

TREATMENT OF SPENT CAUSTIC USING IONIC LIQUIDS

by

Muhammad Ashraf Sabri

A Thesis presented to the Faculty of the
American University of Sharjah
College of Engineering
In Partial Fulfillment
of the Requirements
for the Degree of

Master of Science in
Chemical Engineering

Sharjah, United Arab Emirates

April 2017

Approval Signatures

We, the undersigned, approve the Master's Thesis of Muhammad Ashraf Sabri.

Thesis Title: Treatment of Spent Caustic Using Ionic Liquids.

Signature

Date of Signature

(dd/mm/yyyy)

Dr. Taleb Hassan Ibrahim
Professor, Department of Chemical Engineering
Thesis Advisor

Dr. Paul Nancarrow
Associate Professor, Department of Chemical Engineering
Thesis Committee Member

Dr. Yehya Amin El Sayed
Associate Professor, Department of Biology, Chemistry and Environmental Science
Thesis Committee Member

Dr. Naif Darwish
Head, Department of Chemical Engineering

Dr. Mohamed El-Tarhuni
Associate Dean for Graduate Affairs and Research, College of Engineering

Dr. Richard Schoephoerster
Dean, College of Engineering

Dr. Khaled Assaleh
Interim Vice Provost for Research and Graduate Studies

Acknowledgement

I would like to express my gratitude to my advisor Prof. Taleb Hassan Ibrahim for his guidance, supervision of my research, continuous support, tolerance and encouragement throughout the MScHE studies. In short, I cannot imagine a better mentor and supervisor for my studies and research.

I would like to extend my gratitude towards Dr. Mustafa Ibrahim Khamis who always induced further motivation in me for research. His remarks and imperative discussions always enhanced curiosity and stimulated me to go the extra mile.

Special thanks to Dr. Yehya ElSayed for his support, clear recommendations and help without any hesitation every time. The work would not have been done so impeccably without his support.

My sincere thanks to Mr. Ziad Sara (Chemistry department) who helped me to develop experimental skills and have hands-on experience on several equipment. I am highly obliged by his kind behaviour and eagerness to assist in experimental work.

I would like to thank Dr. Paul Nancarrow for his suggestions and discussions on ionic liquids. Furthermore, I would like to thank all my professors who taught me the graduate level courses. In addition, I would like to extend my appreciation to the Department of Chemical Engineering for the award of graduate teaching assistantship.

I would like to appreciate the assistance provided by librarians, research staff particularly Miss Alanna Ross regarding access to scholarly articles and journals.

Finally sincere appreciation for my parents for their encouragement and help in all matters of life. Special thanks to my friend Mr. Husnain for his help during the early stages of MScHE studies.

Dedication

To a special person in my life to whom I have dedicated all my years yet to come

Abstract

Treatment of spent caustic (SC) wastes from downstream of refineries and petrochemical industries is not only complex but also highly expensive due to its content of high concentration of hazardous compounds, high pH, variations in the waste composition and the need to comply with the environmental regulations. Owing to the presence of pollutants such as sulfides, mercaptans and phenols, SC is known to be among the most difficult class of wastes to be treated and disposed. Several existing technologies have been applied to treat SC; however, they require extreme operation conditions of pressure and temperature. These methods are neither environment friendly nor cost effective. Thus, efforts are directed toward removal of specific pollutants particularly phenols, sulfides and mercaptans from SC streams in simple and environment-friendly manner. In this work, two hydrophobic ionic liquids (IL), tetrahexylammoniumdihexyl-sulfosuccinate (IL1) and trioctylmethylammonium salicylate (IL2), were used to treat industrial SC at room temperature using both bench-scale batch contactor and sequential batch contactor modes. UV-Vis spectroscopy, gas chromatography coupled with mass spectrometry (GC-MS) and chemical oxygen demand (COD) analysis were employed for SC characterization. The chemical composition and the COD values of SC were determined before and after treatment with IL1 and IL2. The operating conditions for extraction were optimized. The results reveal that both ionic liquids have the same optimum phase ratio and initial pH of 1.0 and 1.7, respectively. The optimum contact time for IL1 and IL2 is less than 6.0 minutes and 1.0 minute, respectively. Under these optimum conditions, IL1 and IL2 are able to reduce the COD level from 6.4×10^4 mg/L to 63 mg/L and the phenol level from 3.2×10^2 mg/L to 0.032 mg/L in SC. Thiol and benzaldehyde concentrations after treatment are brought below the detection limit of the GC-MS. Thus, this work highlights the high potential of ILs as an alternative SC treatment solution compared to the current complex industrial processes that require drastic operation conditions, use of hazardous chemicals and long contact times for SC treatment. The results of this work assure that the use of ILS for SC treatment is highly efficient, environmentally friendly, simple and novel.

Search Terms: Spent Caustic, Ionic liquids, Liquid-Liquid Extraction, phenol, Sequential Batch Contactors, Organics.

