Atlas, 1975), which increased the mobility

of oil molecules in soil, weakened the oil adhesion, and made them more accessible for desorption by the surfactant solution. (Bi et al., 2020). The high temperature increased the micelle diameter and micelle core volume, which improved the solubilization of oil components and enhanced the oil amount dissolved in the micellar phase. Moreover, the increase in the diffusion rate of oil molecules and Brownian movement of solvent components and the decrease in van der Waals interaction forces between oil and soil particles were also indicated at high temperatures (Wang et al., 2019). As a result, the oil removal was enhanced at high temperatures. Based on the experimental data, 25°C should be the optimal temperature for the oil removal process. This result is comparable to previous studies, where a rhamnolipid biosurfactant was used at a temperature of about 23.5°C for soil remediation (Olasanmi and Thring, 2020).

In summary, the optimum operating parameters for the batch experiment included shaking speed of 60 rpm for 60 min, biosurfactant: nanoparticle ratio of 10:1 (wt%: wt%), pH 7, and temperature of 25°C (or room temperature). These operating parameters would be used for all batch experiments.

4.5.8. Effect of order of chemical addition

The influence of chemical order was carried out in four experiment sets (Figure 29). In the first set, oil-contaminated soil was mixed with particles in the tube, and the surfactant was added to the mixture. In the second set, oil-contaminated soil was mixed with the surfactant, and particles were added to the mixture. In the third set, particles and the surfactant were mixed in the tube, and oil-contaminated soil was added to the mixture. In the fourth set, oil-contaminated soil and particles and surfactant were mixed at the same time in the tube.

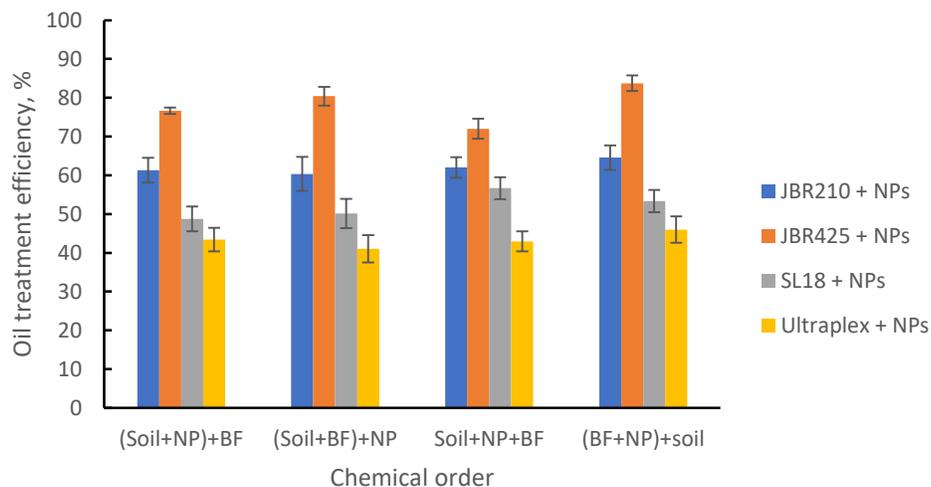


Figure 29. Effect of chemical order on the oil treatment efficiency

Among the four sets of chemical order, adding soil to the mixture of surfactant and nanoparticles showed a slightly higher oil treatment efficiency. During the sonication of surfactant/nanoparticle suspension, ROS, such as HO^* and HO_2^* , were formed due to the Fenton reactions, which was determined by the reduction of the ROS probe compound (pCBA) (Chen and Jafvert, 2010). Therefore, oil pollutants were degraded by these ROS after adding contaminated oil to the suspension (Joo et al., 2008; Murgueitio et al., 2018). Meanwhile, sonication of soil with nanoparticles or surfactants did not produce ROS. Hence, the order of (soil + nanoparticle) + biosurfactant and (soil + biosurfactant) + nanoparticle showed a lower treatment efficiency than the order of (biosurfactant + nanoparticle) + soil. In the case of adding soil, nanoparticle, and biosurfactant at the same time, the soil did not distribute evenly due to the presence of competitive nanoparticles in the solution, resulting in slightly lower treatment efficiency. However, the difference in treatment efficiency is not significant.

4.5.9. Effect of particle size

New Fe/Cu particles were prepared by a slow method (Morales-Luckie et al., 2008) with an average particle size of about 200 nm (Malvern Zetasizer Nano ZS, USA). The effect of particle size was measured by comparing 20 nm Fe/Cu particles (old particles) with 200 nm Fe/Cu particles (new particles) at the same experimental conditions.

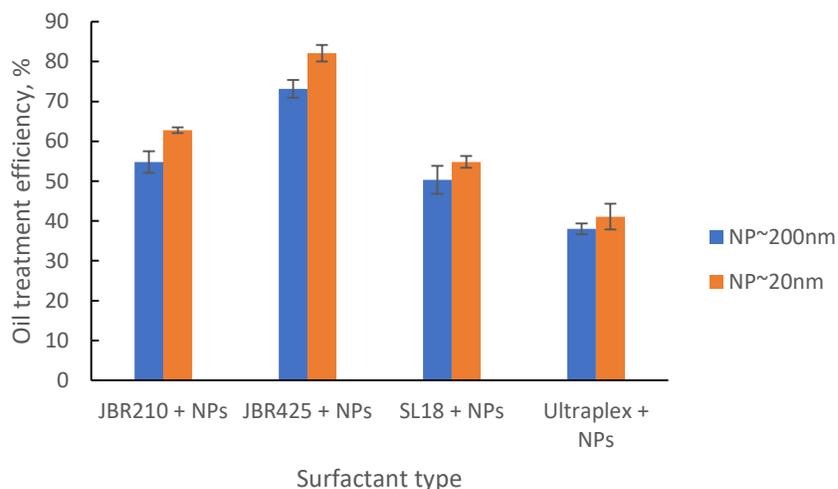


Figure 30. Effect of particle size on the oil treatment efficiency

As presented in Figure 30, the treatment by 20 nm particles is somewhat higher than 200 nm particles. For JBR 425, the oil treatment efficiency by 20 nm Fe/Cu particles was about 9% higher than 200 nm Fe/Cu particles. This result could be explained by the larger specific surface area of 20 nm Fe/Cu particles, which promoted the interaction of petroleum hydrocarbons and nanoparticles in the mixture, leading to a higher remediation rate (Chang et al., 2007). However,

the different remediation rate was only significant for JBR 210 and JBR 425 rhamnolipid biosurfactants.

4.5.10. Effect of ionic strength

In a surfactant and nanoparticle-containing aqueous solution, ionic strength plays a vital role in the effectiveness of surfactants. The influence of ionic strength was carried out by adding NaCl and CaCl₂, two of the most common cations in soil, to the mixture containing biosurfactants, nanoparticles, and contaminated soil (Figure 30). In particular, 0.001-0.1 mol.L⁻¹ of NaCl and CaCl₂, representing the concentration of cations in soil, were separately added to the biosurfactant/nanoparticle mixture (Enyoh and Isiuku, 2020). The presence of these inorganic salts can weaken the electrostatic repulsions between biosurfactant molecules and increase the biosurfactant viscosity, which may decrease the CMC value of the system. As a result, the affinity between micelles and oil molecules is improved, resulting in greater solubilization and desorption of oil from the contaminated soil (Wang et al., 2019). In this study, different amounts of salt concentration were used, whereas neither biosurfactant nor nanoparticle was present in the control sample.

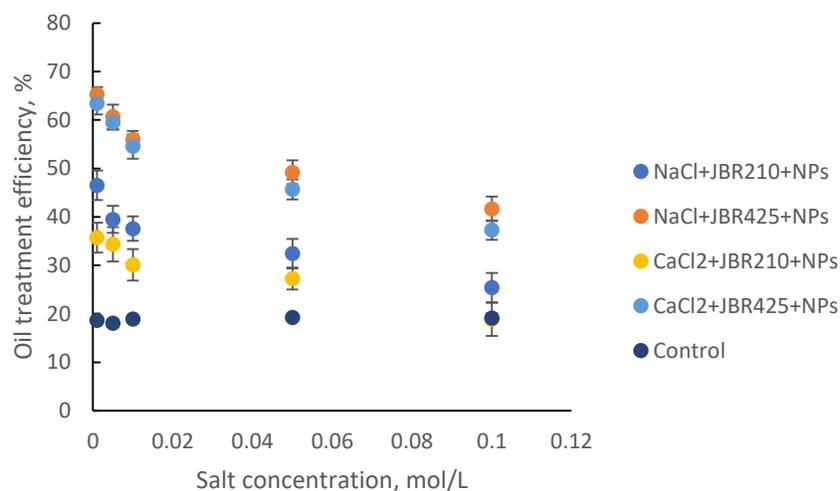


Figure 31. Effect of ionic strength on the oil treatment efficiency

The oil treatment efficiency was about 19% in all control samples (Figure 31). For surfactant and nanoparticle-containing samples, the higher salt concentration lowered oil treatment efficiency. The high salt concentration or high ionic strength created more competitive factors in the mixture, together with the reduction of CMC value of the hybrid system, which could prevent the oil desorption from the soil, leading to a lower remediation rate (Bi et al., 2020). In particular, the presence of inorganic salts might cause chemical bonds between Na^+ and Ca^{2+} ions and surfactant headgroups, which inhibited the contact of oil components and surfactant molecules, resulting in a lower oil treatment efficiency (Wang et al., 2019). Moreover, the addition of salt concentration made the electrical double layer, which related to the oil adsorption on salt ions, at the surfactant monolayer interface more compressed, resulting in delaying the surfactant molecules movement at the interface and reducing the oil treatment efficiency (Eicke and Meier, 1996).

In addition, the influence of CaCl_2 on the oil treatment efficiency is different from NaCl . Instead of causing a more substantial reduction of electrostatic repulsion between ionic headgroups

than Na^+ , Ca^{2+} ions might significantly contact surfactant molecules, producing more precipitation and consuming more surfactant, resulting in less soil remediation rate (Wang et al., 2019). Moreover, the potentially intense attraction between Ca^{2+} ions and water molecules may cause the hydration of Ca^{2+} by water molecules, making the Ca^{2+} ions likely to stay in an aqueous solution. Due to the interaction of solvent and surfactant, the surfactant concentration will be decreased, which will reduce the solubilization of oil compounds, resulting in lower oil treatment efficiency (Yekeen et al., 2017). In addition, Ca^{2+} can also influence the double layer differently than the monovalent Na^+ , leading to the difference in the oil treatment efficiency (Wang et al., 2019).

4.5.11. Effect of surfactant combinations

Based on previous results, rhamnolipid biosurfactant JBR 425 demonstrated the highest oil treatment efficiency. Therefore, it was used as the fixed surfactant in all experiments. Adding one surfactant to another may change the properties of mixed surfactants, such as aggregation number, micellization of the surfactant, and solubilization capacity of the micelle (Nagarajan and Wang, 2000; Wang et al., 2019).

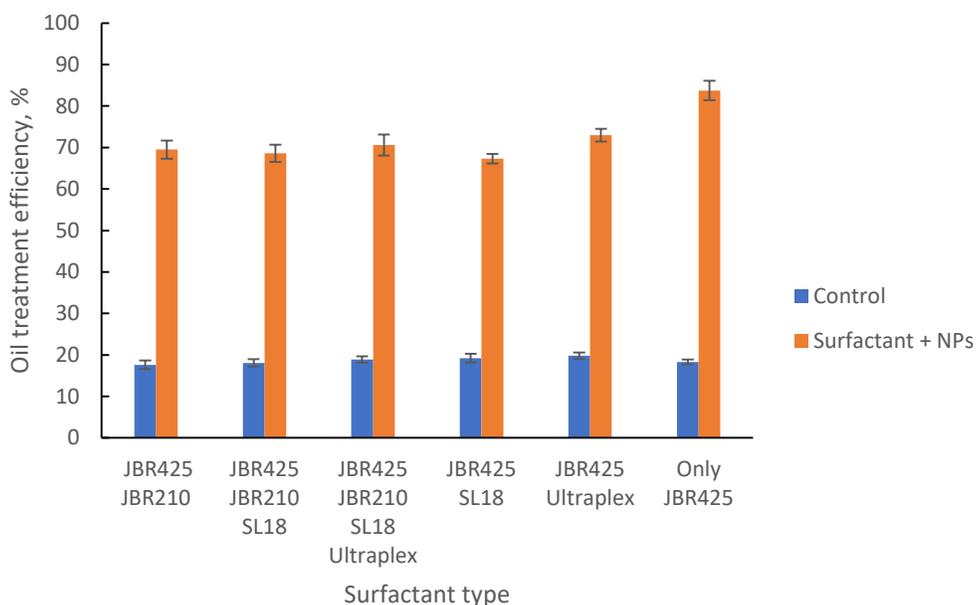


Figure 32. Effect of surfactant mixtures on the oil treatment efficiency

It was found that the hybrid systems decreased the overall oil treatment efficiency by 9-14% compared to using only JBR 425, as indicated in Figure 32. Among different surfactants, the combination of rhamnolipid biosurfactant JBR 425 and nonionic surfactant Ultrplex demonstrated the maximum remediation efficiency, while JBR 425/SL 18 showed the least remediation efficiency. However, the difference in treatment efficiency was not significant. Due to the nonionic characteristic of the Ultrplex surfactant, it can be mixed with an anionic surfactant, such as rhamnolipid or sophorolipid biosurfactant, to have synergistic effects (Rosen and Kunjappu, 2012; Liu et al., 2020). In particular, the micelles formed by JBR425-Ultrplex may weaken the electrostatic and space repulsion compared to the same surfactant type (Zhou and Zhu, 2008), which will reduce the CMC and loss due to adsorption and precipitation (Zhou and Zhu, 2005; Wei et al., 2015). As a result, the JBR425-Ultrplex mixture showed a higher oil treatment efficiency than other mixed surfactant solutions. Simultaneously, mixing the anionic surfactant

with another anionic surfactant is not suitable because of a complementary reaction (Befkadu and Quanyuan, 2018). In addition, SL 18 displayed a lower soil remediation rate than JBR 425 and JBR 210. Therefore, the mixture of SL18/JBR425 demonstrated the lowest soil remediation percentage.

4.5.12. Reuse of nanoparticles

The results from ICP-MS showed that about 90% of Fe and Cu nanoparticles remained in the tube after each experiment. These nanoparticles were reused by adding new surfactants and contaminated soil for a new experiment. The decrease of nanoparticle amount in the tube after each time reuse was found by the FTIR analysis. The oil treatment efficiency by reused nanoparticles is exhibited in Figure 33.

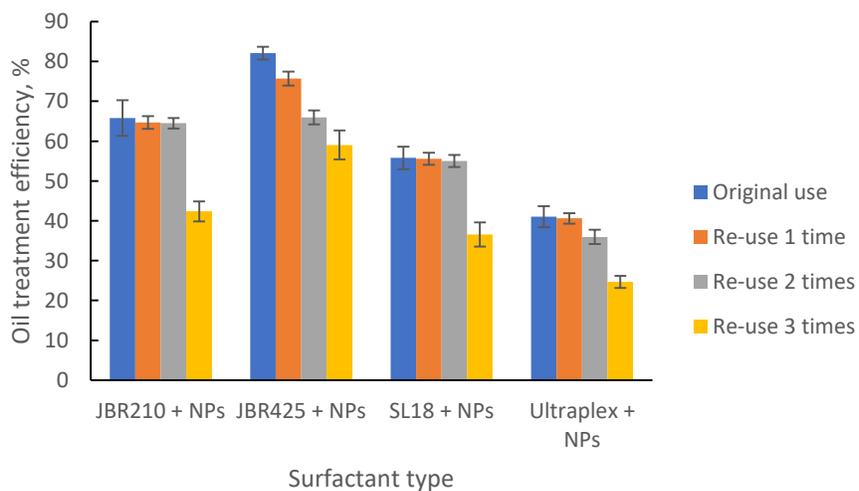


Figure 33. Reuse of nanoparticles for soil remediation

As shown in Figure 33, oil removal by the surfactant/nanoparticle decreased after each reuse time of nanoparticles for all surfactant types. After four cycles, the oil treatment efficiency by the suspension of JBR425 with nanoparticles was 59%. This treatment rate was still higher than the control experiment (~18%), which indicated the effective remediation by the suspension of surfactant/reuse-nanoparticle after three-time reuse. In all samples, rhamnolipid biosurfactant JBR 425 showed the highest remediation performance due to its greatest attachment to reused nanoparticles (Figure3). In addition, its ability to improve the oil solubilization also contributed to the high oil treatment efficiency (Lai et al., 2009; Mulligan, 2021). Therefore, nanoparticles can be effectively reused three times for oil remediation from the soil.

4.6. Column experiments

The column experiments investigated the performance of biosurfactant/nanoparticle suspension to stimulate in-situ remediation of oil-contaminated soil. The maximum operating parameters from the batch experiments include the biosurfactant: nanoparticle: soil ratio of 13:1:4 (volume: volume: mass), pH 7, and room temperature were used in the column experiments.

4.6.1. Foam quality and stability

Rhamnolipid biosurfactant/nanoparticle mixture can produce high foam quality at low biosurfactant and nanoparticle concentrations. The effect of rhamnolipid biosurfactant JBR425 concentration on foam quality and stability at pH 7 was investigated (Figure 34). After about three hours, the foams completely collapsed. In the presence of 1 wt% Fe/Cu nanoparticles, the increase of rhamnolipid concentration from 0.5 vol% to 2 vol% would lead to higher foam stability from

20 min to 33 min, 25 min to 40 min, and 18 min to 35 min at 85%, 95%, and 99% foam quality, respectively. In other words, foam quality influenced the foam stability at different rhamnolipid biosurfactant concentrations. This result was comparable to previous studies, where rhamnolipid biosurfactant JBR425 showed a higher foamability than other commercial surfactants (Mulligan and Wang, 2006; Mulligan and Eftekhari, 2003).

Besides, the raise of foam quality from 85% to 95% and from 95% to 99% leads to the increase and slight decrease of foam stability, respectively. In other words, the foam stability is dependent on the foam quality. At higher foam quality, the larger air portion or bubble size of foam is significant, while the liquid films are smaller. As a result, the capillary flow decreases, and the lamellar film between adjoining bubbles will be collapsed, leading to a higher foam stability (Kornev et al., 1999). However, if the foam quality is too high, the break of large bubbles due to the heterogeneous size distribution of gas bubbles inside a foam will reduce the foam stability. In addition, the liquid film may be charged due to the use of an anionic rhamnolipid biosurfactant. Hence, the overlapping of these similar charged electric double layers can resist liquid film thinning and improve foam stability (Chang, 2016).

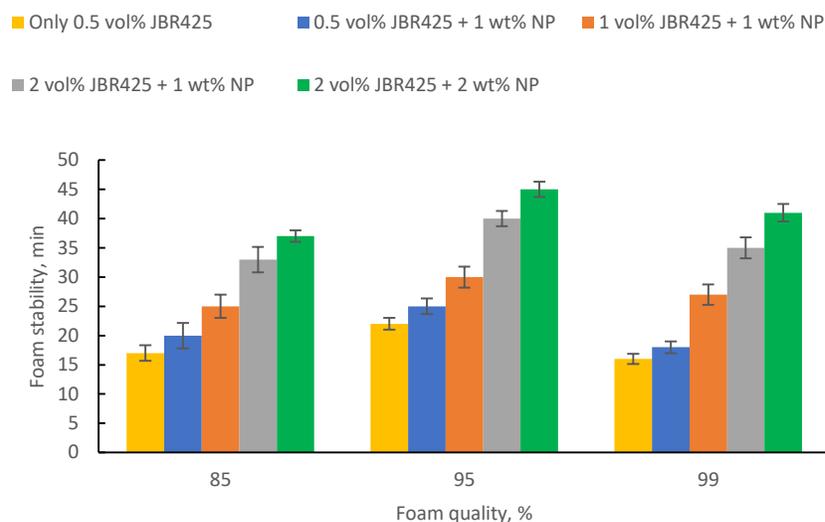


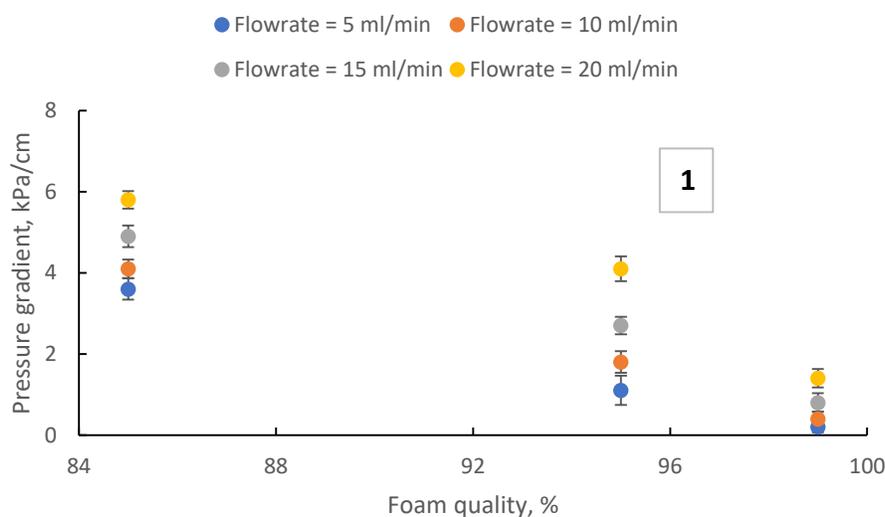
Figure 34. Effect of foam quality and biosurfactant concentration on foam stability

The foam stability observed with only 0.5 vol% rhamnolipid biosurfactant JBR425 was lower than in the presence of nanoparticles at all foam quality values. This result reflects the role of nanoparticles in enhancing foam stability. The accumulation of nanoparticles at the surfactant-water interface may form a thick layer, preventing the coalescence and stabilizing the liquid films in the foam (Binks, 2017). The adsorption of colloidal particles at liquid-liquid interfaces also enhances foam stability by reducing bubble breakage in the porous particle surface (Gonzenbach et al., 2006; Sun et al., 2015). The hydrophobic interaction of rhamnolipid molecules and nanoparticle surface may decrease the surface charge and improve the adsorption of more uncharged particles on the bubble surface, resulting in higher foam stability (Karthick et al., 2019a; Karthick et al., 2019b). The synergistic effect of biosurfactant and nanoparticle also played a vital role in generating high foam stability or strong foam. In particular, the formation of fine bubbles may contribute to a high surface area for the gas-liquid interface to adsorb more nanoparticles on their surface, leading to higher foam stability (Li and Prigiobbe, 2021). Moreover, the mechanism

of foam formation in the presence of nanoparticles and biosurfactant is similar to only biosurfactant, which resembles the previous paper (Li and Prigiobbe, 2020). Besides, the higher nanoparticle dosage improved the foam stability due to the synergistic effect reported in Figure 34 (Li and Prigiobbe, 2021). Nonetheless, too many particles may block the pore space, leading to lower treatment efficiency by the system (Kim et al., 2015). Hence, 1 vol% rhamnolipid and 1 wt% nanoparticles were selected for future experiments.

4.6.2. Evaluation of pressure gradient in the soil column

The pressure change in the soil column due to the biosurfactant foam/nanoparticle mixture at various conditions was measured (Figure 35). The pressure gradient change in the soil column depends on the flowrate, foam quality, and biosurfactant concentration. In particular, pressure gradient increased with the increase of flowrate and biosurfactant concentration and reduction of foam quality. During the continuous flow, tiny bubbles with thin films created by low foam quality are hard to be broken down when moving through the soil layer, leading to high pressure gradients.



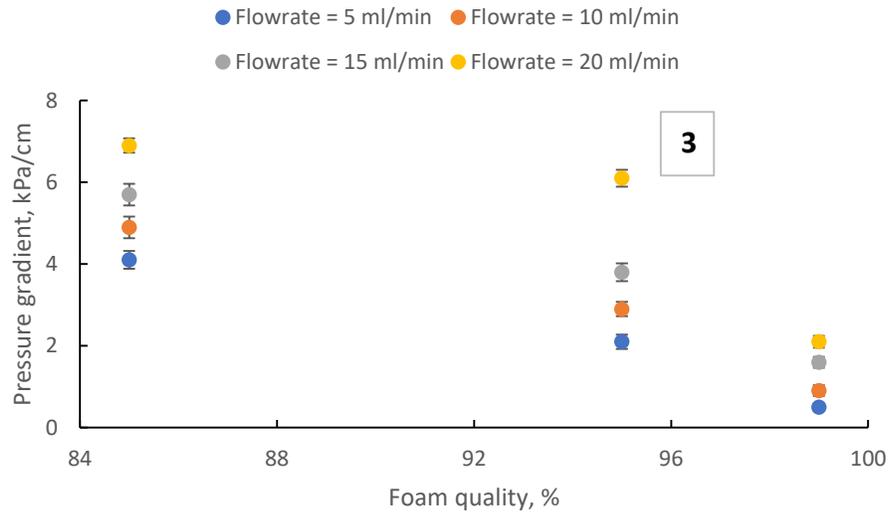
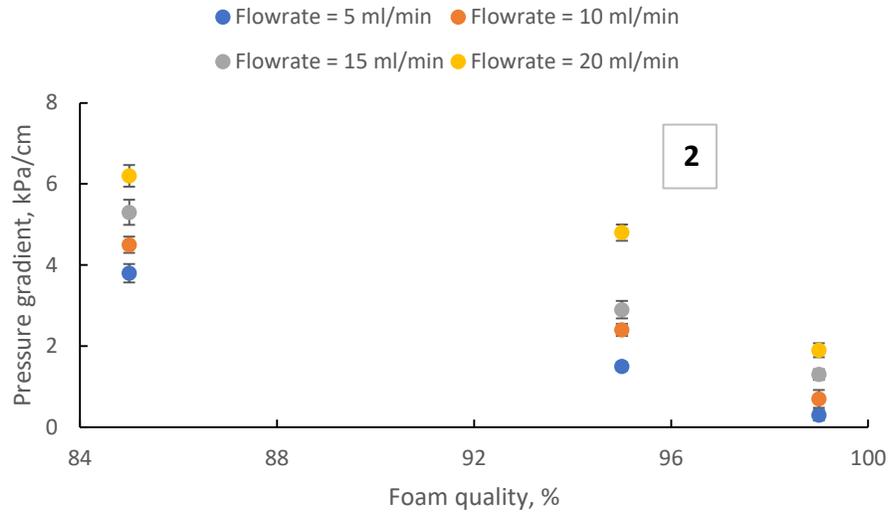


Figure 35. Effect of flowrate, foam quality, and biosurfactant concentration on pressure gradient (1: 0.5 vol% biosurfactant; 2: 1 vol% biosurfactant; 3: 2 vol% biosurfactant)

In addition, a high biosurfactant concentration may form more viscous emulsions or disperse fine materials in the soil column, which can cause column plugging and improve the pressure gradient (Wang and Mulligan, 2004). However, the effect of biosurfactant concentration on the

pressure gradient is not significant (Figure 35). Meanwhile, an increase in flowrate reduced the effective viscosity of foam, resulting in a high-pressure gradient (Chowdiah et al., 1998). These results indicated that a low biosurfactant concentration at a small flowrate might create a high-quality foam, maintaining a low-pressure gradient in the soil column. Therefore, 1 vol% rhamnolipid biosurfactant and 10 ml/min flowrate were used for other experiments to decrease the pressure gradient while maintaining good foam quality and stability. Moreover, a small flowrate would reduce the energy consumption, which is beneficial for the system to apply at large field scale.

Besides, the increase of foam quality led to the decrease of hydraulic conductivity. In particular, the hydraulic conductivity for 85%, 95%, and 99% foam quality was 6.7×10^{-4} , 1.3×10^{-4} , and 0.4×10^{-4} cm/s, respectively. In addition, these values are lower than the hydraulic conductivity of contaminated soil (9.7×10^{-3} cm/s). These results are similar to previous studies (Karthick et al., 2019b; Zheng and Jang, 2016; Mulligan and Wang, 2006; Wang and Mulligan, 2004).

4.6.3. Effect of flowrate

Flowrate is one of the most critical factors affecting treatment efficiency. In this experiment, the effect of flowrate was examined on the treatment efficiency (Figure 36). In general, the increase of flowrate decreased the oil treatment efficiency in all samples. In particular, the highest oil treatment efficiency was obtained at the flowrate less than 10 mL/min after 20 pore volumes of injection of the biosurfactant foam/nanoparticle foam mixture into the column. The same results were also achieved for the solution containing biosurfactant/nanoparticle suspension, only JBR425 biosurfactant and only nanoparticles, while the removal performance by DI water was the same

under different flowrates. At the flowrate of less than 10 mL/min, the contact time between contaminated soil and solution was sufficient for the treatment process, resulting in the high treatment efficiency. Conversely, if the flowrate is greater than 10 mL/min, the contact time will be shorter, lowering the remediation performance. Therefore, 10 mL/min was selected as the optimal flowrate for the next column experiments.

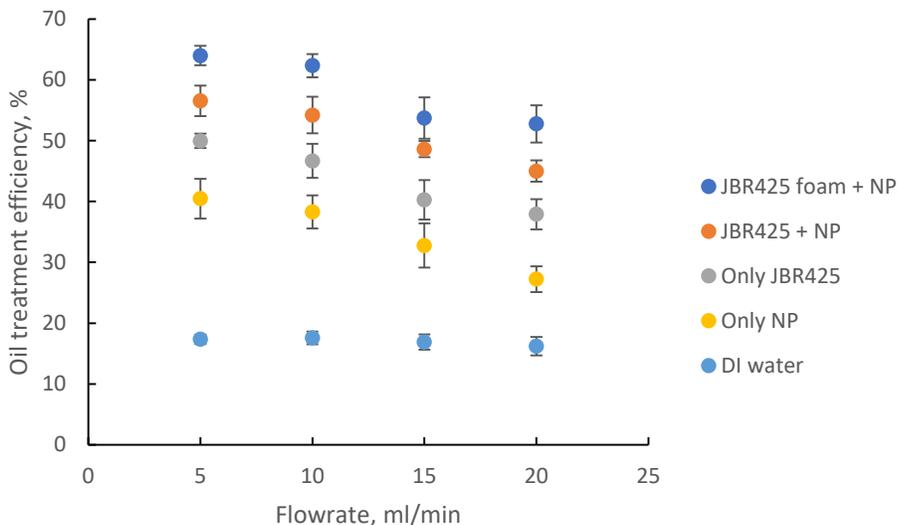


Figure 36. Effect of flowrate on the oil treatment efficiency in a column

Based on these results, the correlation coefficient for each condition was calculated (Table 9).

Table 9. Correlation coefficient of flowrate and treatment efficiency

Condition	Correlation coefficient
JBR425 foam + nanoparticle	-0.97
JBR425 + nanoparticle	-0.99
Only JBR425	-0.95
Only nanoparticle	-0.95

DI water	-0.89
----------	-------

From Table 9, the correlation coefficient by each experimental condition was high. In other words, four experimental solutions showed a strong correlation between flowrate and oil treatment efficiency. Moreover, the presence of nanoparticle made the correlation stronger, whereas the mixture of JBR425 and nanoparticles demonstrated the higher correlation.

The biosurfactant/nanoparticle suspension showed a higher oil treatment efficiency than only biosurfactant or only nanoparticles at all flow rates. This result can be explained by the synergistic effects between biosurfactant and nanoparticle in the suspension, which improved the stability and reactivity of both biosurfactant and nanoparticles, resulting in higher removal efficiency (Yekeen et al., 2020). The biosurfactant displayed a higher oil treatment performance than the nanoparticle solution, which reflected the effectiveness of biosurfactant micelles for remediation of oil pollutants in soil. In addition, nanoparticles adherence on the tube also contributed to the lower treatment efficiency than the biosurfactant solution alone.

Among the two mixtures, biosurfactant foam/nanoparticle solution demonstrated higher remediation productivity than biosurfactant/nanoparticle suspension. It can be explained by the more significant nanoparticle amount adsorbed on each bubble surface, which will likely adsorb or reduce more oil pollutants, resulting in higher treatment efficiency. Moreover, the higher transport of biosurfactant foam/nanoparticle mixture through the soil may enhance its interaction with oil pollutants and increase soil remediation effectiveness (Yu et al., 2015). The attachment of oil droplets to the foam to form the oil layer by electrostatic force (Huang et al., 2021), the decrease of pressure to detach the trapped oil due to supersaturation (Hewage et al., 2021), and the increase of absolute zeta potential of the soil column due to the foam formation may improve the repulsion

forces between oil and soil particles, which may favorably release oil droplets from the soil surface and increase the treatment effectiveness (Ma, 2021). This result is similar to previous studies, whereas surfactant foam shows a higher soil contaminant remediation productivity (Karthick et al., 2019; Karthick and Chattopadhyay, 2017; Mulligan and Eftekhari, 2003).

4.6.4. Change in oil concentration in the soil column

After treatment with the biosurfactant foam/nanoparticle, biosurfactant/nanoparticle suspension, only biosurfactant foam, only biosurfactant, and only nanoparticles, the change in oil content was investigated through a fixed-bed soil column under the same conditions. In other words, they are the breakthrough curves of oil pollutants transported through the soil column. As indicated in Figure 37, the oil extraction curves showed peaks after specific pore volumes, followed by a gradual decrease. In particular, the peak appeared after three, five, seven, eight, and eight pore volumes for the soil column with biosurfactant foam/nanoparticle mixture, biosurfactant/nanoparticle suspension, only biosurfactant foam, only biosurfactant, and only nanoparticles, respectively. Based on the curve, maximum oil treatment efficiency by biosurfactant foam/nanoparticle, biosurfactant/nanoparticle, only biosurfactant foam, only biosurfactant, and nanoparticle-amended soil was about 3 times, 2.5 times, 2.1 times, 2 times, and 1.5 times more than DI water, respectively.