Table of Contents

Abstract.....	6
List of Figures.....	10
List of Tables.....	11
Chapter 1: Introduction.....	12
1.1. Overview.....	12
1.2. Thesis Objective.....	12
1.3. Research Contribution.....	13
1.4. Thesis Organization.....	13
Chapter 2: Literature Survey.....	14
2.1. Spent Caustic (SC).....	14
2.2. Spent Caustic Classification.....	14
2.3. Environmental Concerns.....	15
2.4. Spent Caustic Treatment Methods.....	16
2.4.1. Thermal treatment.....	16
2.4.2. Chemical treatment.....	17
2.5. Non-conventional Treatment Processes.....	22
2.6. Liquid-liquid Extraction.....	24
2.6.1. Solvent selection.....	24
2.6.2. Factors for effective separation.....	25
2.6.3. Distribution coefficient.....	25
2.7. Ionic Liquid in Solvent Extractions.....	26
2.8. Phenol Removal using Ionic Liquids.....	27
Chapter 3: Experimental Setup and Methodology.....	28
3.1. Materials.....	28
3.2. Instrumentation.....	28

3.3. Methods	28
3.3.1. Preparation of tetrahexylammonium dihexylsulfosuccinate..	28
3.3.2. Preparation of trioctylmethyammonium salicylate	29
3.3.3. UV-Vis spectroscopy	29
3.3.3.1. <i>Standard solutions of spent caustic.</i>	29
3.3.3.2. <i>Liquid- liquid extraction by ionic liquids.</i>	29
3.3.4. Quantitative and qualitative analysis of pollutants in SC.	29
3.3.5. Removal efficiencies and distribution coefficients.	30
Chapter 4: Results and Discussion.....	31
4.1. Spent Caustic UV-Spectra and Calibration Curve.....	31
4.2. Ionic Liquid Selection.....	32
4.3. Effect of Phase Ratio	32
4.4. Effect of Contact Time	33
4.5. Effect of pH	35
4.6. Optimum Parameters	36
4.7. Sequential Batch Contactors.....	37
4.8. Multiple Usage.....	38
4.9. Compositional Analysis using GC-MS	38
4.10. Regeneration	42
4.11. Process Intensification and Recommendations	44
4.12. Suggestions and Recommendations	47
Chapter 5: Conclusions	51
References.....	53
Appendix.....	62
A.1 Structure of Compounds	62
A.2 Distribution Coefficients of Phenols and Aromatic Compounds for ILs	65
A.3 $E_T(30)$ values for solvents	66

A.4 Major Compounds present in industrial SC before and after treatment using GC-MS spectroscopy by the procedure EPA-3510c and EPA-8270d.....	67
Vita	72

List of Figures

Figure 2.1: Fenton Process	22
Figure 4.1: Spectra of spent caustic at different COD concentrations	31
Figure 4.2: Calibration curve for concentration of spent caustic	31
Figure 4.3: Effect of phase ratio on the removal percentage of pollutants from SC. Parameters: initial pH, stirring speed and contact time were 13, 2500 rpm and 10 minutes, respectively.....	33
Figure 4.4: Effect of contact time on the removal percentage of pollutants from sc. Parameters: initial pH, stirring speed and phase ratio were 13, 2500 rpm and 1, respectively	34
Figure 4.5: Effect of pH on the removal percentage of pollutants from SC. Parameters: phase ratio and stirring speed were 1 and 2500 rpm, respectively. The contact time for IL1 and IL2 was 4 minutes and 1 minute, respectively	35
Figure 4.6: Spent caustic before treatment (A) and after treatment (B) with IL2. Parameters: Contact time: 1 min, stirring speed: 2500 ppm and pH of 1.7.....	37
Figure 4.7: GC-MS profiles for SC (spent caustic without any treatment) and SC_IL1 (spent caustic after treatment with IL1) for (a) bench-scale batch experiment with phase ratio one (b) sequential batch contactor with phase ratio of 2. The LLE parameters in terms of time, pH and stirring speed were 6 min, 1.7 and 2500 rpm, respectively.	39
Figure 4.8: GC-MS profiles for SC (spent caustic without any treatment) and SC_IL2 (spent caustic after treatment with IL2) for (a) bench-scale batch experiment with phase ratio one (b) sequential batch contactor with phase ratio of 2. The LLE parameters in terms of phase ratio, time, pH and stirring speed were 1, 1 min, 1.7 and 2500 rpm, respectively	40
Figure 4.9: TG curves of SC, ILs and used ILs.....	44
Figure 4.10: COD remaining after SC treatment using IL1 and IL2 at different phase ratios. Parameters: pH = 1.55 and contact time: 1 minute (IL2), 4 minutes (IL1).....	45
Figure 4.11: Non-conventional Spent Caustic Treatment Technique.....	50

List of Tables

Table 2.1: Characterization of Spent Caustic.....	14
Table 2.2: Types of WAO, operating parameters and oxidation of contaminants	17
Table 4.1: Percentage removal of major impurities from SC as determined by GC-MS.	41
Table 4.2: COD comparison of SC before and after treatment with respective IL	42
Table 4.3: COD comparison of SC before and after treatment with respective IL. Parameters: pH = 1.55, contact time = 1 minute (IL2), 4 minutes (IL1), mixing speed = 2500 rpm.....	46
Table 4.4: Number of stages required for percentage removal exceeding 99.99 % with respective IL. Parameters: pH = 1.55, contact time = 1 minute (IL2), 4 minutes (IL1), mixing speed = 2500 rpm.....	47

Chapter 1: Introduction

Chapter 1 presents a short overview of spent caustic (SC), its generation and the problems associated with developing an environment friendly treatment. The objectives of the research work as well as the research contributions are summarized. Finally, structure of the thesis and its chapters is presented.