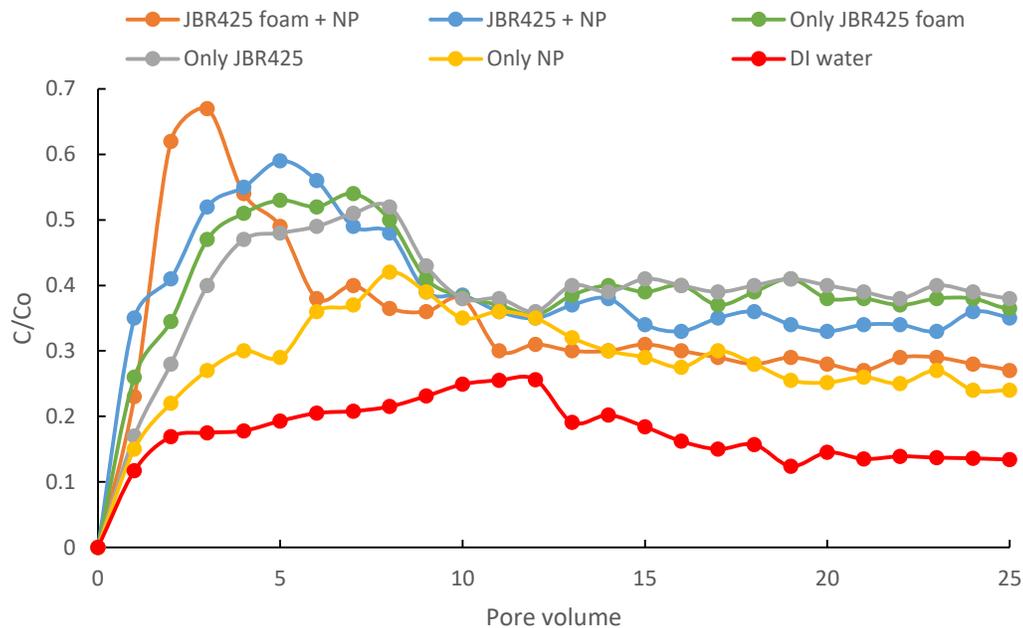


Figure 37. Breakthrough curves of oil pollutants in the soil column under different treatments according to pore volume

The breakthrough curves of the material-amended soil column were narrow, while the breakthrough curve of DI water was a broad and diffuse infiltration front. This behavior indicated that the oil concentration in the effluent (after the soil column) firstly increased in time due to the effective remediation properties of treatment solutions. After most of the oil pollutants were removed from the soil column, less oil concentration would present in the effluent, leading to decreased oil concentration over time. When a steady state was reached, the clean soil was saturated, and the oil concentration in the effluent attained equilibrium. The equilibrium point of biosurfactant foam/nanoparticle mixture was lower than biosurfactant/nanoparticle suspension, only biosurfactant foam, only biosurfactant, and only nanoparticles reflecting its higher remediation capacity under the same experimental conditions. Moreover, the oil treatment by

biosurfactant/nanoparticle was higher than by only biosurfactant foam, only biosurfactant, and only nanoparticle. This result was due to the synergistic effect between biosurfactant and nanoparticle, which improved the transport and reactivity while decreasing the adsorption in soil, led to a higher oil removal performance (Vu and Mulligan, 2022b). In addition, the generation of micelles at high biosurfactant concentrations also prevented biosurfactant sorption in the soil column and contributed to a higher oil removal efficiency. These results also reflected the effectiveness in oil removal by the biosurfactant foam/nanoparticle mixture, biosurfactant/nanoparticle suspension, biosurfactant foam, biosurfactant, and nanoparticle-amended soil column. Meanwhile, control experiments (with DI water) expressed a low oil pollutants treatment efficiency due to the low solubility of oil in water (50 mg/l at 20 °C). Hence, the minor removal performance of oil pollutants by water flushing was negligible.

The results from ICP-MS indicated that 13% of Fe/Cu nanoparticles were found in the effluent after the column experiment. In addition, a small number of nanoparticles was observed to attach to the inner surface of the tube and column. In other words, more than 80% of Fe/Cu nanoparticles stayed in the soil column in the presence of the filter at the bottom of the soil column, which reduced (through the reactive oxygen species) or were adsorbed on to the contaminated soil in the soil column. These results are similar to other studies (Vu and Mulligan, 2022c; Karthick et al., 2019; Babae et al., 2018). Meanwhile, more than 20% of nanoparticles were found in the effluent in the absence of the filter at the soil column bottom. These results showed a high distribution and transport of nanoparticles in the column due to their weak adsorption to the soil particles (Zhang et al., 2019; Soares et al., 2018).

Besides, the CMC value of the effluent (through surface tension measurement) was also measured to determine the possible loss of surfactant after the treatment process (Chu, 2002). The

results showed an increase of about 40% of the CMC value for rhamnolipid biosurfactant, which suggested the surfactant loss during the experiments due to the attachment or adsorption to the soil particles or nanoparticles. This result is similar to the batch experiments, in which the CMC value of rhamnolipid biosurfactant increased 47% with the presence of nanoparticles and soil. In fact, the change in CMC value may be due to the micelle structure. However, methods for direct measurement of surfactant concentration adsorbed on soil are complicated and controversial (Garcia-Cervilla et al., 2022; Ishiguro and Koopal, 2016). Therefore, it can be concluded that a partial amount of surfactant was lost during the treatment processes.

4.6.5. Mechanisms of surfactant-nanoparticle oil removal

The GC analysis showed that most oil components in the soil were removed. In particular, C13-C29 oil components are treated while C1-C12 and C30-C40 are not remediated (Figure 38). In addition, up to 25%, 18%, 5%, and 13% of oil pollutants are degraded by biosurfactant foam/nanoparticle mixture, biosurfactant/nanoparticle suspension, only biosurfactant, and only nanoparticle, respectively. This result can be explained by the inert status of C1-C12 and C30-C40 oil pollutants that prevent their degradation. In other words, after the treatment process, most of the oil pollutants were solubilized, while a small part of oil pollutants was degraded by surfactant/nanoparticle suspension in batch and column experiments.

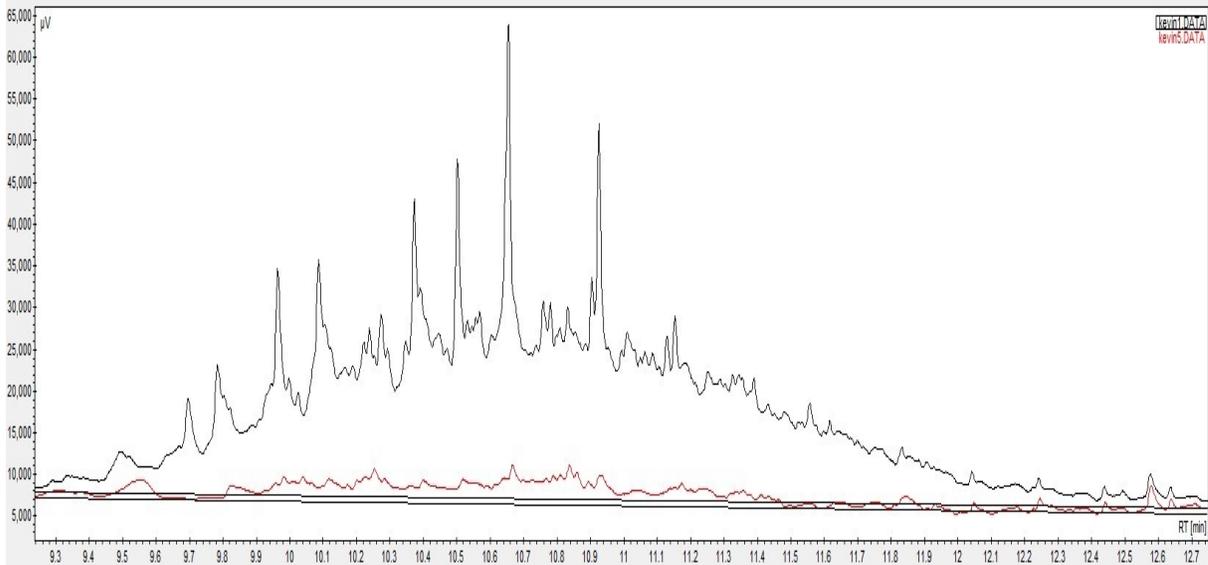


Figure 38. GC analysis for oil compounds before (black) and after (red) treatment process

Among different types of treatment, biosurfactant foam/nanoparticle mixture demonstrated the highest treatment efficiency. It can be concluded that foam has a greater tendency to extract more oil pollutants from the soil, leading to a higher removal efficiency (Mulligan and Eftekhari, 2003). Based on these results, the mechanism of oil removal by surfactant-nanoparticle can be proposed in Figure 39.

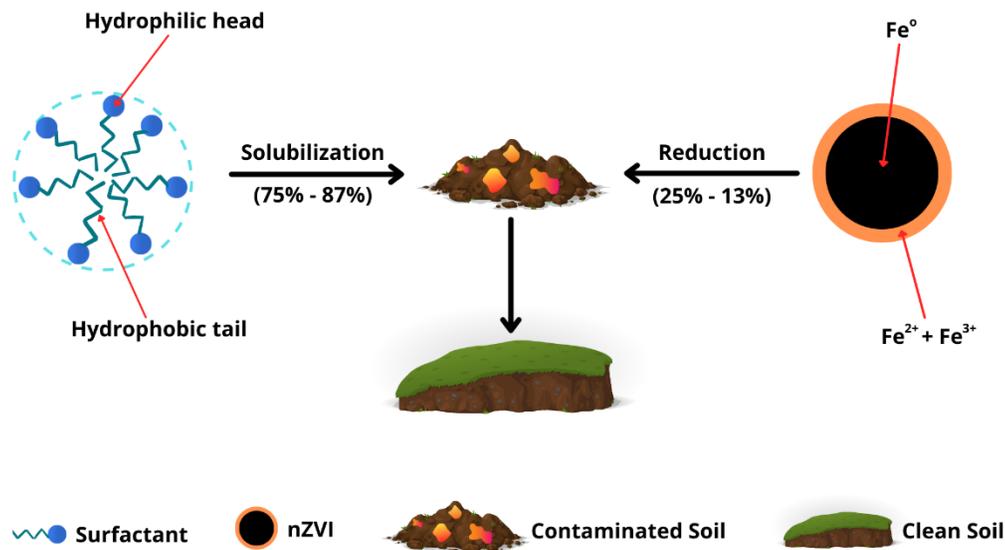


Figure 39. Proposed mechanism of oil removal by surfactant-nanoparticle

Experimental results for the treatment efficiency of oil pollutants were used to determine the overall mass balance to determine the mechanisms of oil pollutant removal. Oil concentration measurement showed a good correlation for the oil mass balances during the experiments. In particular, only 2%, 2%, 3%, and 1% of oil pollutants were not accounted for by analyses of the biosurfactant foam/nanoparticle mixture, biosurfactant/nanoparticle suspension, only biosurfactant, and only nanoparticle, respectively (Table 10), which was expected due to the analytical or human errors (Mulligan and Wang, 2006). In other words, oil pollutants are hard to volatilize because of their high sorption to the soil, which is similar to the result of the previous study (Kamath et al., 2004). Furthermore, the similar oil content in the original soil after 7 and 14 days suggests that the effect of aging process of contamination on oil volatilization can be small (Tang et al., 2012). Besides, some oil compounds might have already volatilized due to the contamination in the soil. The degradation efficiency of oil pollutants also contributes to the unaccounted removal efficiency of oil pollutants in the overall mass balance.

Table 10. Mass balance for oil pollutants after column experiment

Type of treatment	Removed in the effluent, %	Retained in soil column, %	Unaccounted removal, %
JBR425 foam +NP	67	31	2
JBR425 + NP	59	39	2
Only JBR425	52	45	3
Only NP	42	57	1

4.7. Limitations

Some limitations may appear when using the biosurfactant for in-situ soil remediation. First, high biosurfactant concentrations, usually greater than critical micelle concentration, are required to obtain effective stabilization. Second, the mobility of biosurfactant/nanoparticle suspension may be lowered in the actual soil. Third, fast biosurfactant desorption into water under the soil may occur after injecting the biosurfactant/nanoparticle suspension, reducing the stabilization. Fourth, non-targeted contaminants can be solubilized or mobilized by adding biosurfactants, resulting in lower treatment efficiency.

The stability of biosurfactant-stabilized Fe/Cu nanoparticles is another concern. It is caused by the attraction and repulsion forces of nanoparticle surfaces in various fluids. To avoid nanoparticle aggregation or obtain a stable suspension, the repulsion force should be greater than the attraction force (Kazemzadeh et al., 2019). Some of the main parameters that strongly affect the formation of a stable nanoparticle suspension are charge density and functionalized nanoparticle surface. In

principle, the higher the absolute zeta potential value, the higher the stability and suspension of nanoparticles due to the improvement of electrostatic repulsion force between nanoparticles.

Nonetheless, the zeta potential value may decrease the nanoparticle stability and increase the surface charge density of nanoparticles, leading to higher attraction forces between nanoparticles and existing ions. Therefore, both the zeta potential and charge density of nanoparticles play an essential role in the stability of nanoparticles.

Some other available limitations are the competitive sorption between organic compounds and biosurfactants on nanoparticle surfaces due to the electrostatic attraction force (Yu et al., 2012), limiting the contact time of nanoparticles and contaminants. As a result, the nanoparticle surface can be oxidized over time, which will decrease the reactivity of nanoparticles, resulting in lower removal effectiveness. However, the adsorption of biosurfactant molecules on the nanoparticle surface will increase the organic contaminant amount accumulation on the nanoparticle surface, leading to improved treatment efficiency (Zhang et al., 2011).

The potential toxicity of biosurfactant/nanoparticle suspension is another concern. After about one month, due to the reaction with adsorbed contaminants or NOM, part of carboxymethyl cellulose-stabilized nZVI can be converted to iron minerals under subsurface conditions, which may adsorb toxic chemicals like chromium or arsenic and cause adverse effects on the environment (Johnson et al., 2013). In addition, the iron materials may induce cytotoxicity for microorganisms (Lee et al., 2008). Their effect on cellular viability and functionality of soil microorganisms is small and dependent on the dose and species (Fajardo et al., 2012). They may also deposit on the roots and cause phytotoxicity for the plant. In particular, the membrane pores are blocked, limiting the root function to uptake water and nutrients, resulting in plant death (Ma et al., 2013). Nevertheless, it should be noted that the biosurfactant is of very low toxicity (Mulligan, 2021).

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In this research, biosurfactant/nanoparticle suspension and biosurfactant foam/nanoparticle mixture were prepared and used for remediation of oil-contaminated soil. Through a simple method, Fe/Cu bimetallic nanoparticles were successfully produced with an average diameter of less than 20 nm, while Fe content was higher than Cu. The appearance of iron oxide and copper oxide was confirmed by XRD analysis. The combination of biosurfactant and nanoparticles limited nanoparticle surface oxidation and inhibited nanoparticle aggregation, which improved their transport and reactivity in soil. The oil treatment efficiency was significantly enhanced through the solubilization/mobilization by biosurfactant and reduction/adsorption by nanoparticles. In particular, the oil remediation efficiency by rhamnolipid biosurfactant/nanoparticle suspension was up to 84% and followed the first-order reaction. Rhamnolipid biosurfactant was more effective than sophorolipid biosurfactant and nonionic surfactant in oil removal, with and without nanoparticles. For batch experiments, optimum operating parameters included biosurfactant: nanoparticle ratio of 10:1 (wt%: wt%), pH 7, shaking speed 60 rpm for 60 minutes at room temperature (25°C). The addition of inorganic salt created more competitive factors in the mixture, which inhibited the contact of oil and surfactant molecules and reduced the soil remediation performance. The presence of other surfactants decreased the treatment productivity by 9-14% compared to using only rhamnolipid biosurfactant. After three cycles, nanoparticles were reused with a remediation efficiency of 59% by rhamnolipid biosurfactant.

For the column experiments, biosurfactant foam/nanoparticle and biosurfactant/nanoparticle mixtures were effectively used to remediate oil-contaminated soil, whereas the highest treatment efficiency was 67%, 59%, and 52% for rhamnolipid biosurfactant foam/nanoparticle, rhamnolipid biosurfactant/nanoparticle, and only rhamnolipid biosurfactant, respectively. The oil removal productivity decreased with the increase of flowrate due to the shorter contact time between the foam mixture and oil droplets. The breakthrough curves of oil pollutants in the soil column also suggested that the foam mixture's maximum oil treatment efficiency was higher than biosurfactant/nanoparticle suspension and only biosurfactant. The overall mass balances after the column experiments were good, whereas the highest unaccounted removal efficiency of oil pollutants was 3%. In addition, up to 25% and 18% of oil pollutants were degraded by biosurfactant foam/nanoparticle mixture and biosurfactant/nanoparticle suspension, respectively. Therefore, the main mechanism of oil removal was solubilization. Besides, an increase in the CMC value of the effluent indicated the loss of a certain amount of surfactant after each experiment. The nanoparticles were proven to be highly distributed and transported in the soil column. These results suggested that biosurfactant/Fe-Cu nanoparticle suspension can be effectively used to remediate oil from contaminated soil. However, more investigation into the production costs, in-situ production, and the stabilization of nanoparticles in surfactants before the remediation processes will be required to evaluate the efficiency of this method in full-scale applications.

The outcomes from this work will significantly benefit the soil remediation field. Many contaminated sites are likely to cause an immediate or long-term threat to human health and the environment or exceed allowable levels stated in policies and regulations. Due to the oil production process, soil contamination leads to a sustainable site remediation technology to reuse the contaminated land areas. Concerns about toxicity and environmental impact by traditional

chemical approaches drive the demand for more sustainable treatment alternatives. Among those options, biosurfactants produced from environmentally renewable resources are preferred due to their biodegradability and minimum waste generation. This work will provide an environmentally friendly method for removing oil from contaminated soil.

5.2. Future research

Future studies may investigate the synthesis, characterization, and use of other bimetallic nanoparticles, such as Fe/Ni, Fe/Pd, with biosurfactants for remediation of oil-contaminated soil. The new results may be compared with Fe/Cu nanoparticles to find the optimal nanoparticles for soil remediation. In addition, different soil types, for example, sandy-silt or fine sand, will be utilized to evaluate the effectiveness of these methods under various conditions and their potential application range. In addition, the effectiveness of this method under various environmental conditions, such as low temperature, will be studied to evaluate its potential application range.

Further research should focus on applying this method in field scale and improving models to predict the movement and interactions between surfactant-stabilized nanoparticles and soil components and contaminants. More research will be required regarding the in-situ generation of biosurfactants, reduction of production costs, and recycling and reuse of surfactants and nanoparticles. In addition, the post-treatment process for the effluent needs more study. While biosurfactants are highly biodegradable and nanoparticles can be reused or used for other remediation processes, oil pollutants in the effluent will need further treatment. Therefore, different bioremediation methods will be used to completely remove the oil pollutants.

In addition, the transport and delivery into the soil have not been fully understood. This approach, however, is not appropriate for less permeable soil and sediment. More studies will be required for the particle stabilization plan, which may improve the transport of surfactant-stabilized nanoparticles to contaminated sites. Besides, the size and reactivity of particles may be inhibited by the high concentration of DOM and soil leachate, respectively. Likewise, the oxidation of the nZVI surface owing to reactions with soil particles is another concern (Zhang et al., 2011).

Although the understanding of the fate and transport of nanoparticles in the soil is restricted, previous studies show that the application of stabilized nanoparticles may alter the biogeochemical properties of soil, resulting in an effect on the stability of soil contaminants. Meanwhile, soil's geochemical and biochemical conditions may significantly change the characteristics of nanoparticles. Therefore, more monitoring data on the long-term stability of soil contaminants (e.g., metals, organic hydrocarbons) in the field tests are essential to evaluating the remediation effectiveness and advancing the treatment design. The effect of pH on the particle size and zeta potential will be also determined.

The limited lifetime of stabilized nanoparticles and reactivity of soil contaminants due to sorption/desorption and diffusion makes this technique only available for contaminants with high desorption. Hence, there is a need to diminish the corrosion of nanoparticles by water, such as by using different stabilizers simultaneously, to protect the reactivity of nanoparticles. Furthermore, the synergistic or antagonistic effects of Fe/Cu nanoparticles on soil microorganisms need further research to determine the mechanisms of the treatment process.

The potential risks of this method to the environment should be considered for the broad application. Our understanding of the long-term effect of delivered Fe/Cu nanoparticles and surfactants on the biota under various conditions is limited. Therefore, more studies on their

toxicity and impacts on biological systems are necessary before applying them to the broader environment. Notably, more effective technologies for monitoring the surfactant-particle mixture and more peer-reviewed and validated data from field-scale applications are required to evaluate this method.

The relationship between the fate and transport of surfactant/nanoparticle suspension and the environmental conditions should be further investigated. It will give more information about the effect of surfactants and nanoparticles on the mobility of other soil constituents in the field and more details about the transformation of surfactants and nanoparticles in soil. In addition, the influence of delivered nanoparticles on the soil hydraulic conductivity for a long time also needs more research. Hence, it is necessary to develop models to predict the movement of surfactant-stabilized nanoparticles in soil. More studies relating to the potential chemical transformation of nanoparticles will be required to obtain better results for the models.

Moreover, more studies are needed to evaluate the valuable lifetime of nanoparticles and surfactants in the mixture under different field conditions, sustainability assessment of surfactant/nanoparticle mixture in case studies. Collaboration between research and the industry community will be desired to deal with those challenges. The chemical and colloidal features of the mixture, which relate to nanoparticle reactivity and selectivity, also need further evaluation to obtain a higher treatment efficiency. More studies for the remediation of other contaminants are needed to evaluate the treatment efficiency of the mixture.

Lastly, more research will be required regarding the in-situ generation of biosurfactants, reduction of production costs, and recycling and reuse of biosurfactants and nanoparticles.

REFERENCES

- Abatenh, E., Gizaw, B., Tsegaye, Z., & Wassie, M. (2017). The role of microorganisms in bioremediation-A review. *Open Journal of Environmental Biology*, 2(1), 38-46. doi: 10.17352/ojeb.000007.
- Abdel-Shafy, H. I., & Mansour, M. S. (2016). A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egyptian Journal of Petroleum*, 25(1), 107-123.
- Adam, G. (2001) A study into the potential of phytoremediation for diesel fuel contaminated soil. PhD thesis, University of Glasgow.
- Agamuthu, P., Abioye, O. P., & Aziz, A. A. (2010). Phytoremediation of soil contaminated with used lubricating oil using *Jatropha curcas*. *Journal of Hazardous Materials*, 179(1-3), 891-894.
- Agarry, S., & Latinwo, G. K. (2015). Biodegradation of diesel oil in soil and its enhancement by application of bioventing and amendment with brewery waste effluents as biostimulation-bioaugmentation agents. *Journal of Ecological Engineering*, 16(2), 82-91. doi:10.12911/22998993/1861.
- Al-Daher, R., Al-Awadhi, N., & El-Nawawy, A. (1998). Bioremediation of damaged desert environment using the windrow soil pile system in Kuwait. *Environment International*, 24(1-2), 175-180.
- Al Zubaidi, I., & Al Tamimi, A. (2018). Soil remediation from waste lubricating oil. *Environmental Technology & Innovation*, 9, 151-159.

- Ali, N., Bilal, M., Khan, A., Ali, F., & Iqbal, H. M. (2020). Effective exploitation of anionic, nonionic, and nanoparticle-stabilized surfactant foams for petroleum hydrocarbon contaminated soil remediation. *Science of the Total Environment*, 704, 135391.
- Alvarez-Bernal, D., Garcia-Diaz, E. L., Contreras-Ramos, S. M., & Dendooven, L. (2006). Dissipation of polycyclic aromatic hydrocarbons from soil added with manure or vermicompost. *Chemosphere*, 65(9), 1642-1651.
- Amjad, A., Di, G., Mahar, A., Ping, W., Feng, S., Ronghua, L. I., & Zhang, Z. (2017). Mycoremediation of potentially toxic trace elements-a biological tool for soil cleanup: a review. *Pedosphere*, 27(2), 205-222.
- Anderson, A., & Mitchell, P. (2003). Treatment of mercury-contaminated soil, mine waste and sludge using silica micro-encapsulation. Paper presented at the *TMS Annual Meeting, Extraction and Processing Division*, 265-274.
- Anderson, C., & Juday, G. (2016). Mycoremediation of petroleum: a literature review. *Journal of Environmental Science and Engineering: A*, 5, 397-405.
- Artiola, J. F., Brusseau, M. L., & Pepper, I. L. (2004). *Environmental monitoring and characterization*. Academic Press, 335-356. ISBN: 978-0-12-064477-3. doi:10.1016/B978-0-12-064477-3.X5000-0.
- Asgari, A. R., Nabizadeh, R., Mahvi, A. H., Nasser, S., Dehghani, M. H., Nazmara, S., & Yaghmaeian, K. (2017). Remediation of total petroleum hydrocarbons using combined in-vessel composting and oxidation by activated persulfate. *Global Journal of Environmental Science and Management*, 3(4), 373-384.
- Atagana, H. I. (2008). Compost bioremediation of hydrocarbon-contaminated soil inoculated with organic manure. *African Journal of Biotechnology*, 7(10), 1516-1525.

- Atlas, R. M. (1975). Effects of temperature and crude oil composition on petroleum biodegradation. *Applied Microbiology*, 30(3), 396-403.
- Atlas, R. M. (1981). Microbial degradation of petroleum hydrocarbons: an environmental perspective. *Microbiological Reviews*, 45(1), 180-209.
- Atlas, R. M., & Philp, J. (2005). *Bioremediation. Applied microbial solutions for real-world environmental cleanup*. ASM press.
- Auffan, M., Rose, J., Bottero, J., Lowry, G. V., Jolivet, J., & Wiesner, M. R. (2009). Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective. *Nature Nanotechnology*, 4(10), 634-641.
- Azeez, O. M., Anigbogu, C. N., Akhigbe, R. E., Saka, W. A. (2015). Cardiotoxicity induced by inhalation of petroleum products. *Journal of African Association of Physiological Sciences*, 3(1), 14-17.
- Azizi, A. B., Liew, K. Y., Noor, Z. M., & Abdullah, N. (2013). Vermiremediation and mycoremediation of polycyclic aromatic hydrocarbons in soil and sewage sludge mixture: a comparative study. *International Journal of Environmental Science and Development*, 4(5), 565-568.
- Azubuiké, C. C., Chikere, C. B., & Okpokwasili, G. C. (2016). Bioremediation techniques—classification based on site of application: principles, advantages, limitations and prospects. *World Journal of Microbiology and Biotechnology*, 32(11), 1-18.
- Ba-Naimoon, M. S., & Hamid, A. M. (2016). Stabilization/Solidification (S/S) technique and its applications in Saudi Arabia. *International Journal of Environment and Sustainability*, 5(1), 46-50.

Babae, Y., Mulligan, C. N., & Rahaman, M. S. (2018). Arsenic immobilization in soil using starch-stabilized Fe/Cu nanoparticles: a case study in treatment of a chromated copper arsenate (CCA)-contaminated soil at lab scale. *Journal of Soils and Sediments*, 18(4), 1610-1619. doi:10.1007/s11368-017-1882-2.

Bailey, K. L., Tilton, F., Jansik, D. P., Ergas, S. J., Marshall, M. J., Miracle, A. L., & Wellman, D. M. (2012). Growth inhibition and stimulation of *Shewanella oneidensis* MR-1 by surfactants and calcium polysulfide. *Ecotoxicology and Environmental Safety*, 80, 195-202.

Ballesteros, S., Rincón, J. M., Rincón-Mora, B., & Jordán, M. M. (2017). Vitrification of urban soil contamination by hexavalent chromium. *Journal of Geochemical Exploration*, 174, 132-139.

Banaszkiewicz, K., & Marcinkowski, T. (2017). Use of cement-fly ash-based stabilization techniques for the treatment of waste containing aromatic contaminants. Paper presented at the *E3S Web of Conferences*, 22 00009.

Banerji, S. K., Zappi, M. E., Teeter, C. L., Gunnison, D., Cullinane, M. J., Morgan, R. T. (1995). *Bioremediation of soils contaminated with petroleum hydrocarbons using bioslurry reactors*. US Army Engineer Waterways Experiment Station. NSNL: 7540-01-280-5500, 40-57.

Baragaño, D., Alonso, J., Gallego, J. R., Lobo, M. C., & Gil-Díaz, M. (2020). Zero valent iron and goethite nanoparticles as new promising remediation techniques for As-polluted soils. *Chemosphere*, 238, 124624.

Bardos, P., Bone, B., Elliott, D., Hartog, N., Henstock, J., & Nathanail, P. (2011). A risk/benefit approach to the application of iron nanoparticles for the remediation of contaminated sites in the environment. *Department of Environmental Food Rural Affiliation*.

- Bardos, P., Bone, B., Daly, P., Elliott, D., Jones, S., Lowry, G., & Merly, C. (2014). A risk/benefit appraisal for the application of nano-scale zero valent iron (nZVI) for the remediation of contaminated sites. *WP9 NanoRem*.
- Basnet, M., Ghoshal, S., & Tufenkji, N. (2013). Rhamnolipid biosurfactant and soy protein act as effective stabilizers in the aggregation and transport of palladium-doped zerovalent iron nanoparticles in saturated porous media. *Environmental Science & Technology*, *47*(23), 13355-13364.
- Bates, E., & Hills, C. (2015). Stabilization and solidification of contaminated soil and waste: A manual of practice. *Édit Media H*. Corpus ID: 114229023.
- Befkadu, A. A., & Quanyuan, C. (2018). Surfactant-enhanced soil washing for removal of petroleum hydrocarbons from contaminated soils: a review. *Pedosphere*, *28*(3), 383-410.
- Bennett, P., He, F., Zhao, D., Aiken, B., & Feldman, L. (2010). In situ testing of metallic iron nanoparticle mobility and reactivity in a shallow granular aquifer. *Journal of Contaminant Hydrology*, *116*(1-4), 35-46. doi:10.1016/j.jconhyd.2010.05.006.
- Benyahia, F., & Embaby, A. S. (2016). Bioremediation of crude oil contaminated desert soil: effect of biostimulation, bioaugmentation and bioavailability in biopile treatment systems. *International Journal of Environmental Research and Public Health*, *13*(2), 219.
- Besha, A. T., Bekele, D. N., Naidu, R., & Chadalavada, S. (2018). Recent advances in surfactant-enhanced In-Situ Chemical Oxidation for the remediation of non-aqueous phase liquid contaminated soils and aquifers. *Environmental Technology & Innovation*, *9*, 303-322.
- Betancur, S., Carrasco-Marín, F., Pérez-Cadenas, A. F., Franco, C. A., Jiménez, J., Manrique, E. J., Quintero, H., Cortés, F. B. (2019). Effect of magnetic iron core-carbon shell nanoparticles in

chemical enhanced oil recovery for ultralow interfacial tension region. *Energy Fuels* 33:4158–4168. <https://doi.org/10.1021/acs.energyfuels.9b00426>.

Bhatnagar, S., & Kumari, R. (2013). Bioremediation: a sustainable tool for environmental management—a review. *Annual Research & Review in Biology*, 3(4), 974-993.

Bhattacharjee, S., Basnet, M., Tufenkji, N., & Ghoshal, S. (2016). Effects of rhamnolipid and carboxymethylcellulose coatings on reactivity of palladium-doped nanoscale zerovalent iron particles. *Environmental Science & Technology*, 50(4), 1812-1820.

Bi, H., An, C., Chen, X., Owens, E., & Lee, K. (2020). Investigation into the oil removal from sand using a surface washing agent under different environmental conditions. *Journal of Environmental Management*, 275, 111232. doi:10.1016/j.jenvman.2020.111232.

Bikoko, T., & Okonta, F. N. (2016). Binder systems for the stabilization/solidification of contaminated soils—a review. *Electronic Journal of Geotechnical Engineering*, 21, 9927-9960.

Brown, D. M., Okoro, S., van Gils, J., van Spanning, R., Bonte, M., Hutchings, T., Linden, O., Egbuche, U., Bruun, K. B., & Smith, J. W. (2017). Comparison of landfarming amendments to improve bioremediation of petroleum hydrocarbons in Niger Delta soils. *Science of the Total Environment*, 596, 284-292.

Byström, A., & Hirtz, M. (2002). Phytoremediation of Petroleum Hydrocarbon-Contaminated Soils with *Salix Viminalis*. Thesis, Chalmers University of Technology.

Camenzuli, D., & Freidman, B. L. (2015). On-site and in situ remediation technologies applicable to petroleum hydrocarbon contaminated sites in the Antarctic and Arctic. *Polar Research*, 34(1), 24492.

Camenzuli, D., & Gore, D. B. (2013). Immobilization and encapsulation of contaminants using silica treatments: A review. *Remediation Journal*, 24(1), 49-67.

Canada Environmental Protection Service, Technical Services Branch. (1984). Manual for spills of hazardous materials. Technical Services Branch, Environmental Protection Service, Environment Canada. <https://publications.gc.ca/site/fra/463890/publication.html>. Accessed 18 December 2021.

Cartmill, A. D., Cartmill, D. L., & Alarcón, A. (2014). Controlled release fertilizer increased phytoremediation of petroleum-contaminated sandy soil. *International Journal of Phytoremediation*, *16*(3), 285-301.

Chachina, S. B., Voronkova, N. A., & Baklanova, O. N. (2016). Biological remediation of the petroleum and diesel contaminated soil with earthworms *Eisenia fetida*. *Procedia Engineering*, *152*, 122-133.

Chaithawiwat, K., Vangnai, A., McEvoy, J. M., Pruess, B., Krajangpan, S., & Khan, E. (2016). Impact of nanoscale zero valent iron on bacteria is growth phase dependent. *Chemosphere*, *144*, 352-359.

Chang, M., Shu, H., Hsieh, W., & Wang, M. (2007). Remediation of soil contaminated with pyrene using ground nanoscale zero-valent iron. *Journal of the Air & Waste Management Association*, *57*(2), 221-227.

Chen, C., & Jafvert, C. T. (2010). Photoreactivity of carboxylated single-walled carbon nanotubes in sunlight: reactive oxygen species production in water. *Environmental Science & Technology*, *44*(17), 6674-6679.

Chen, J., Al-Abed, S. R., Ryan, J. A., & Li, Z. (2001). Effects of pH on dechlorination of trichloroethylene by zero-valent iron. *Journal of Hazardous Materials*, *83*(3), 243-254.

Chen, K., Chang, Y., & Chiou, W. (2016). Remediation of diesel-contaminated soil using in situ chemical oxidation (ISCO) and the effects of common oxidants on the indigenous microbial

community: a comparison study. *Journal of Chemical Technology & Biotechnology*, 91(6), 1877-1888.

Chen, Q., Li, J., Wu, Y., Shen, F., & Yao, M. (2013). Biological responses of Gram-positive and Gram-negative bacteria to nZVI (Fe 0), Fe 2 and Fe 3. *RSC Advances*, 3(33), 13835-13842.

Cho, Y., & Choi, S. (2010). Degradation of PCE, TCE and 1,1,1-TCA by nanosized FePd bimetallic particles under various experimental conditions. *Chemosphere*, 81(7), 940-945. <https://doi.org/10.1016/j.chemosphere.2010.07.054>

Chu, W. (2003). Remediation of contaminated soils by surfactant-aided soil washing. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, 7(1), 19-24.

Comba, S., & Sethi, R. (2009). Stabilization of highly concentrated suspensions of iron nanoparticles using shear-thinning gels of xanthan gum. *Water Research*, 43(15), 3717-3726.

Cook, R. L., & Hesterberg, D. (2013). Comparison of trees and grasses for rhizoremediation of petroleum hydrocarbons. *International Journal of Phytoremediation*, 15(9), 844-860.

Cornelissen, G., Schaanning, M., Gunnarsson, J. S., & Eek, E. (2016). A large-scale field trial of thin-layer capping of PCDD/F-contaminated sediments: Sediment-to-water fluxes up to 5 years post-amendment. *Integrated Environmental Assessment and Management*, 12(2), 216-221.

Costa, A. S., Romão, L., Araújo, B. R., Lucas, S., Maciel, S., Wisniewski Jr, A., & Alexandre, M. d. R. (2012). Environmental strategies to remove volatile aromatic fractions (BTEX) from petroleum industry wastewater using biomass. *Bioresource Technology*, 105, 31-39.