1.1. Overview

Diluted sodium hydroxide solutions are commonly used in refineries and petrochemical industry to treat various petroleum products by removing organic acids such as phenols and naphthenic acids, sulfur compounds such as hydrogen sulfide and mercaptans and acid gases such as carbon dioxide from hydrocarbon streams [1-5]. Treatment processes such as Dualayer gasoline production, ferrocynide process, electrolytic mercaptans, mercapsol process and lye treatment using diluted caustic results in the formation of waste solution stream referred as SC [5, 6]. SC generation is not only common in refineries and petrochemical industry but is also generated in other industries such as plastic manufacturing and pulp and paper [7].

SC waste contains high concentrations of carbonates, sulfides, phenols, mercaptides and other emulsified and soluble organic compounds [5, 7, 8]. In oil refineries, the SC may contain compounds such as phenols, mercaptans, amines and thiols with variable concentrations depending on the crude oil source [5, 9, 10].

SC is considered to be a major concern for the environment as well as industrial production facilities. This is due to their noxious and hazardous properties and being very difficult class of industrial waste to handle, treat and dispose. Such complications are associated with their high pH values, high concentration of pollutants and the presence of a wide range of compounds of different chemistries introduced from diverse sources at different times [2, 5, 7]

1.2. Thesis Objective

Several technologies were developed for the treatment of SC mainly to remove phenols. These technologies are highly uneconomical and require utilization of hazardous materials. In this study, hydrophobic room temperature ionic liquids (ILs) will be examined and tested for their potential application as extraction solvents for pollutants in caustic water. Therefore, liquid-liquid based extraction will be applied for

the removal of pollutants from waste water under consideration. Therefore, the main objective of this research is to treat SCs with appropriate ILs and to determine the optimum operating conditions for liquid-liquid extraction. Advanced analytical methods will be applied to determine the variation in the SC before and after treatment from qualitative and quantitative aspects.

1.3. Research Contribution

The research contribution are summarized below

- Characterization of the industrial SC and investigation of its treatment using suitable IL.
- Evaluation of the removal efficiency of phenol and other toxic compounds present in industrial SC using ILs.
- Determination of the optimum operating parameters such as phase ratio (volume of SC treatment to volume of IL used), time, temperature and pH.
- Characterization of the SC, before and after treatment with ILs.
- Evaluation of the efficiency of the process

1.4. Thesis Organization

Chapter 2 presents a detailed literature survey of SC, its generation in industry, characteristics, environmental impacts and the conventional techniques utilized for its treatment. It also includes the description of ILs, their characteristics and potential towards environment friendly removal of toxic compounds such as phenols. Chapter 3 describes the instrumentation and the experimental work carried out for the treatment of SC and the techniques utilized for quantitative and qualitative analysis before and after treatment. Chapter 4 demonstrates the various results and discussions on the quantitative and qualitative removal of pollutants from SC using ILs. Identification of the pollutants in SC, determined using GC-MS spectroscopy, are presented in this chapter. Chapter 5 summarizes the conclusions of this research work and provide the main findings and recommendations for future investigations.

Chapter 2: Literature Survey

2.1. Spent Caustic (SC)

SC is an industrial waste generated by petrochemical industries and is mainly generated by scrubbing of gasoline, light petroleum gas (ethylene, LPG), kerosene and diesel with diluted caustic solution [1-5].

2.2. Spent Caustic Classification

The classification of SC depends not only on the industry generating it but also on the fuel sources that caustic treats [5, 11, 12]. Typically refineries treat these SCs collectively rather than separately. SC streams from different processes are mixed together, called mixed SC, and then treated [5, 10-12]. The SCs are produced by the scrubbing of gasoline, light petroleum gas (ethylene, LPG) and mercaptan-extraction of middle distillates (kerosene and diesel), respectively. SCs are broadly classified into three types namely phenolic/cresylic, sulfidic, and naphthenic. Phenolic caustics have high concentrations of phenols and cresols, sulfidic caustics are highly concentrated in sulfides and mercaptans, while naphthenic caustics contains naphthenic acids and other polycyclic aliphatic organic compounds in high concentrations [2, 5, 13]. The typical constituents and characteristics of these caustics has been presented in Table 2.1.

Table 2.1: Characterization of Spent Caustic

Spent Caustic	Phenolic/ Cresylic SC	Sulfidic SC	Naphthenic SC	Ref.
Major constituent	Phenols Cresols	Sulfides Mercaptans	Polycyclic aliphatic organic compounds	[2, 5, 13]
Production source	scrubbing of gasoline	scrubbing of light petroleum gas (ethylene, LPG)	scrubbing of kerosene and diesel	[2, 5, 13]
Phenols (g/L)	14 – 20	Less than 2	2 – 10	[5, 7, 14]
Sulfides (g/L)	Up to 64	2 – 53	Less than 1	[5, 9, 14]
Total organic content, TOC (g/L)	23 – 60	0.02 – 4	11 – 25	[14, 15]
Chemical oxygen demand, COD (g/L)	165 – 230	7 – 110	50 – 100	[14, 15]
pH	12 – 14	13 – 14	12 – 14	[5, 15]

2.3. Environmental Concerns

SCs, due to their high concentrations of toxic compounds (such as mercaptans, phenols and sulfides) and high pH, are a major concern for environment. Handling, treatment and disposal of SC is not only difficult but also complicated due to large variations in this waste stream and the toxic chemicals present within that need to be treated or removed before the stream is allowed to discharge to the water resources [7].