Covino, S., D'Annibale, A., Stazi, S. R., Cajthaml, T., Čvančarová, M., Stella, T., & Petruccioli, M. (2015). Assessment of degradation potential of aliphatic hydrocarbons by autochthonous filamentous fungi from a historically polluted clay soil. *Science of the Total Environment*, 505, 545-554.

- Crane, R. A., & Scott, T. B. (2012). Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. *Journal of Hazardous Materials*, 211, 112-125.
- Cristaldi, A., Conti, G. O., Jho, E. H., Zuccarello, P., Grasso, A., Copat, C., & Ferrante, M. (2017). Phytoremediation of contaminated soils by heavy metals and PAHs. A brief review. *Environmental Technology & Innovation*, 8, 309-326.
- Cullen, L. G., Tilston, E. L., Mitchell, G. R., Collins, C. D., & Shaw, L. J. (2011). Assessing the impact of nano-and micro-scale zerovalent iron particles on soil microbial activities: particle reactivity interferes with assay conditions and interpretation of genuine microbial effects. *Chemosphere*, 82(11), 1675-1682.
- Dabke, S. V. (2013). Vermi-remediation of heavy metal-contaminated soil. *Journal of Health and Pollution*, 3(4), 4-10.
- Dadrasnia, A., Shahsavari, N., & Emenike, C. U. (2013). *Remediation of contaminated sites*. Intech Rijeka. doi:10.5772/51591.
- Das, N., & Chandran, P. (2011). Microbial degradation of petroleum hydrocarbon contaminants: an overview. *Biotechnology Research International*, 2011(10), 1-13.
- Devold, H. (2013). *Oil and gas production handbook: an introduction to oil and gas production, transport, refining and petrochemical industry*. ABB Oil and Gas. ISBN 978-82-997886-3-2.
- Deshpande, S., Shiau, B. J., Wade, D., Sabatini, D. A., & Harwell, J. H. (1999). Surfactant selection for enhancing ex situ soil washing. *Water Research*, 33(2), 351-360.
- Dias, R. L., Ruberto, L., Calabró, A., Balbo, A. L., Del Panno, M. T., & Mac Cormack, W. P. (2015). Hydrocarbon removal and bacterial community structure in on-site biostimulated biopile systems designed for bioremediation of diesel-contaminated Antarctic soil. *Polar Biology*, 38(5), 677-687.

- Doong, R., & Lei, W. (2003). Solubilization and mineralization of polycyclic aromatic hydrocarbons by *Pseudomonas putida* in the presence of surfactant. *Journal of Hazardous Materials*, 96(1), 15-27.
- Ecobiol, J. (2006). Phytoremediation: processes and mechanisms. *Journal of Ecobiology*, 18(1), 33-38.
- Eicke, H., & Meier, W. (1996). Interfacial charge transport in water-in-oil microemulsions stabilized by ionic-non-ionic surfactant mixtures. *Biophysical Chemistry*, 58(1-2), 29-37.
- Ekperusi, O. A., & Aigbodion, F. I. (2015). Bioremediation of petroleum hydrocarbons from crude oil-contaminated soil with the earthworm: *Hyperiodrilus africanus*. *Biotech*, 5(6), 957-965.
- El-Temseh, Y. S., & Joner, E. J. (2012a). Ecotoxicological effects on earthworms of fresh and aged nano-sized zero-valent iron (nZVI) in soil. *Chemosphere*, 89(1), 76-82.
- El-Temseh, Y. S., & Joner, E. J. (2012b). Impact of Fe and Ag nanoparticles on seed germination and differences in bioavailability during exposure in aqueous suspension and soil. *Environmental Toxicology*, 27(1), 42-49.
- Elijah, A.A. (2022). A Review of the Petroleum Hydrocarbons Contamination of Soil, Water and Air and the Available Remediation Techniques, Taking into Consideration the Sustainable Development Goals. Earthline. *Journal of Chemical Sciences*, 7(1), 97-113. <https://doi.org/10.34198/ejcs.7122.97113>.
- Elliott, D. W., & Zhang, W. (2001). Field assessment of nanoscale bimetallic particles for groundwater treatment. *Environmental Science & Technology*, 35(24), 4922-4926.
- Elsgaard, L., Petersen, S. O., & Deboisz, K. (2001). Effects and risk assessment of linear alkylbenzene sulfonates in agricultural soil. 1. Short-term effects on soil

microbiology. *Environmental Toxicology and Chemistry: An International Journal*, 20(8), 1656-1663.

Enyoh, C. E., & Isiuku, B. O. (2020). Characterisation of some soils from flood basin in Amakohia, Owerri, Nigeria. *International Journal of Environmental Analytical Chemistry*, 102(8), 1-20. doi:10.1080/03067319.2020.1773455.

Esbaugh, A. J., Mager, E. M., Stieglitz, J. D., Hoenig, R., Brown, T. L., French, B. L., Linbo, T. L., Lay, C., Forth, H., & Scholz, N. L. (2016). The effects of weathering and chemical dispersion on Deepwater Horizon crude oil toxicity to mahi-mahi (*Coryphaena hippurus*) early life stages. *Science of the Total Environment*, 543, 644-651.

Fabbricino, M., Ferraro, A., Luongo, V., Pontoni, L., & Race, M. (2018). Soil washing optimization, recycling of the solution, and ecotoxicity assessment for the remediation of Pb-contaminated sites using EDDS. *Sustainability*, 10(3), 636.

Fajardo, C., Ortíz, L. T., Rodríguez-Membibre, M. L., Nande, M., Lobo, M. C., & Martin, M. (2012). Assessing the impact of zero-valent iron (ZVI) nanotechnology on soil microbial structure and functionality: a molecular approach. *Chemosphere*, 86(8), 802-808.

Fajardo, C., Saccà, M. L., Martinez-Gomariz, M., Costa, G., Nande, M., & Martin, M. (2013). Transcriptional and proteomic stress responses of a soil bacterium *Bacillus cereus* to nanosized zero-valent iron (nZVI) particles. *Chemosphere*, 93(6), 1077-1083.

Fang, L. I., Qingjie, H., Fujun, M. A., Yuting, W. U., Fasheng, L. I., & Qingbao, G. U. (2016). Stabilization/solidification of petroleum contaminated soil using biochar-cement. *Chinese Journal of Environmental Engineering*, 10(11), 6739-6745.

- Feitz, A. J., Joo, S. H., Guan, J., Sun, Q., Sedlak, D. L., & Waite, T. D. (2005). Oxidative transformation of contaminants using colloidal zero-valent iron. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 265(1-3), 88-94.
- Fernandez-Luqueno, F., Thalasso, F., Luna-Guido, M. L., Ceballos-Ramírez, J. M., Ordoñez-Ruiz, I. M., & Dendooven, L. (2009). Flocculant in wastewater affects dynamics of inorganic N and accelerates removal of phenanthrene and anthracene in soil. *Journal of Environmental Management*, 90(8), 2813-2818.
- Garcia-Cervilla, R., Santos, A., Romero, A., & Lorenzo, D. (2022). Simultaneous addition of surfactant and oxidant to remediate a polluted soil with chlorinated organic compounds: Slurry and column experiments. *Journal of Environmental Chemical Engineering*, 10(3), 107625. <https://doi.org/10.1016/j.jece.2022.107625>
- García-Junco, M., De Olmedo, E., & Ortega-Calvo, J. (2001). Bioavailability of solid and non-aqueous phase liquid (NAPL)-dissolved phenanthrene to the biosurfactant-producing bacterium *Pseudomonas aeruginosa* 19SJ. *Environmental Microbiology*, 3(9), 561-569.
- Geng, B., Jin, Z., Li, T., & Qi, X. (2009). Kinetics of hexavalent chromium removal from water by chitosan-Fe⁰ nanoparticles. *Chemosphere*, 75(6), 825-830.
- Gennadiev, A. N., Pikovskii, Y. I., Tsibart, A. S., & Smirnova, M. A. (2015). Hydrocarbons in soils: origin, composition, and behavior. *Eurasian Soil Science*, 48(10), 1076-1089.
- Gil-Díaz, M., Álvarez, M. A., Alonso, J., & Lobo, M. C. (2020). Effectiveness of nanoscale zero-valent iron for the immobilization of Cu and/or Ni in water and soil samples. *Scientific Reports*, 10(1), 1-10.

- Gomez, F., & Sartaj, M. (2014). Optimization of field scale biopiles for bioremediation of petroleum hydrocarbon contaminated soil at low temperature conditions by response surface methodology (RSM). *International Biodeterioration & Biodegradation*, 89, 103-109.
- Gouda, A. H., El-Gendy, A. S., El-Razek, T., & El-Kassas, H. I. (2016). Evaluation of phytoremediation and bioremediation for sandy soil contaminated with petroleum hydrocarbons. *Int J Environ Sci Dev*, 7(7), 490-493.
- Guarino, C., Spada, V., & Sciarrillo, R. (2017). Assessment of three approaches of bioremediation (Natural Attenuation, Landfarming and Bioaugmentation–Assisted Landfarming) for a petroleum hydrocarbons contaminated soil. *Chemosphere*, 170, 10-16.
- Gutzkow, K. B. (2015). Genotoxicity, mutagenicity and carcinogenicity and REACH. *Norwegian Institute Of Public Health, ICAW*, 1-28.
- He, F., Zhang, M., Qian, T., & Zhao, D. (2009). Transport of carboxymethyl cellulose stabilized iron nanoparticles in porous media: Column experiments and modeling. *Journal of Colloid and Interface Science*, 334(1), 96-102. doi:10.1016/j.jcis.2009.02.058.
- He, F., & Zhao, D. (2005). Preparation and characterization of a new class of starch-stabilized bimetallic nanoparticles for degradation of chlorinated hydrocarbons in water. *Environmental Science & Technology*, 39(9), 3314-3320. doi:10.1021/es048743y.
- He, F., & Zhao, D. (2007). Manipulating the size and dispersibility of zerovalent iron nanoparticles by use of carboxymethyl cellulose stabilizers. *Environmental Science & Technology*, 41(17), 6216-6221. doi:10.1021/es0705543.
- He, F., Zhao, D., Liu, J., & Roberts, C. B. (2007). Stabilization of Fe-Pd nanoparticles with sodium carboxymethyl cellulose for enhanced transport and dechlorination of trichloroethylene in soil and

groundwater. *Industrial & Engineering Chemistry Research*, 46(1), 29-34.
doi:10.1021/ie0610896.

He, F., & Zhao, D. (2008). Hydrodechlorination of trichloroethene using stabilized Fe-Pd nanoparticles: Reaction mechanism and effects of stabilizers, catalysts and reaction conditions. *Applied Catalysis B: Environmental*, 84(3), 533-540.
doi:10.1016/j.apcatb.2008.05.008.

He, F., Zhao, D., & Paul, C. (2010). Field assessment of carboxymethyl cellulose stabilized iron nanoparticles for in situ destruction of chlorinated solvents in source zones. *Water Research*, 44(7), 2360-2370. doi:10.1016/j.watres.2009.12.041.

Hellstrom, A. (2004). Uptake of organic pollutants in plants. Department of Environment and Assessments, Swedish University of Agricultural Sciences, Uppsala.

Henn, K. W., & Waddill, D. W. (2006). Utilization of nanoscale zero-valent iron for source remediation—A case study. *Remediation Journal: The Journal of Environmental Cleanup Costs, Technologies & Techniques*, 16(2), 57-77.

Hildebrand, H., Kühnel, D., Potthoff, A., Mackenzie, K., Springer, A., & Schirmer, K. (2010). Evaluating the cytotoxicity of palladium/magnetite nano-catalysts intended for wastewater treatment. *Environmental Pollution*, 158(1), 65-73.

Hobson, A. M., Frederickson, J., & Dise, N. B. (2005). CH₄ and N₂O from mechanically turned windrow and vermicomposting systems following in-vessel pre-treatment. *Waste Management*, 25(4), 345-352.

Hreniuc, M., Coman, M., & Cioruta, B. (2015). Considerations regarding the soil pollution with oil products in Sacel-Maramures. *Scientific Research & Education in the Air Force*, 28-30.

<http://www.oil-gasportal.com/environmental-issues/petroleum-contaminated-soils-remediation-technologies>.

Ishiguro, M., & Koopal, L. K. (2016). Surfactant adsorption to soil components and soils. *Advances in Colloid and Interface Science*, 231, 59-102. <https://doi.org/10.1016/j.cis.2016.01.006>

Ivshina, I. B., Kuyukina, M. S., Krivoruchko, A. V., Elkin, A. A., Makarov, S. O., Cunningham, C. J., Peshkur, T. A., Atlas, R. M., & Philp, J. C. (2015). Oil spill problems and sustainable response strategies through new technologies. *Environmental Science: Processes & Impacts*, 17(7), 1201-1219.

Jang, K., Cho, S., Scok, S., Kong, W., Kim, G., & Sung, J. (2009). Screening of biodegradable function of indigenous ligno-degrading mushroom using dyes. *Mycobiology*, 37(1), 53-61.

Jankaite, A., & Vasarevičius, S. (2005). Remediation technologies for soils contaminated with heavy metals. *Journal of Environmental Engineering and Landscape Management*, 13(2), 109-113.

Jia, L., Ou, Z., & Ouyang, Z. (2005). Ecological Behavior of Linear Alkylbenzene Sulfonate (LAS) in Soil-Plant Systems. *Pedosphere*, 15(2), 216-224.

Jiang, Y., Brassington, K. J., Prpich, G., Paton, G. I., Semple, K. T., Pollard, S. J., & Coulon, F. (2016). Insights into the biodegradation of weathered hydrocarbons in contaminated soils by bioaugmentation and nutrient stimulation. *Chemosphere*, 161, 300-307.

Johnson, R. L., Nurmi, J. T., O'Brien Johnson, G. S., Fan, D., O'Brien Johnson, R. L., Shi, Z., Salter-Blanc, A. J., Tratnyek, P. G., & Lowry, G. V. (2013). Field-scale transport and transformation of carboxymethylcellulose-stabilized nano zero-valent iron. *Environmental Science & Technology*, 47(3), 1573-1580.

- Joo, S. H., & Zhao, D. (2008). Destruction of lindane and atrazine using stabilized iron nanoparticles under aerobic and anaerobic conditions: Effects of catalyst and stabilizer. *Chemosphere*, 70(3), 418-425. <https://doi.org/10.1016/j.chemosphere.2007.06.070>.
- Kalantary, R. R., Mohseni-Bandpi, A., Esrafil, A., Nasser, S., Ashmogh, F. R., Jorfi, S., & Ja'fari, M. (2014). Effectiveness of biostimulation through nutrient content on the bioremediation of phenanthrene contaminated soil. *Journal of Environmental Health Science and Engineering*, 12(1), 1-9.
- Kalmykova, Y., Moona, N., Strömval, A., & Björklund, K. (2014). Sorption and degradation of petroleum hydrocarbons, polycyclic aromatic hydrocarbons, alkylphenols, bisphenol A and phthalates in landfill leachate using sand, activated carbon and peat filters. *Water Research*, 56, 246-257.
- Kamath, R., Rentz, J. A., Schnoor, J. L., & Alvarez, P. (2004). Phytoremediation of hydrocarbon-contaminated soils: principles and applications. *Studies in surface science and catalysis* (pp. 447-478). Elsevier.
- Kanel, S. R., Nepal, D., Manning, B., & Choi, H. (2007). Transport of surface-modified iron nanoparticle in porous media and application to arsenic (III) remediation. *Journal of Nanoparticle Research*, 9(5), 725-735. doi:10.1007/s11051-007-9225-7.
- Kanel, S. R., Goswami, R. R., Clement, T. P., Barnett, M. O., & Zhao, D. (2008). Two dimensional transport characteristics of surface stabilized zero-valent iron nanoparticles in porous media. *Environmental Science & Technology*, 42(3), 896-900. doi:10.1021/es071774j.
- Kang, S., & Choi, W. (2009). Oxidative degradation of organic compounds using zero-valent iron in the presence of natural organic matter serving as an electron shuttle. *Environmental Science & Technology*, 43(3), 878-883. doi:10.1021/es801705f.

- Kang, W., Cheong, J., Kim, K., Chae, H., & Chang, C. (2012). Restoration of petroleum-contaminated soils by field-scale soil washing system. Paper presented at the *International Conference on Environmental Science and Technology IPCBEE*, 30
- Kanga, S. A., Bonner, J. S., Page, C. A., Mills, M. A., & Autenrieth, R. L. (1997). Solubilization of naphthalene and methyl-substituted naphthalenes from crude oil using biosurfactants. *Environmental Science & Technology*, 31(2), 556-561.
- Kao, C. M., Chen, C. Y., Chen, S. C., Chien, H. Y., & Chen, Y. L. (2008). Application of in situ biosparging to remediate a petroleum-hydrocarbon spill site: Field and microbial evaluation. *Chemosphere*, 70(8), 1492-1499.
- Karanfil, T., & Kilduff, J. E. (1999). Role of granular activated carbon surface chemistry on the adsorption of organic compounds. 1. Priority pollutants. *Environmental Science & Technology*, 33(18), 3217-3224.
- Karn, B., Kuiken, T., & Otto, M. (2009). Nanotechnology and in situ remediation: a review of the benefits and potential risks. *Environmental Health Perspectives*, 117(12), 1813-1831.
- Kastanek, F., Topka, P., Soukup, K., Maleterova, Y., Demnerova, K., Kastanek, P., & Solcova, O. (2016). Remediation of contaminated soils by thermal desorption; effect of benzoyl peroxide addition. *Journal of Cleaner Production*, 125, 309-313.
- Kastner, M., & Miltner, A. (2016). Application of compost for effective bioremediation of organic contaminants and pollutants in soil. *Applied Microbiology and Biotechnology*, 100(8), 3433-3449.
- Kazemzadeh, Y., Shojaei, S., Riazi, M., & Sharifi, M. (2019). Review on application of nanoparticles for EOR purposes: A critical review of the opportunities and challenges. *Chinese Journal of Chemical Engineering*, 27(2), 237-246.