Deep well injection has been traditionally practiced for a very long time but, due to voluminous discharge of SCs and the long term effects of this practice, is prohibited now. The higher chain chemicals sediment in the soil, degrade at a very slow rate and contaminate the surroundings and the soil itself [16]. Thus, this disposal method is becoming practically and environmentally unacceptable in almost all parts of the world. The environmental standards for discharge of wastes are becoming stricter so as to preserve the water resources and the aquatic life within it. These environmental standards encompass the allowable discharge levels of each pollutant thus affecting the SC treatment methods and system design [7, 17].

Hazardous wastes are termed for wastes that can be potentially harmful for environment and human health according to Environmental Protection Agency [18]. The classification of different wastes depends on their specific characteristic. Ignitability (D001), corrosivity (D002), reactivity (D003) and toxicity (D004 – D043) are the basic four characteristics upon which the waste can be termed as hazardous waste as per EPA Hazardous Waste Codes [17, 18].

SC is highly corrosive (pH 12 – 14), reactive due to the presence of sulfides, and highly toxic due to high salinity and phenolic contents [17]. Pollutants such as mercaptans and sulfides have strong odors with threshold odor limit is in parts per billion [19]. Phenols adversely affect the biological treatment systems even in concentrations below 400 mg/L [2, 7]. They not only inhibit the removal of ammonia, phosphorous and COD but also hinder the settling of sludge [7]. Hydrogen sulfide with a concentration below 30 mg/L can paralyze the sense of smell of the individual and can cause death even at concentrations of 700 mg/L [19].

Due to these characteristics of SC streams, these waste water streams are difficult to handle, treat and dispose in an environment friendly manner [2, 5]. Consequently, the treatment of SC is inevitably demanding and expensive. The present

work is an effort to reduce the expense and difficulties in the treatment and disposal of SC in an environment friendly way.

2.4. Spent Caustic Treatment Methods

SC treatment is receiving a lot of concern from industries as well as environmental regulatory bodies to minimize the toxic compounds as much as it can be. For the same purpose, various efforts have been carried out for the development, enhancement and maturity of SC treatment. Many efforts has been based on the effort to obtain zero discharge rate with minimum economic constraints

The main objective of SC treatment is to lower the concentration of pollutants below the allowable discharge limits as per the environmental regulations. Maximum allowable discharge limit of phenol and sulfides is 0.1 mg/L [18]. To satisfy the EPA and other environmental regulations, the waste streams are mostly subjected to various treatment techniques depending on the concentration and the composition of the SCs. The most efficient method is selected based on the above-mentioned criteria and can also be selected on the basis of COD concentration.

Incineration is well-suited for wastes having concentrations above 200 g/L. Wet air oxidation (WAO) is considered to be best for concentrations range of 20 – 200 g/L while advanced oxidation (AOPs) is implemented for values below 20 g/L [20].

2.4.1. Thermal treatment

2.4.1.1. Wet air oxidation. WAO is the oxidation of inorganic and organic substances in the waste caustic stream by means of air or oxygen at elevated pressures and temperatures with or without the use of catalyst [21, 22]. This technology is able to destroy the toxic chemicals in the SCs as it breaks down the complex structures into simple compounds such as carbon dioxide and water [21]. Though WAO has been reported to be able to destroy 99% of the present pollutants, however few pollutants form intermediate compounds and are not completely oxidized. The effluent concentration using WAO process can be decreased below 0.002 g/L in the case of total phenols and 0.001 g/L in the case of sulfides [23]. The major drawback of this method is its high operational cost due to high temperature and pressure and these elevated conditions also pose a potential safety concern. The catalytic WAO is preferred over non-catalytic WAO as it decreases the temperature and pressure conditions required for the oxidation of the present pollutants [22]. Yet the cost of catalyst and its regeneration

is quite high [24]. Thus for this technique to be economically feasible, low cost and highly stable catalysts need to be used. Allowance of onsite treatment of SC without generation of odorous gases is a major advantage of WAO.

WAO can be divided into three types depending on the desired effluent characteristics namely; low temperature WAO, medium temperature WAO and high temperature WAO. The operational parameters and the oxidization ability of each WAO system has been mentioned in Table 2.2.

Table 2.2: Types of WAO, operating parameters and oxidation of contaminants

WAO	Pressure (bar)	Temperature (K)	Oxidation of contaminants	Reference
Low operating conditions	1.72 – 6.89	373 – 473	sulfides	[2, 25]
Medium operating conditions	20.7 – 41.4	473 – 533	Naphthenic SC, sulfides and mercaptans	[2, 22]
High operating conditions	48.3 – 75.8	533 – 593	sulfides, mercaptans , organic contaminant (cresylic acids)	[2, 10, 26]

2.4.1.2. Incineration. In case of pollutant concentration exceeding 200 g/L, incineration is employed. This gas-phase oxidation method converts the waste into stable states by decomposition. It is mentioned to provide the ultimate oxidation of pollutants at the expense of high energy requirements and high toxic emissions. These high energy requirements make the process undesirable and uneconomical [5].