- Khan, F. I., Husain, T., & Hejazi, R. (2004). An overview and analysis of site remediation technologies. *Journal of Environmental Management*, 71(2), 95-122.
- Keenan, C. R., Goth-Goldstein, R., Lucas, D., & Sedlak, D. L. (2009). Oxidative stress induced by zero-valent iron nanoparticles and Fe (II) in human bronchial epithelial cells. *Environmental Science & Technology*, 43(12), 4555-4560.
- Kim, E., Le Thanh, T., & Chang, Y. (2014). Comparative toxicity of bimetallic Fe nanoparticles toward *Escherichia coli*: mechanism and environmental implications. *Environmental Science: Nano*, 1(3), 233-237.
- Kim, J., Lee, A. H., & Chang, W. (2018). Enhanced bioremediation of nutrient-amended, petroleum hydrocarbon-contaminated soils over a cold-climate winter: The rate and extent of hydrocarbon biodegradation and microbial response in a pilot-scale biopile subjected to natural seasonal freeze-thaw temperatures. *Science of the Total Environment*, 612, 903-913.
- Kim, J. Y., Park, H., Lee, C., Nelson, K. L., Sedlak, D. L., & Yoon, J. (2010). Inactivation of *Escherichia coli* by nanoparticulate zerovalent iron and ferrous ion. *Applied and Environmental Microbiology*, 76(22), 7668-7670.
- Kluck, C., & Achari, G. (2004). Chemical oxidation techniques for in situ remediation of hydrocarbon impacted soils. *Environmental Engineering*, 2004, 1-8.
- Kocur, C. M., Chowdhury, A. I., Sakulchaicharoen, N., Boparai, H. K., Weber, K. P., Sharma, P., Krol, M. M., Austrins, L., Peace, C., & Sleep, B. E. (2014). Characterization of nZVI mobility in a field scale test. *Environmental Science & Technology*, 48(5), 2862-2869. doi:10.1021/es4044209.

- Koran, K. M., Venosa, A. D., & Luedeker, C. (2008). Evaluation of detergency, interfacial tension and contact angle for five surface washing agents. Paper presented at the *International Oil Spill Conference, 2008*(1) 785-789.
- Kretzschmar, R., Barmettler, K., Grolimund, D., Yan, Y., Borkovec, M., & Sticher, H. (1997). Experimental determination of colloid deposition rates and collision efficiencies in natural porous media. *Water Resources Research*, 33(5), 1129-1137. doi:10.1029/97WR00298.
- Kretzschmar, R., Borkovec, M., Grolimund, D., & Elimelech, M. (1999). Mobile subsurface colloids and their role in contaminant transport. *Advances in Agronomy*, 66, 121-193. doi:10.1016/S0065-2113(08)60427-7.
- Kumar, A., Prasad, M. N., Maiti, S. K., & Favas, P. J. (2018). Mycoremediation for mine site rehabilitation. *Bio-Geotechnologies for Mine Site Rehabilitation*. Elsevier, 233-260.
- Kuyukina, M. S., Ivshina, I. B., Makarov, S. O., Litvinenko, L. V., Cunningham, C. J., & Philp, J. C. (2005). Effect of biosurfactants on crude oil desorption and mobilization in a soil system. *Environment International*, 31(2), 155-161.
- Kvesitadze, E., Sadunishvili, T., & Kvesitadze, G. (2009). Mechanisms of organic contaminants uptake and degradation in plants. *World Acad Sci Eng Technol*, 55(6), 458-468.
- Lai, C., Huang, Y., Wei, Y., & Chang, J. (2009). Biosurfactant-enhanced removal of total petroleum hydrocarbons from contaminated soil. *Journal of Hazardous Materials*, 167(1-3), 609-614.
- Lawal, A. T. (2017). Polycyclic aromatic hydrocarbons. A review. *Cogent Environmental Science*, 3(1), 1339841.

- Lee, C., Kim, J. Y., Lee, W. I., Nelson, K. L., Yoon, J., & Sedlak, D. L. (2008). Bactericidal effect of zero-valent iron nanoparticles on *Escherichia coli*. *Environmental Science & Technology*, 42(13), 4927-4933. doi:10.1021/es800408u.
- Li, Q., Chen, X., Zhuang, J., & Chen, X. (2016). Decontaminating soil organic pollutants with manufactured nanoparticles. *Environmental Science and Pollution Research*, 23(12), 11533-11548.
- Li, X., Du, Y., Wu, G., Li, Z., Li, H., & Sui, H. (2012). Solvent extraction for heavy crude oil removal from contaminated soils. *Chemosphere*, 88(2), 245-249.
- Li, Z., Greden, K., Alvarez, P. J., Gregory, K. B., & Lowry, G. V. (2010). Adsorbed polymer and NOM limits adhesion and toxicity of nano scale zerovalent iron to *E. coli*. *Environmental Science & Technology*, 44(9), 3462-3467.
- Liang, C. (2010). Cationic and Anionic Carbon Dioxide Responsive Switchable Surfactants. MS Thesis, Queen's University, Kingston, Ontario, Canada.
- Liang, Q., & Zhao, D. (2014). Immobilization of arsenate in a sandy loam soil using starch-stabilized magnetite nanoparticles. *Journal of Hazardous Materials*, 271, 16-23.
- Liao, S., Ghosh, A., Becker, M. D., Abriola, L. M., Cápiro, N. L., Fortner, J. D., & Pennell, K. D. (2021). Effect of rhamnolipid biosurfactant on transport and retention of iron oxide nanoparticles in water-saturated quartz sand. *Environmental Science: Nano*, 8(1), 311-327.
- Lim, M. W., Von Lau, E., & Poh, P. E. (2016). A comprehensive guide of remediation technologies for oil contaminated soil—present works and future directions. *Marine Pollution Bulletin*, 109(1), 14-45.

- Limbach, L. K., Wick, P., Manser, P., Grass, R. N., Bruinink, A., & Stark, W. J. (2007). Exposure of engineered nanoparticles to human lung epithelial cells: influence of chemical composition and catalytic activity on oxidative stress. *Environmental Science & Technology*, *41*(11), 4158-4163.
- Lin, C., Lee, C., & Chiu, W. (2005). Preparation and properties of poly(acrylic acid) oligomer stabilized superparamagnetic ferrofluid. *Journal of Colloid and Interface Science*, *291*(2), 411-420. <https://doi.org/10.1016/j.jcis.2005.05.023>
- Liu, G., Zhong, H., Yang, X., Liu, Y., Shao, B., & Liu, Z. (2018). Advances in applications of rhamnolipids biosurfactant in environmental remediation: A review. *Biotechnology and Bioengineering*, *115*(4), 796-814.
- Liu, J., Wei, K., Xu, S., Cui, J., Ma, J., Xiao, X., Xi, B., & He, X. (2020). Surfactant-enhanced remediation of oil-contaminated soil and groundwater: A review. *Science of the Total Environment*, 144142.
- Liu, J., Zhang, H., Yao, Z., Li, X., & Tang, J. (2019). Thermal desorption of PCBs contaminated soil with calcium hydroxide in a rotary kiln. *Chemosphere*, *220*, 1041-1046.
- Lowry, G. V., & Reinhard, M. (1999). Hydrodehalogenation of 1-to 3-carbon halogenated organic compounds in water using a palladium catalyst and hydrogen gas. *Environmental Science & Technology*, *33*(11), 1905-1910.
- Lozhkomoev, A. S., Lerner, M. I., Pervikov, A. V., Kazantsev, S. O., & Fomenko, A. N. (2018). Development of Fe/Cu and Fe/Ag bimetallic nanoparticles for promising biodegradable materials with antimicrobial effect. *Nanotechnologies in Russia*, *13*(1), 18-25.
- Luna, M., Gastone, F., Tosco, T., Sethi, R., Velimirovic, M., Gemoets, J., Muyshondt, R., Sapion, H., Klaas, N., & Bastiaens, L. (2015). Pressure-controlled injection of guar gum stabilized

microscale zerovalent iron for groundwater remediation. *Journal of Contaminant Hydrology*, 181, 46-58. doi:10.1016/j.jconhyd.2015.04.007.

Ma, J., Yang, Y., Dai, X., Li, C., Wang, Q., Chen, C., Yan, G., & Guo, S. (2016). Bioremediation enhances the pollutant removal efficiency of soil vapor extraction (SVE) in treating petroleum drilling waste. *Water, Air, & Soil Pollution*, 227(12), 1-10.

Ma, X., Gurung, A., & Deng, Y. (2013). Phytotoxicity and uptake of nanoscale zero-valent iron (nZVI) by two plant species. *Science of the Total Environment*, 443, 844-849.

Maier, R. M., & Soberon-Chavez, G. (2000). Pseudomonas aeruginosa rhamnolipids: biosynthesis and potential applications. *Applied Microbiology and Biotechnology*, 54(5), 625-633.

Makkar, R. S., & Rockne, K. J. (2003). Comparison of synthetic surfactants and biosurfactants in enhancing biodegradation of polycyclic aromatic hydrocarbons. *Environmental Toxicology and Chemistry: An International Journal*, 22(10), 2280-2292.

Maletić, S., Dalmacija, B., & Rončević, S. (2013). Petroleum hydrocarbon biodegradability in soil—implications for bioremediation. *Hydrocarbon*, 43.

Mancera-López, M. E., Esparza-García, F., Chávez-Gómez, B., Rodríguez-Vázquez, R., Saucedo-Castaneda, G., & Barrera-Cortés, J. (2008). Bioremediation of an aged hydrocarbon-contaminated soil by a combined system of biostimulation–bioaugmentation with filamentous fungi. *International Biodeterioration & Biodegradation*, 61(2), 151-160.

Mao, J., & Guan, W. (2016). Fungal degradation of polycyclic aromatic hydrocarbons (PAHs) by *Scopulariopsis brevicaulis* and its application in bioremediation of PAH-contaminated soil. *Acta Agriculturae Scandinavica, Section B—Soil & Plant Science*, 66(5), 399-405.

Mao, X., Jiang, R., Xiao, W., & Yu, J. (2015). Use of surfactants for the remediation of contaminated soils: a review. *Journal of Hazardous Materials*, 285, 419-435.

- Margesin, R., Labbe, D., Schinner, F., Greer, C. W., & Whyte, L. G. (2003). Characterization of hydrocarbon-degrading microbial populations in contaminated and pristine alpine soils. *Applied and Environmental Microbiology*, 69(6), 3085-3092.
- Mar Gil-Díaz, M., Pérez-Sanz, A., Angeles Vicente, M., & Carmen Lobo, M. (2014). Immobilisation of Pb and Zn in Soils Using Stabilised Zero-valent Iron Nanoparticles: Effects on Soil Properties. *Clean–Soil, Air, Water*, 42(12), 1776-1784.
- McCutcheon, S. C., & Schnoor, J. L. (2004). *Phytoremediation: transformation and control of contaminants*. John Wiley & Sons.
- Meegoda, J. N. (1999). Stabilization/solidification of petroleum-contaminated soils with asphalt emulsions. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, 3(1), 46-55.
- Megharaj, M., & Naidu, R. (2017). Soil and brownfield bioremediation. *Microbial Biotechnology*, 10(5), 1244-1249.
- Mendez-Natera, J. R., Roque, K. Z. C., & Otahola-Gómez, V. A. (2004). Effect of oil concentration and contamination period on seed germination of corn (*Zea mays* L.) cv. Himeca 95. Universidad de Oriente Press. ISSN: 1317-9152.
- Meskar, M. (2018). Treatment of petroleum contaminated soil using supercritical fluid extraction (SFE) technology. *Ph.D. Thesis. Ottawa-Carleton Institute for Civil Engineering, University of Ottawa, Canada*.
- Miyazawa, T., Itaya, M., Burdeos, G. C., Nakagawa, K., & Miyazawa, T. (2021). A Critical Review of the Use of Surfactant-Coated Nanoparticles in Nanomedicine and Food Nanotechnology. *International Journal of Nanomedicine*, 16, 3937.

Moldes, A. B., Paradelo, R., Rubinos, D., Devesa-Rey, R., Cruz, J. M., & Barral, M. T. (2011). Ex situ treatment of hydrocarbon-contaminated soil using biosurfactants from *Lactobacillus pentosus*. *Journal of Agricultural and Food Chemistry*, 59(17), 9443-9447.

Moldoveanu, S. C. (2019). Chapter 2 - Pyrolysis of Hydrocarbons. In S. C. Moldoveanu (Ed.), *Pyrolysis of Organic Molecules (Second Edition)* (pp. 35-161). Elsevier. <https://doi.org/10.1016/B978-0-444-64000-0.00002-0>.

Morales-Luckie, R.A., Sanchez-Mendieta, V., Arenas-Alatorre, J.A., López-Castañares, R., Perez-Mazariego, J.L., Marquina-Fabrega, V., and Gómez, R.W. (2008). One-step aqueous synthesis of stoichiometric Fe–Cu nanoalloy. *Materials Letters*, 62(26):4195-4197. <https://doi.org/10.1016/j.matlet.2008.06.039>.

Morselli, L., De Robertis, C., Luzi, J., Passarini, F., & Vassura, I. (2008). Environmental impacts of waste incineration in a regional system (Emilia Romagna, Italy) evaluated from a life cycle perspective. *Journal of Hazardous Materials*, 159(2-3), 505-511.

Morselli, L., Setti, L., Iannuccilli, A., Maly, S., Dinelli, G., & Quattroni, G. (1999). Supercritical fluid extraction for the determination of petroleum hydrocarbons in soil. *Journal of Chromatography A*, 845(1-2), 357-363.

Mueller, N. C., Braun, J., Bruns, J., Černík, M., Rissing, P., Rickerby, D., & Nowack, B. (2012). Application of nanoscale zero valent iron (NZVI) for groundwater remediation in Europe. *Environmental Science and Pollution Research*, 19(2), 550-558.

Mueller, N. C., & Nowack, B. (2010). Nanoparticles for remediation: solving big problems with little particles. *Elements*, 6(6), 395-400.

Mulligan, C. N. (2005). Environmental applications for biosurfactants. *Environmental Pollution*, 133(2), 183-198. doi:10.1016/j.envpol.2004.06.009.

- Mulligan, C. N. (2007). Rhamnolipid biosurfactants: solubility and environmental issues. *Thermodynamics, solubility and environmental issues*. Elsevier, 279-298.
- Mulligan, C. N. (2021). Sustainable remediation of contaminated soil using biosurfactants. *Frontiers in Bioengineering and Biotechnology*, 9, 195. doi:10.3389/fbioe.2021.635196.
- Mulligan, C. N., Sharma, S. K., & Mudhoo, A. (2019). Biosurfactants: research trends and applications. CRC press, Boca Raton.
- Mulligan, C. N., Gibbs, B. F. (2004). Types, production and applications of biosurfactants. *Proceedings-Indian National Science Academy Part B*, 70(1), 31-56.
- Mulligan, C. N., Sharma, S. K., & Mudhoo, A. (2019). Biosurfactants: research trends and applications. CRC press, Boca Raton.
- Mulligan, C. N., Yong, R. N., & Gibbs, B. F. (2001). Surfactant-enhanced remediation of contaminated soil: a review. *Engineering Geology*, 60(1-4), 371-380.
- Murgueitio, E., Cumbal, L., Abril, M., Izquierdo, A., Debut, A., & Tinoco, O. (2018). Green synthesis of iron nanoparticles: Application on the removal of petroleum oil from contaminated water and soils. *Journal of Nanotechnology*, 2018 (4), 1-8.
- Murugesan, K., Bokare, V., Jeon, J., Kim, E., Kim, J., & Chang, Y. (2011). Effect of Fe–Pd bimetallic nanoparticles on *Sphingomonas* sp. PH-07 and a nano-bio hybrid process for triclosan degradation. *Bioresource Technology*, 102(10), 6019-6025.
- Nagarajan, R., & Wang, C. (2000). Theory of surfactant aggregation in water/ethylene glycol mixed solvents. *Langmuir*, 16(12), 5242-5251.

- Nasehi, S. A., Uromeihy, A., Nikudel, M. R., & Morsali, A. (2016). Use of nanoscale zero-valent iron and nanoscale hydrated lime to improve geotechnical properties of gas oil contaminated clay: a comparative study. *Environmental Earth Sciences*, 75(9), 733. doi:10.1007/s12665-016-5443-6.
- Nel, A., Xia, T., Mädler, L., & Li, N. (2006). Toxic potential of materials at the nanolevel. *Science*, 311(5761), 622-627.
- Njoku, K. L., Nomba, E. U., & Olatunde, A. M. (2017). Vermiremediation of crude oil contaminated soil using *Eudrillus euginae* and *Lumbricus terrestris*. *Journal of Biological and Environmental Sciences*, 11(31), 43-50.
- Njoku, K. L., Yussuf, A., Akinola, M. O., Adesuyi, A. A., Jolaoso, A. O., & Adedokun, A. H. (2016). Mycoremediation of petroleum hydrocarbon polluted soil by *Pleurotus pulmonarius*. *Ethiopian Journal of Environmental Studies and Management*, 9(1), 865-875.
- Nguyen, T. T., & Sabatini, D. A. (2011). Characterization and emulsification properties of rhamnolipid and sophorolipid biosurfactants and their applications. *International Journal of Molecular Sciences*, 12(2), 1232-1244.
- Nwankwegu, A. S., & Onwosi, C. O. (2017). Bioremediation of gasoline contaminated agricultural soil by bioaugmentation. *Environmental Technology & Innovation*, 7, 1-11.
- Ogunneye, A. L., Omoboyowa, D. A., Sonibare, A. L., Adebusuyi, A. J., & Faniran, T. P. (2014). Hepatotoxic and nephrotoxic effects of petroleum fumes on petrol attendants in Ibadan, Nigeria. *Nigerian Journal of Basic and Applied Sciences*, 22(3-4), 57-62.
- Olasanmi, I. O., & Thring, R. W. (2020). Evaluating rhamnolipid-enhanced washing as a first step in remediation of drill cuttings and petroleum-contaminated soils. *Journal of Advanced Research*, 21, 79-90.

- Ossai, I. C., Ahmed, A., Hassan, A., & Hamid, F. S. (2020). Remediation of soil and water contaminated with petroleum hydrocarbon: A review. *Environmental Technology & Innovation*, 17, 100526. doi:10.1016/j.eti.2019.100526.
- Pacwa-Płociniczak, M., Płaza, G. A., Piotrowska-Seget, Z., & Cameotra, S. S. (2011). Environmental applications of biosurfactants: recent advances. *International Journal of Molecular Sciences*, 12(1), 633-654.
- Palmroth, M. R., Pichtel, J., & Puhakka, J. A. (2002). Phytoremediation of subarctic soil contaminated with diesel fuel. *Bioresource Technology*, 84(3), 221-228.
- Paria, S. (2008). Surfactant-enhanced remediation of organic contaminated soil and water. *Advances in Colloid and Interface Science*, 138(1), 24-58. doi:10.1016/j.cis.2007.11.001.
- Pardoe, H., Chua-anusorn, W., St. Pierre, T. G., & Dobson, J. (2001). Structural and magnetic properties of nanoscale iron oxide particles synthesized in the presence of dextran or polyvinyl alcohol. *Journal of Magnetism and Magnetic Materials*, 225(1), 41-46. [https://doi.org/10.1016/S0304-8853\(00\)01226-9](https://doi.org/10.1016/S0304-8853(00)01226-9)
- Parish, C. (2013). Agency for toxic substances and disease registry. *U.S. Department of health and human services*. <https://www.atsdr.cdc.gov/index.html>. Accessed 08 May 2022.
- Paustenbach, D. J., Panko, J. M., Scott, P. K., & Unice, K. M. (2006). A methodology for estimating human exposure to perfluorooctanoic acid (PFOA): a retrospective exposure assessment of a community (1951–2003). *Journal of Toxicology and Environmental Health, Part A*, 70(1), 28-57.
- Pekdemir, T., Copur, M., & Urum, K. (2005). Emulsification of crude oil–water systems using biosurfactants. *Process Safety and Environmental Protection*, 83(1), 38-46.

- Pawlett, M., Ritz, K., Dorey, R. A., Rocks, S., Ramsden, J., & Harris, J. A. (2013). The impact of zero-valent iron nanoparticles upon soil microbial communities is context dependent. *Environmental Science and Pollution Research*, 20(2), 1041-1049.
- Pennell, K. D., Abriola, L. M., & Weber Jr, W. J. (1993). Surfactant-enhanced solubilization of residual dodecane in soil columns. 1. Experimental investigation. *Environmental Science & Technology*, 27(12), 2332-2340. doi:10.1021/es00048a005.
- Pilon-Smits, E. (2005). Phytoremediation. *Annual Reviews of Plant Biology*, 56, 15-39.
- Phenrat, T., Liu, Y., Tilton, R. D., & Lowry, G. V. (2009a). Adsorbed polyelectrolyte coatings decrease Fe⁰ nanoparticle reactivity with TCE in water: conceptual model and mechanisms. *Environmental Science & Technology*, 43(5), 1507-1514.
- Phenrat, T., Long, T. C., Lowry, G. V., & Veronesi, B. (2009b). Partial oxidation (“aging”) and surface modification decrease the toxicity of nanosized zerovalent iron. *Environmental Science & Technology*, 43(1), 195-200.
- Poi, G., Aburto-Medina, A., Mok, P. C., Ball, A. S., & Shahsavari, E. (2017). Large scale bioaugmentation of soil contaminated with petroleum hydrocarbons using a mixed microbial consortium. *Ecological Engineering*, 102, 64-71.
- Prakash, V., Saxena, S., Sharma, A., Singh, S., & Singh, S. K. (2015). Treatment of oil sludge contamination by composting. *Journal of Bioremediation & Biodegradation*, 6(3), 1-6.
- Priyadarshane, M., Mahto, U., & Das, S. (2022). Mechanism of toxicity and adverse health effects of environmental pollutants. *Microbial Biodegradation and Bioremediation*. Elsevier, 33-53.
- Quinn, J., Elliott, D., O'Hara, S., & Billow, A. (2009). Use of nanoscale iron and bimetallic particles for environmental remediation: A review of field-scale applications. *ACS Symposium Series*, 1027(15), 263-283. doi:10.1021/bk-2009-1027.ch015.

- Quinn, J., Geiger, C., Clausen, C., Brooks, K., Coon, C., O'Hara, S., Krug, T., Major, D., Yoon, W., & Gavaskar, A. (2005). Field demonstration of DNAPL dehalogenation using emulsified zero-valent iron. *Environmental Science & Technology*, 39(5), 1309-1318. doi:10.1021/es0490018.
- Rahman, K., Banat, I. M., Thahira, J., Thayumanavan, T., & Lakshmanaperumalsamy, P. (2002). Bioremediation of gasoline contaminated soil by a bacterial consortium amended with poultry litter, coir pith and rhamnolipid biosurfactant. *Bioresource Technology*, 81(1), 25-32.
- Ramirez, M. I., Arevalo, A. P., Sotomayor, S., & Bailon-Moscoso, N. (2017). Contamination by oil crude extraction–Refinement and their effects on human health. *Environmental Pollution*, 231, 415-425. doi:10.1016/j.envpol.2017.08.017.
- Ren, X., Zeng, G., Tang, L., Wang, J., Wan, J., Wang, J., Deng, Y., Liu, Y., & Peng, B. (2018). The potential impact on the biodegradation of organic pollutants from composting technology for soil remediation. *Waste Management*, 72, 138-149.
- Rock, S. (1997). Phytoremediation. *Standard Handbook of Hazardous Waste Treatment and Disposal*, 93-112.
- Rosen, M. J., & Kunjappu, J. T. (2012). Surfactants and interfacial phenomena. *John Wiley & Sons*.
- Rusin, M., Gospodarek, J., & Nadgórska-Socha, A. (2015). The effect of petroleum-derived substances on the growth and chemical composition of *Vicia faba L.* *Polish Journal of Environmental Studies*, 24(5), 2157-2166. doi:10.15244/pjoes/41378.
- Saborimanesh, N., & Mulligan, C. N. (2018). Dispersion of weathered biodiesel, diesel, and light crude oil in the presence of sophorolipid biosurfactant in seawater. *Journal of Environmental Engineering*, 144(5), 04018028.

- Saccà, M. L., Fajardo, C., Costa, G., Lobo, C., Nande, M., & Martín, M. (2014). Integrating classical and molecular approaches to evaluate the impact of nanosized zero-valent iron (nZVI) on soil organisms. *Chemosphere*, *104*, 184-189.
- Saccà, M. L., Fajardo, C., Nande, M., & Martín, M. (2013). Effects of nano zero-valent iron on *Klebsiella oxytoca* and stress response. *Microbial Ecology*, *66*(4), 806-812.
- Saleh, N., Sirk, K., Liu, Y., Phenrat, T., Dufour, B., Matyjaszewski, K., Tilton, R. D., & Lowry, G. V. (2007). Surface modifications enhance nanoiron transport and NAPL targeting in saturated porous media. *Environmental Engineering Science*, *24*(1), 45-57. doi:10.1089/ees.2007.24.45.
- Sang, L., Wang, G., Liu, L., Bian, H., Jiang, L., Wang, H., Zhang, Y., Zhang, W., Peng, C., & Wang, X. (2021). Immobilization of Ni (II) at three levels of contaminated soil by rhamnolipids modified nano zero valent iron (RL@ nZVI): Effects and mechanisms. *Chemosphere*, *276*, 130139.
- Sankula, K., Kota, S., & Nissankarrao, S. (2014). Supercritical fluid technology: green chemistry for the 21st century. *The Pharma Innovation*, *3*(5, Part A), 19.
- Saum, L., Jiménez, M. B., & Crowley, D. (2018). Influence of biochar and compost on phytoremediation of oil-contaminated soil. *International Journal of Phytoremediation*, *20*(1), 54-60.
- Sayara, T., Borràs, E., Caminal, G., Sarrà, M., & Sánchez, A. (2011). Bioremediation of PAHs-contaminated soil through composting: Influence of bioaugmentation and biostimulation on contaminant biodegradation. *International Biodeterioration & Biodegradation*, *65*(6), 859-865.
- Schaefer, M., & Juliane, F. (2007). The influence of earthworms and organic additives on the biodegradation of oil contaminated soil. *Applied Soil Ecology*, *36*(1), 53-62.

- Schnoor, J. L., Light, L. A., McCutcheon, S. C., Wolfe, N. L., & Carreia, L. H. (1995). Phytoremediation of organic and nutrient contaminants. *Environmental Science & Technology*, 29(7), 318-323.
- Schrick, B., Blough, J. L., Jones, A. D., & Mallouk, T. E. (2002). Hydrodechlorination of trichloroethylene to hydrocarbons using bimetallic nickel– iron nanoparticles. *Chemistry of Materials*, 14(12), 5140-5147.
- Shan, B., Zhang, Y., Cao, Q., Kang, Z., & Li, S. (2014). Growth responses of six leguminous plants adaptable in Northern Shaanxi to petroleum contaminated soil. *Huan Jing Ke Xue*, 35(3), 1125-1130.
- Sharma, H. D., & Reddy, K. R. (2004). Geoenvironmental engineering: site remediation, waste containment, and emerging waste management technologies. *John Wiley & Sons*. ISBN: 978-0-471-21599-8.
- Sharma, N., Ghosh, A., Fortner, J. D., & Giammar, D. E. (2020). Modeling performance of rhamnolipid-coated engineered magnetite nanoparticles for U (vi) sorption and separation. *Environmental Science: Nano*, 7(7), 2010-2020.
- Silva, A., Delerue-Matos, C., & Fiúza, A. (2005). Use of solvent extraction to remediate soils contaminated with hydrocarbons. *Journal of Hazardous Materials*, 124(1-3), 224-229.
- Silva, M. G., Volcão, L. M., Seus, E. R., Machado, M. I., Mirlean, N., Baisch, P., & da Silva Júnior, F. (2021). Comparative evaluation of different bioremediation techniques for crude oil-contaminated soil. *International Journal of Environmental Science and Technology*, 1-12.
- Simpanen, S., Dahl, M., Gerlach, M., Mikkonen, A., Malk, V., Mikola, J., & Romantschuk, M. (2016). Biostimulation proved to be the most efficient method in the comparison of in situ soil

remediation treatments after a simulated oil spill accident. *Environmental Science and Pollution Research*, 23(24), 25024-25038.

Sin, H. S., & Gwon, O. S. (2000). The simultaneous analysis of benzene, toluene, ethylbenzene, o, m, p-xylenes and total petroleum hydrocarbons in soil by GC-FID after ultra-sonication. *Bulletin of the Korean Chemical Society*, 21(11), 1101-1105.

Singh, B., Bhattacharya, A., Channashettar, V. A., Jeyaseelan, C. P., Gupta, S., Sarma, P. M., Mandal, A. K., & Lal, B. (2012). Biodegradation of oil spill by petroleum refineries using consortia of novel bacterial strains. *Bulletin of Environmental Contamination and Toxicology*, 89(2), 257-262.

Singh, R., Manickam, N., Mudiam, M. K. R., Murthy, R. C., & Misra, V. (2013). An integrated (nano-bio) technique for degradation of γ -HCH contaminated soil. *Journal of Hazardous Materials*, 258, 35-41.

Sinha, R. K., Bharambe, G., & Ryan, D. (2008). Converting wasteland into wonderland by earthworms—a low-cost nature's technology for soil remediation: a case study of vermiremediation of PAHs contaminated soil. *The Environmentalist*, 28(4), 466-475.

Soares, A., Ramos, S., Albergaria, T., & Delerue-Matos, C. (2018). Green zero valent iron nanoparticles dispersion through a sandy column using different injection sequences. *Science of the Total Environment*, 637-638, 935-942. <https://doi.org/10.1016/j.scitotenv.2018.05.096>.

Song, H., & Carraway, E. R. (2005). Reduction of chlorinated ethanes by nanosized zero-valent iron: kinetics, pathways, and effects of reaction conditions. *Environmental Science & Technology*, 39(16), 6237-6245.

- Song, S., Su, Y., Adeleye, A. S., Zhang, Y., & Zhou, X. (2017). Optimal design and characterization of sulfide-modified nanoscale zerovalent iron for diclofenac removal. *Applied Catalysis B: Environmental*, 201, 211-220.
- Souza, E. C., Vessoni-Penna, T. C., & de Souza Oliveira, Ricardo Pinheiro. (2014). Biosurfactant-enhanced hydrocarbon bioremediation: An overview. *International Biodeterioration & Biodegradation*, 89, 88-94.
- Speight, J. G. (2006). The chemistry and technology of petroleum. *CRC press*. ISBN:9780429118494. doi:10.1201/9781420008388.
- Størdal, I. F., Olsen, A. J., Jenssen, B. M., Netzer, R., Altin, D., & Brakstad, O. G. (2015). Biotransformation of petroleum hydrocarbons and microbial communities in seawater with oil dispersions and copepod feces. *Marine Pollution Bulletin*, 101(2), 686-693.
- Straube, W. L., Nestler, C. C., Hansen, L. D., Ringleberg, D., Pritchard, P. H., & Jones-Meehan, J. (2003). Remediation of polyaromatic hydrocarbons (PAHs) through landfarming with biostimulation and bioaugmentation. *Acta Biotechnologica*, 23(2-3), 179-196.
- Su, C., Puls, R. W., Krug, T. A., Watling, M. T., O'Hara, S. K., Quinn, J. W., & Ruiz, N. E. (2013). Travel distance and transformation of injected emulsified zerovalent iron nanoparticles in the subsurface during two and half years. *Water Research*, 47(12), 4095-4106. doi:10.1016/j.watres.2012.12.042.
- Su, Y., Jassby, D., Zhang, Y., Keller, A. A., & Adeleye, A. S. (2020). Comparison of the colloidal stability, mobility, and performance of nanoscale zerovalent iron and sulfidated derivatives. *Journal of Hazardous Materials*, 396, 122691.
- Swiatkowska-Warkocka, Z. (2021). Bimetal CuFe Nanoparticles—Synthesis, Properties, and Applications. *Applied Sciences*, 11(5), 1978.

- Tabrizian, P., Ma, W., Bakr, A., & Rahaman, M. S. (2019). pH-sensitive and magnetically separable Fe/Cu bimetallic nanoparticles supported by graphene oxide (GO) for high-efficiency removal of tetracyclines. *Journal of Colloid and Interface Science*, 534, 549-562.
- Tang, J., Lu, X., Sun, Q., & Zhu, W. (2012). Aging effect of petroleum hydrocarbons in soil under different attenuation conditions. *Agriculture, Ecosystems & Environment*, 149, 109-117.
- Thome, A., Reginatto, C., Cecchin, I., & Colla, L. M. (2014). Bioventing in a residual clayey soil contaminated with a blend of biodiesel and diesel oil. *Journal of Environmental Engineering*, 140(11), 06014005.
- Tilston, E. L., Collins, C. D., Mitchell, G. R., Princiville, J., & Shaw, L. J. (2013). Nanoscale zerovalent iron alters soil bacterial community structure and inhibits chloroaromatic biodegradation potential in Aroclor 1242-contaminated soil. *Environmental Pollution*, 173, 38-46.
- Tosco, T., Papini, M. P., Viggi, C. C., & Sethi, R. (2014). Nanoscale zerovalent iron particles for groundwater remediation: a review. *Journal of Cleaner Production*, 77, 10-21.
- Tratnyek, P. G., Salter-Blanc, A. J., Nurmi, J. T., Amonette, J. E., Liu, J., Wang, C., Dohnalkova, A., & Baer, D. R. (2011). Reactivity of zerovalent metals in aquatic media: Effects of organic surface coatings. *Aquatic Redox Chemistry* (pp. 381-406). ACS Publications.
- Trulli, E., Morosini, C., Rada, E. C., & Torretta, V. (2016). Remediation in situ of hydrocarbons by combined treatment in a contaminated alluvial soil due to an accidental spill of LNAPL. *Sustainability*, 8(11), 1086.
- Tuhuloula, A., Altway, A., Juliastuti, S. R., & Suprpto, S. (2018). Biodegradation of soils contaminated with naphthalene in petroleum hydrocarbons using bioslurry reactors. Paper presented at the *IOP Conference Series: Earth and Environmental Science*, 175(1) 012014.

Ulfig, K., Plaza, G., Worsztynowicz, A., Manko, T., Tien, A. J., & Brigmon, R. L. (2003). Keratinolytic Fungi as Indicators of Hydrocarbon Contamination and Bioremediation Progress in a Petroleum Refinery. *Polish Journal of Environmental Studies*, 12(2), 245-250.

Ulfig, K., Przysaś, W., Płaza, G., & Miksch, K. (2006). Biodegradation of petroleum hydrocarbons by keratinolytic fungi. Soil and water pollution monitoring, protection and remediation. *Springer*, 553-564.

Urum, K., Pekdemir, T., & Gopur, M. (2003). Optimum conditions for washing of crude oil-contaminated soil with biosurfactant solutions. *Process Safety and Environmental Protection*, 81(3), 203-209. doi:10.1205/095758203765639906.

Urum, K., & Pekdemir, T. (2004). Evaluation of biosurfactants for crude oil contaminated soil washing. *Chemosphere*, 57(9), 1139-1150. doi:10.1016/j.chemosphere.2004.07.048.