2.4.2. Chemical treatment

2.4.2.1. Neutralization followed by air stripping. Neutralizing SCs generates the original elements of the SC components. Mercaptans, sulfur, phenol and hydrogen sulfide are produced as a result of neutralization that needs to be stripped for recovery and are treated as valuable product while the sour gases required proper handling procedures. This technique is quite simple and economically viable, but lacks

efficiency in removing majority of the organic components in the SCs. The COD after neutralization is often high enough to suggest further treatment by another technique [7].

2.4.2.2. Chemical oxidation. The major purpose of this method is to oxidize the pollutants so that they can either be degraded to simple compounds or form intermediates or compounds that can be readily removed from the system. This method involves the transfer of electrons from contaminants (electron donor) to the oxidant (electron receptor). In biological treatment processes, microorganisms referred to as natural oxidants carry out the oxidation. In chemical oxidation, a variety of oxidizers is added in the stream in a variety of ways depending upon the concentration and the composition of the waste stream.

Chemical oxidation is broadly classified into two main categories namely, classical chemical oxidation and advanced oxidation processes (AOPs).

2.4.2.2.1. Classical chemical oxidation. Addition of oxidizer such as chlorine dioxide, oxygen, chlorine, ozone, permanganate and hydrogen peroxide to the waste aqueous stream is termed as classical approach to chemical oxidation. Each of these oxidizers has different advantages and disadvantages depending on the removal efficiency and economy of the treatment that need to be estimated before its utilization for particular waste stream treatment. The classical approach is implemented in various industries for a variety of purposes such as to improve the water quality and wastewater treatment.

2.4.2.2.2. Advanced oxidation processes (AOPs). AOPs utilize the mechanism for the formation of highly reactive radicals (hydroxyl) in sufficient amount to oxidize the complex toxic contaminants in the wastewater [27-29]. These hydroxyl radicals are generated using strong oxidants (such as hydrogen peroxide and ozone) with or without the use of catalysts (transition metals, titanium oxide). Energy sources such as ultraviolet radiation have also been employed with any of the strong oxidants for the generation of such radicals. The AOPs can be applied at normal conditions of pressure and temperature and are able to reduce the concentration from ppm to few ppb [30]. These AOPs have the ability to oxidize majority of chemicals and brings the COD and TOD of the waste water to the discharge limits when operated at controlled conditions such as temperature, pressure and pH [31].

The AOPs coupled with other technique for final treatment of wastewater is another option when the AOP alone is not sufficient to bring the toxic chemicals concentration within the discharge limits. This method reduces the economic feasibility and increases the complexity of treatment process [32, 33].

AOP is a promising straightforward technique that can be implemented to treat various toxic compounds simultaneously and complete the mineralization of pollutants [33-35]. Owing to the presence of large quantity of radicals generated, the reaction rates are fast enough to complete the reaction in limited time interval [33, 35]. In spite of all these benefits, high capital cost and need of high controlled parameters are a pitfall of this technique [33, 35].

Selection of particular AOP depends on various parameters such as treatment objectives, inlet concentrations, outlet concentration requirement or removal required, site considerations, composition of the waste stream and the cost of the process to be employed [31].

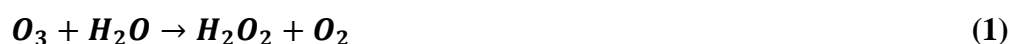
Depending on the variety of chemical present in the SC, high variation in concentration and high volumes, it is evident that no process can be employed individually for the treatment and complete removal of the toxics. Thus in order to minimize the energy requirements, operating costs and higher removal efficiency different combination of AOPs have been proposed and documented to be well suited and efficient for the SC treatment [31-33].

Such combinations are hydrogen peroxide with UV and hydrogen peroxide with ozone. Both are quite effective for the processes in which the feed characteristics and composition is prone to vary [33]. Combination of hydrogen peroxide, ozone and UV is highly efficient in terms of SC treatment but has a disadvantage of very high operational costs due to the use of two costly oxidants [33].

Fenton's method has been implemented widely due to its high advantages. The only major disadvantage of this process is the hazards associated with hydrogen peroxide. The advantages include the complete destruction of the pollutants that is the main objective to treat SCs, ability to oxidize various pollutants and high efficiency. Thus up to date Fenton's method is not only widely implemented technique but also is also highly recommended for SC treatment [30, 33].

One of the industrial examples of SC treatment by Fenton's method with few modifications is called Oxidation with Hydrogen Peroxide (OHP) and this treatment method is employed by "FMC Foret".

Ozone and ultraviolet radiation (O_3/UV): Hydroxyl radical formation is a two-step process in this technique. The photolysis of ozone generates hydrogen peroxide which further reacts with ozone to create the radicals [28]. The equations can be summarized as below; the first reaction is carried out in the presence of UV.

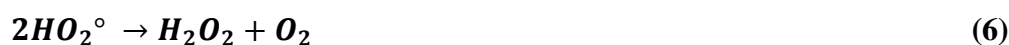


The main parameters affecting the efficiency of this technique are ozone concentration, pH of the system and UV dosage [27, 28, 36]. Oxidation potential of hydroxyl radicals generated from this technique is greater than the oxidation potential of hydrogen peroxide and ozone [37]. Pollutant removal using ozone/UV technique is quite higher than other AOPs since the oxidation can occur from any of the four oxidants, i.e. oxygen, hydroxyl radical, ozone and hydrogen peroxide [36].

Hydrogen peroxide and ultraviolet radiation (H_2O_2/UV): This technique generates hydroxyl radicals either with the photolysis or with the decomposition of H_2O_2 [27, 28, 31, 37-39]. The main reaction, under the influence of UV, is given by [37, 39]



The complete reactions and propagation steps are mentioned below with the last reaction to be the termination step [39].



The reaction is pH dependent and higher amounts of hydroxyl ions are generated at high pH values [31]. The concentration of hydrogen peroxide in the system should be kept as minimum as possible to ensure that the hydroxyl radical production is through photolysis and the technique is economical as higher usage of hydrogen

peroxide can offset the economical balance of the technique [28]. Other parameters include temperature, reactor contact time, pressure, hydrogen peroxide dosage and UV lamp intensity [27, 38]. Similar to the previous technique, this technique provides better removal of pollutants than hydrogen peroxide alone.

Ozone with hydrogen peroxide system: Ozone with hydrogen peroxide system has been characterized by the enhancement of hydroxyl radical generation [40]. The hydroxyl radical generation rate using this system is far superior to the ozone, ozone/water systems and hydrogen peroxide systems [40]. Ozone reacts with hydrogen peroxide in a variety of steps with the main result summarized as follows [28]



The technique provides much better results as higher pH values than at acidic conditions [31]. The system is superior to UV/H₂O₂ system as it is not affected by any turbidity present in the system or solutions [41].

Ultrasound systems: The use of ultrasound systems for the generation of hydroxyl radicals is quite interesting. The propagation of high frequency ultrasound waves through SCs and other wastewaters generates alternating cycles of expansion and compression thus induces acoustic cavitations [42, 43]. The nucleating, growth and collapsing of micro-bubbles in the wastewater is capable of producing high pressures (up to 500 atm) and extreme temperature (up to 5200 K) thus breaking water molecules producing hydroxyl radicals [42, 43]. The main factors affecting the generation of hydroxyl radicals from ultrasound systems are ultrasound intensity, ultrasound frequency, pressure and temperature of the waste stream [44]. Higher ultrasound frequency generates higher cavitations in liquid and thus higher rates of hydroxyl radicals production can be achieved at higher sonication frequencies [27]. Ultrasound systems accompanied with hydrogen peroxide or ozone has shown better results than any of these three alone for wastewater treatments [27, 28, 43].

Fenton's Reagent: Fenton's reagent has been immensely used for the treatment of inorganic and organic industrial wastes such as SCs. The reaction is based on the formation of hydroxyl radicals or organocomplexes iron (ferryl ion) [1, 45-47]. The oxidation system has been successfully implemented for the degradation of non-biodegradable matters and toxic wastes with high energy efficiency and can be effectively used to degrade the matter to be used for biological treatment [1]. Different

literatures are present to provide useful insight into the Fenton chemistry and its application to industrial wastewater treatment including SC treatment [1, 48].

Figure 2.1 shows a typical Fenton reactor which is normally stirrer reactor coated with acid-resistant material as the Fenton reagent used is highly corrosive [1]. The main chemicals involved are ferrous sulfate and hydrogen peroxide. The addition of chemicals is done through metering pumps. pH is adjusted to optimum conditions depending on the feed concentrations, the optimum pH is mostly 3 – 4, and the peroxide to catalyst ratio is 5:1 w/w basis. Sulfuric acid is added to wastewater for acidic conditions, followed by the addition of catalyst and then pH is adjusted to the optimum values for optimum results. Hydrogen peroxide is added slowly to ensure temperature control and minimum hydrogen peroxide usage in the system since additional hydrogen peroxide may cause issues with the downstream biological systems. Neutralization of effluent is carried out for pH adjustments followed by flocculation tank and separation tank for TDS adjustments. The effluent after TDS adjustment can be sent to secondary biological treatment plants [1].