Urum, K., Pekdemir, T., & Çopur, M. (2004). Surfactants treatment of crude oil contaminated soils. *Journal of Colloid and Interface Science*, 276(2), 456-464. doi:10.1016/j.jcis.2004.03.057.

US Environmental Protection Agency, 2001. A Citizen's Guide to Solvent Extraction. US Environmental Protection Agency, Washington, DC. <https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=10002SQ1.TXT>. Accessed 08 May 2022.

US Environmental Protection Agency (2005). Toxics release inventory (TRI) report. <https://www.epa.gov/toxics-release-inventory-tri-program/2005-tri-public-data-release-materials>. Accessed 06 May 2022.

US Environmental Protection Agency, 2006. In-situ treatment technologies for contaminated soil. In: Engineering Forum Issue Paper. Solid Wates and Emergency Response 5203P, EPA 542/F-06/013.

US Environmental Protection Agency (2007). Treatment technologies for site cleanup: Annual status report. <https://www.epa.gov/remedytech/treatment-technologies-site-cleanup-annual-status-report-twelfth-edition>. Accessed 18 December 2021.

Valentin, L., Nousiainen, A., & Mikkonen, A. (2013). Introduction to organic contaminants in soil: concepts and risks. *Emerging Organic Contaminants in Sludges* (pp. 1-29). Springer. doi:10.1007/698_2012_208

Van der Heul, R M. (2011). Environmental degradation of petroleum hydrocarbons. Faculty of Medicine Master Thesis, Utrecht University.

Varanasi, P., Fullana, A., & Sidhu, S. (2007). Remediation of PCB contaminated soils using iron nano-particles. *Chemosphere*, 66(6), 1031-1038. doi:10.1016/j.chemosphere.2006.07.036.

Varjani, S. J. (2017). Microbial degradation of petroleum hydrocarbons. *Bioresource Technology*, 223, 277-286.

Vásquez-Murrieta, M. S., Hernández-Hernández, O. J., Cruz-Maya, J. A., Cancino-Díaz, J. C., & Jan-Roblero, J. (2016). Approaches for removal of PAHs in soils: Bioaugmentation, biostimulation and bioattenuation. *Soil Contamination-Current Consequences and further Solutions*, 329-314.

Vázquez-Luna, D. (2014). Chronic toxicity of weathered oil-contaminated soil. *Environmental risk assessment of soil contamination*, 8-103. doi:10.5772/57253.

Vidonish, J. E., Zygourakis, K., Masiello, C. A., Sabadell, G., & Alvarez, P. J. (2016a). Thermal treatment of hydrocarbon-impacted soils: a review of technology innovation for sustainable remediation. *Engineering*, 2(4), 426-437.

- Vidonish, J. E., Zygourakis, K., Masiello, C. A., Gao, X., Mathieu, J., & Alvarez, P. J. (2016b). Pyrolytic treatment and fertility enhancement of soils contaminated with heavy hydrocarbons. *Environmental Science & Technology*, 50(5), 2498-2506.
- Viisimaa, M., Karpenko, O., Novikov, V., Trapido, M., & Goi, A. (2013). Influence of biosurfactant on combined chemical–biological treatment of PCB-contaminated soil. *Chemical Engineering Journal*, 220, 352-359. doi:10.1016/j.cej.2013.01.041.
- Vin, N., Battin-Leclerc, F., Le Gall, H., Sebbar, N., Bockhorn, H., Trimis, D., & Herbinet, O. (2019). A study of chlorobenzene pyrolysis. *Proceedings of the Combustion Institute*, 37(1), 399-407.
- Vogel, M., Georgi, A., Kopinke, F., & Mackenzie, K. (2019). Sulfidation of ZVI/AC composite leads to highly corrosion-resistant nanoremediation particles with extended life-time. *Science of the Total Environment*, 665, 235-245.
- Vu, K. A. (2013). Rhamnolipid biosurfactant adsorption and transport in biochar amended agricultural soil. *MS Thesis*, Florida State University, Florida, United States.
- Vu, K. A., & Mulligan, C. N. (2020). Synthesis and application of nanoparticles and biosurfactant for oil-contaminated soil removal. *Paper presented at the 73rd Canadian Geotechnical Conference*, 113. <https://geovirtual2020.ca/wp-content/files/113.pdf>. Accessed 07 December 2022.
- Vu, K. A. and Mulligan, C. N. (2022a). Remediation of oil-contaminated soil using Fe/Cu nanoparticles and biosurfactants. *Environmental Technology*, 44(1), 1-13.
- Vu, K. A. and Mulligan, C. N. (2022b). Remediation of organic contaminated soil by Fe-based nanoparticles and surfactants: A review. *Environmental Technology Reviews*, 12(1), 1-26.

Vu, K. A. and Mulligan, C. N. (2022c). Oil removal from contaminated soil by biosurfactants and Fe/Cu nanoparticles. *Paper presented at the Canadian Society for Civil Engineering Annual Conference (CSCE 2022)*.

Vu, K. A. and Mulligan, C. N. (2022d). Preparation of a biosurfactant foam/nanoparticle mixture for removing the oil from soil. *Paper presented at the 44th AMOP Technical Seminar on Environmental Contamination and Response*.

Vu, K. A. and Mulligan, C. N. (2022e). Treatment of oil pollutants in soil using a biosurfactant/nanoparticle suspension. *Paper presented at the 20th Global Joint Seminar on Geo-Environmental Engineering (GEE 2022)*.

Vu, K. A. and Mulligan, C. N. (2022f). Utilization of a biosurfactant foam/nanoparticle mixture for treatment of oil pollutants in soil. *Environmental Science and Pollution Research*, 30(11), 1-14.

Vu, K. A., Tawfiq, K., & Chen, G. (2015a). Rhamnolipid transport in biochar-amended agricultural soil. *Water, Air, & Soil Pollution*, 226(8), 256-264. doi:10.1007/s11270-015-2497-0.

Vu, K., Yang, G., Wang, B., Tawfiq, K., & Chen, G. (2015b). Bacterial interactions and transport in geological formation of alumino-silica clays. *Colloids and Surfaces B: Biointerfaces*, 125, 45-50. doi:10.1016/j.colsurfb.2014.11.015.

Wami, E. N., & Nmegbu, C. (2015). Micro-encapsulation technique for effective remediation of hydrocarbon contaminants. *International Journal of Scientific & Engineering Research*, 6(8), 815-823.

Wang, C., & Zhang, W. (1997). Synthesizing nanoscale iron particles for rapid and complete dechlorination of TCE and PCBs. *Environmental Science & Technology*, 31(7), 2154-2156. doi:10.1021/es970039c.

Wang, M., Zhang, B., Li, G., Wu, T., & Sun, D. (2019). Efficient remediation of crude oil-contaminated soil using a solvent/surfactant system. *RSC Advances*, 9(5), 2402-2411.

Wang, S., Kuo, Y., Hong, A., Chang, Y., & Kao, C. (2016). Bioremediation of diesel and lubricant oil-contaminated soils using enhanced landfarming system. *Chemosphere*, 164, 558-567.

Wang, Y., Zhou, D., Wang, Y., Wang, L., & Cang, L. (2012). Automatic pH control system enhances the dechlorination of 2, 4, 4'-trichlorobiphenyl and extracted PCBs from contaminated soil by nanoscale Fe⁰ and Pd/Fe⁰. *Environmental Science and Pollution Research*, 19(2), 448-457.

Wang, Z., Xu, Y., Zhao, J., Li, F., Gao, D., & Xing, B. (2011b). Remediation of petroleum contaminated soils through composting and rhizosphere degradation. *Journal of Hazardous Materials*, 190(1-3), 677-685.

Wei, Y., Liang, X., Tong, L., Guo, C., & Dang, Z. (2015). Enhanced solubilization and desorption of pyrene from soils by saline anionic–nonionic surfactant systems. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 468, 211-218.

Whang, L., Liu, P. G., Ma, C., & Cheng, S. (2008). Application of biosurfactants, rhamnolipid, and surfactin, for enhanced biodegradation of diesel-contaminated water and soil. *Journal of Hazardous Materials*, 151(1), 155-163.

Whelan, M. J., Coulon, F., Hince, G., Rayner, J., McWatters, R., Spedding, T., & Snape, I. (2015). Fate and transport of petroleum hydrocarbons in engineered biopiles in polar regions. *Chemosphere*, 131, 232-240.

- Wiesner, M. R., Lowry, G. V., Alvarez, P., Dionysiou, D., & Biswas, P. (2006). Assessing the risks of manufactured nanomaterials. *Environmental Science and Technology*, *14*, 4336-4345.
- Wild, A. (1993). Soils and the Environment. *Cambridge University Press*. doi:10.1017/CBO9780511623530.
- Williams, SD., Ladd, DE., Farmer, J. (2006). Fate and transport of petroleum hydrocarbons in soil and ground water at Big South Fork National River and Recreation Area, Tennessee and Kentucky, 2002-2003. *Scientific Investigations Report 2005-5104*. doi:10.3133/sir20055104.
- Wong, M. S., Alvarez, P. J., Fang, Y., Akçin, N., Nutt, M. O., Miller, J. T., & Heck, K. N. (2009). Cleaner water using bimetallic nanoparticle catalysts. *Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology*, *84*(2), 158-166.
- Wu, M., Dick, W. A., Li, W., Wang, X., Yang, Q., Wang, T., Xu, L., Zhang, M., & Chen, L. (2016). Bioaugmentation and biostimulation of hydrocarbon degradation and the microbial community in a petroleum-contaminated soil. *International Biodeterioration & Biodegradation*, *107*, 158-164.
- Wu, M., Li, W., Dick, W. A., Ye, X., Chen, K., Kost, D., & Chen, L. (2017). Bioremediation of hydrocarbon degradation in a petroleum-contaminated soil and microbial population and activity determination. *Chemosphere*, *169*, 124-130.
- Xia, T., Kovoichich, M., Brant, J., Hotze, M., Sempf, J., Oberley, T., Sioutas, C., Yeh, J. I., Wiesner, M. R., & Nel, A. E. (2006). Comparison of the abilities of ambient and manufactured nanoparticles to induce cellular toxicity according to an oxidative stress paradigm. *Nano Letters*, *6*(8), 1794-1807.

- Xie, W., Vu, K., Yang, G., Tawfiq, K., & Chen, G. (2014). *Escherichia coli* growth and transport in the presence of nanosilver under variable growth conditions. *Environmental Technology*, 35(18), 2306-2313. doi:10.1080/09593330.2014.902112.
- Xinhong, G., Ying, T., Wenjie, R., Jun, M. A., Christie, P., & Yongming, L. (2017). Optimization of ex-situ washing removal of polycyclic aromatic hydrocarbons from a contaminated soil using nano-sulfonated graphene. *Pedosphere*, 27(3), 527-536.
- Xu, J., & Bhattacharyya, D. (2005). Membrane-based bimetallic nanoparticles for environmental remediation: Synthesis and reactive properties. *Environmental Progress*, 24(4), 358-366.
- Xu, L., & Wang, J. (2011). A heterogeneous Fenton-like system with nanoparticulate zero-valent iron for removal of 4-chloro-3-methyl phenol. *Journal of Hazardous Materials*, 186(1), 256-264. <https://doi.org/10.1016/j.jhazmat.2010.10.116>.
- Xu, Y., & Zhao, D. (2007). Reductive immobilization of chromate in water and soil using stabilized iron nanoparticles. *Water Research*, 41(10), 2101-2108.
- Yamada-Onodera, K., Mukumoto, H., Katsuyaya, Y., Saiganji, A., & Tani, Y. (2001). Degradation of polyethylene by a fungus, *Penicillium simplicissimum* YK. *Polymer Degradation and Stability*, 72(2), 323-327.
- Yan, W., Lien, H., Koel, B. E., & Zhang, W. (2013). Iron nanoparticles for environmental clean-up: recent developments and future outlook. *Environmental Science: Processes & Impacts*, 15(1), 63-77.
- Yang, G., Wang, B., Vu, K., Tawfiq, K., & Chen, G. (2015). Role of bacterial adhesion in their subsurface deposition and transport: A critical review. *Reviews of Adhesion and Adhesives*, 3(2), 216-252. doi:10.7569/RAA.2015.097305.

- Yedra, A., Barquín, L. F., Sal, J. G., & Pankhurst, Q. A. (2003). Nanoscale alloys prepared by sodium borohydride reduction of aqueous Fe–Cu and Co–Cu solutions. *Journal of Magnetism and Magnetic Materials*, 254, 14-16.
- Yekeen, N., Manan, M. A., Idris, A. K., & Samin, A. M. (2017). Influence of surfactant and electrolyte concentrations on surfactant Adsorption and foaming characteristics. *Journal of Petroleum Science and Engineering*, 149, 612-622.
- Yekeen, N., Padmanabhan, E., Syed, A. H., Sevo, T., & Kanesen, K. (2020). Synergistic influence of nanoparticles and surfactants on interfacial tension reduction, wettability alteration and stabilization of oil-in-water emulsion. *Journal of Petroleum Science and Engineering*, 186, 106779.
- Yu, H., Hermann, S., Schulz, S. E., Gessner, T., Dong, Z., & Li, W. J. (2012). Optimizing sonication parameters for dispersion of single-walled carbon nanotubes. *Chemical Physics*, 408, 11-16.
- Yuanyuan, W., Qixing, Z., Shengwei, P., Lena, Q. M., & Xiaowei, N. (2009). Toxic effects of crude-oil-contaminated soil in aquatic environment on *Carassius auratus* and their hepatic antioxidant defense system. *Journal of Environmental Sciences*, 21(5), 612-617.
- Yuniati, M. D. (2018). Bioremediation of petroleum-contaminated soil: A Review. Paper presented at the *IOP Conference Series: Earth and Environmental Science*, 118(1) 012063.
- Zahed, M. A., Salehi, S., Madadi, R., & Hejabi, F. (2021). Biochar as a sustainable product for remediation of petroleum contaminated soil. *Current Research in Green and Sustainable Chemistry*, 4, 100055.
- Zhang, C. (2019). Soil and groundwater remediation: fundamentals, practices, and sustainability. *John Wiley & Sons*. ISBN: 978-1-119-39315-3.

- Zhang, C., Chen, X., Tan, Y., Feng, Y., & Zhong, Z. (2015). Soil vapor extraction removal of semi volatile organic compounds in soil: a pilot-scale study. Paper presented at the *International Conference on Sustainable Energy and Environmental Engineering*, 180-182.
- Zhang, C., Yan, H., Li, F., Hu, X., & Zhou, Q. (2013). Sorption of short-and long-chain perfluoroalkyl surfactants on sewage sludges. *Journal of Hazardous Materials*, 260, 689-699.
- Zhang, M., He, F., Zhao, D., & Hao, X. (2011). Degradation of soil-sorbed trichloroethylene by stabilized zero valent iron nanoparticles: effects of sorption, surfactants, and natural organic matter. *Water Research*, 45(7), 2401-2414.
- Zhang, M., He, F., Zhao, D., & Hao, X. (2017). Transport of stabilized iron nanoparticles in porous media: Effects of surface and solution chemistry and role of adsorption. *Journal of Hazardous Materials*, 322, 284-291. doi:10.1016/j.jhazmat.2015.12.071.
- Zhang, T., Cheng, J., Tan, H., Luo, S., & Liu, Y. (2022). Particle-size-based elution of petroleum hydrocarbon contaminated soil by surfactant mixture. *Journal of Environmental Management*, 302, 113983.
- Zhang, W., Wang, C., & Lien, H. (1998). Treatment of chlorinated organic contaminants with nanoscale bimetallic particles. *Catalysis Today*, 40(4), 387-395.
- Zhang, Z., Cissoko, N., Wo, J., & Xu, X. (2009). Factors influencing the dechlorination of 2, 4-dichlorophenol by Ni-Fe nanoparticles in the presence of humic acid. *Journal of Hazardous Materials*, 165(1-3), 78-86.
- Zhang, S., Li, X., Yang, Y., Li, Y., Chen, J., & Ding, F. (2019). Adsorption, transformation, and colloid-facilitated transport of nano-zero-valent iron in soils. *Environmental Pollutants and Bioavailability*, 31(1), 208-218.

- Zhao, C., Dong, Y., Feng, Y., Li, Y., & Dong, Y. (2019). Thermal desorption for remediation of contaminated soil: A review. *Chemosphere*, 221, 841-855.
- Zhao, X., Liu, W., Cai, Z., Han, B., Qian, T., & Zhao, D. (2016). An overview of preparation and applications of stabilized zero-valent iron nanoparticles for soil and groundwater remediation. *Water Research*, 100, 245-266. doi:10.1016/j.watres.2016.05.019.
- Zheng, M., Ahuja, M., Bhattacharya, D., Clement, T. P., Hayworth, J. S., & Dhanasekaran, M. (2014). Evaluation of differential cytotoxic effects of the oil spill dispersant Corexit 9500. *Life Sciences*, 95(2), 108-117.
- Zhou, W., & Zhu, L. (2008). Enhanced soil flushing of phenanthrene by anionic–nonionic mixed surfactant. *Water Research*, 42(1-2), 101-108.
- Zhu, B., & Lim, T. (2007). Catalytic reduction of chlorobenzenes with Pd/Fe nanoparticles: reactive sites, catalyst stability, particle aging, and regeneration. *Environmental Science & Technology*, 41(21), 7523-7529.
- Zhu, B., Lim, T., & Feng, J. (2008). Influences of amphiphiles on dechlorination of a trichlorobenzene by nanoscale Pd/Fe: adsorption, reaction kinetics, and interfacial interactions. *Environmental Science & Technology*, 42(12), 4513-451. doi:10.1021/es800227r.