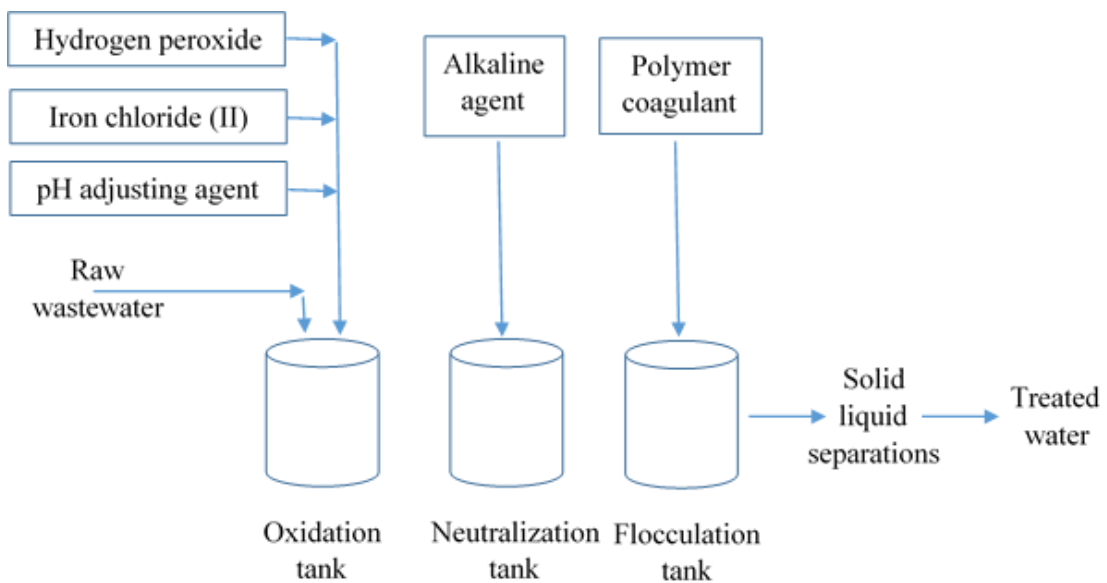


Figure 2.1: Fenton Process [1]

2.5. Non-conventional Treatment Processes

The conventional treatment processes, as mentioned and discussed above, require the use of hazardous chemicals and intense system parameters such as high temperature and pressure that represent another potential safety risk. Furthermore, the

procedure in most cases is complex, energy intensive and costly. Sometimes the excess amount of oxidant (such as hydrogen peroxide) added to break down the toxic chemical in the caustic stream has to be removed before discharge. This presents another problem that requires additional separation step and additional assembly thus complicating the process and increasing treatment costs. As more and more emphasis is being taken on environmental impacts, the treatment processes are becoming more and more expensive than before.

Thus, there is a need to develop technique that is cheap, simple and uses environment friendly chemicals to treat the SC. The main pollutant in SC that is not easily degradable and adversely influences the efficiency of biological treatment processes is phenols. Phenols have been shown to inhibit the growth of natural oxidants in the biological treatment systems even when present in the concentration range of few ppm. Thus, the removal of phenol from the SC stream has always been of major concern to industrialists and researchers.

ILs are termed as environmental friendly and many researchers have shown the ability of ILs to remove phenols from aqueous solutions using ambient conditions and liquid-liquid extraction technique. This method is getting major audience due to its characteristics of being environment friendly, simple and cost effective technique.

The use of hydrophobic ILs that are capable of removing phenols from aqueous solutions has been reported in literature with a removal efficiency exceeding 90 percent. However, these hydrophobic ILs have not been tested for their effectiveness for phenol removal in SC streams. The present work is an effort to treat SC and removal of phenol from this waste stream using different hydrophobic ILs. In work has the potential to create SC treatment process that is simple, economical and complements the environmental standards

ILs are salts with ionic and monomolecular character, representing new category of solvents different from the conventional solvents, normally liquid at room temperature or below 100°C are being studied worldwide both at academic and industrial levels due to their extremely different and useful characteristics [49]. Room temperature ILs are liquid at room temperature and have shown favorable results when used as solvents instead of conventional organic solvents. ILs have shown remarkable characteristics and results when applied in fields such as chemical reactions,

electrochemistry and solvent extractions [49]. Though the applications are fairly wide yet only solvent extractions using IL will be discussed in detail.

2.6. Liquid-liquid Extraction

Liquid-liquid extraction (LLE), known as solvent extraction, is a separation techniques for the separation of desired component (solute) from two immiscible liquids (feed and extractant) based on the solubility of solute in these liquids. Extractant is the solvent used to extract the required component while feed is the liquid from which the solute needs to be extracted. This technique is based on the phase distribution principle which states that a solute can distribute itself between two immiscible liquids in a particular ratio depending upon its activity coefficient in each phase [50, 51]. In industrial application, the extractant can be a mixture of several solvents designed for the extraction of one or more than one solute from the feed [52]. LLE is conventionally used for solvent recovery, product recovery or increasing the solute concentration in extractant. LLE techniques are only preferred in case of non-availability of other viable or economic options due to the fact that this technique necessitate the use of an additional separation step after extraction to separate the solute or the emulsion formed. Typical examples of LLE include separation of heat sensitive and non-volatile compounds, washing of base or acid media from organic stream and removal of phenol, aniline and aromatic compounds from water.

2.6.1. Solvent selection. The choice of solvent is mainly dependent of the solute to be separated and the nature of the feed. The solvent is chosen so as to have maximum solute transfer from feed to the extractant. The characteristics of a solvent are summarized below [53]

- Immiscible with feed
- High affinity towards solute
- Thermally stable
- Low viscosity
- Non-reactive towards other feed components and equipment parts
- Non-flammable and non-toxic
- Non-corrosive to equipment parts
- Economic
- Environment friendly

A variety of solvents is needed to be analyzed and compared before selecting any solvent suitable for the extraction of particular compounds under consideration.

2.6.2. Factors for effective separation. LLE of any system is dependent on a variety of factors including, but not limited to, the interfacial area, rate of mass transfer, viscosity, and affinity of extractant for solute. The extraction efficiency is increased if the interfacial area is increased or the mass transfer resistance is reduced. The mass transfer resistance can be reduced by increasing temperature that reduces the fluid viscosity thus improving mass transfer between the phases. Interfacial area can be increased by decreasing the droplet size [54].

2.6.3. Distribution coefficient. The removal efficiency of solute from feed can be calculated as

$$R = \frac{[S]_o - [S]}{[S]_o} * 100 \quad (9)$$

where R represents the percentage removal efficiency of solute by the extractant which $[S]_o$ and $[S]$ denotes solute concentration in mg/L before and after LLE process.

The molal distribution coefficient in case of completely immiscible liquids is given by equation

$$D = \frac{\gamma_1}{\gamma_2} K \quad (10)$$

where K is a constant in case of complete immiscibility of feed and extractant, γ represents the molal activity coefficient of solute in respective phase and D is the activity coefficient. In case of low concentrations the activity coefficients reach unity and the distribution coefficient becomes constant [50]. The distribution coefficient and the extraction efficiency of solute from feed can be represented as

$$D = P * \left(\frac{R}{100-R} \right) \quad (11)$$

where R is the percentage extraction (removal) efficiency of solute from feed, D is the distribution coefficient and P is the ratio of volume of feed to volume of extractant used.

2.6.4. Applications. Several method have been reported for the removal of organics from aqueous solutions including physical, chemical and biological methods. These methods, in general, are quite expensive, tend to utilize toxic chemicals and offer

limited design flexibility [55-59]. LLE extraction on the other hand is quite simple, less expensive but has some limitations depending upon the choice of solvent [60]. In recent years, LLE has been the focus of attention of researchers. Several papers for the effective removal of dyes, phenols and aromatic compounds researchers have reported [60-66]

2.7. Ionic Liquid in Solvent Extractions

Room Temperature ILs are being preferred and are being focused due to their intrinsic properties of negligible vapor pressure at room temperature, thermal stability, excellent solvation characteristics and easy isolation from the aqueous streams in case of hydrophobic ILs. These characteristics of ILs represent an environment friendly and potential cost effective alternative to the conventional toxic solvents having relatively high vapor pressures [49].

Jingfu et al. demonstrated the excellent abilities of 1-octyl-3-methylimidazolium hexafluorophosphate to be used to extract polycyclic aromatic hydrocarbons from aqueous samples in liquid-phase micro-extraction process [67]. Similarly, polycyclic aromatic hydrocarbons were successfully extracted from sediments using ILs pointing towards the possibility of organic compound extraction from solid matter. The authors suggest the use of microwave assisted extraction for better extraction results [68]. Qingxiang Zhou et al. presented reports regarding the temperature dependent extraction of pyrethroid pesticides using [C₆MIM][PF₆] suggesting the use of IL dispersive liquid phase micro-extraction for increased extraction efficiencies [69].

Yuuki Mochizuki and Katsuyasu Sugawara demonstrated the extraction of organic sulfur from fuels using six different ILs [70]. Mark et al. studied the mechanism of uranium extraction using ILs in liquid-liquid extraction. This study provides insight into the feasibility of IL to replace conventional solvents for the separation of metal ions and uranium by liquid-liquid extraction [71]. Liquid-liquid extraction of toluene from toluene/heptane mixtures using a variety of ILs has been reported with a focus to be applied for extraction of aromatic hydrocarbons from mixtures of aromatic and aliphatic compounds [72]. Kazunori et al. demonstrated the feasibility of utilization of ILs instead of other organic solvent for Lanthanide extraction and selectivity in industrial LLE [73]. Imidazolium-based ILs containing silver tetrafluoroborate have been reported to extract polyunsaturated fatty acid methyl esters from variety of alkanes

successfully demonstrating their ability to replace conventional organic solvents [74]. The use of IL as extraction phase in hollow-fiber based liquid phase micro-extraction has been demonstrated to be able to eliminate the use of toxic organic solvents for lead and nickel determination in biological and environmental samples [75]. Vladimir M. Egorov et al. used quaternary ammonium-based ILs for the extraction of aromatic amines and phenols [76].

2.8. Phenol Removal using Ionic Liquids

Jing Fan et al. carried out the extraction of endocrine-disrupting phenols from their aqueous solutions using ILs and have presented their findings to ascertain the suitability of some ILs to be used as a substitute of volatile organic solvents for LLE [77].

Quaternary ammonium-based and imidazolium-based ILs have been successfully used for the extraction of phenols, preferably partitioned in non-ionized form in ILs, from aqueous solutions [76, 78].

Tetrabutylphosphoniumdioctyl sulfosuccinate, surfactant based IL, showed effective phenol extractions from aqueous solutions due to reduced energy at IL-water phase interface [79]. Partition coefficients in IL-aqueous two-phasic system was measured and correlated for 5 different phenols at 298.2 K. The IL used was 1-Butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) [80]. Deng et al. demonstrated the effect of aqueous pH, chemical structure of phenols and ILs on the extraction ability of ILs to remove phenols from aqueous solutions. Extraction of phenol by trihexyltetradecylphosphonium tetrachloroferrate(III), a synthesized hydrophobic IL, was reported to be more than the non-functionalized ILs [81]. Many other efforts have also been carried out recently for the removal of phenols from aqueous solution using a variety of different ILs [82-84]. Canales et al., in his review, concluded ILs to be competitive alternatives to conventional organic solvents based on their phase behavior, capacities and low viscosities [85].

Up to date, no effort has been reported on the treatment of phenols in SC using ILs as per the literature review. Thus, the objective of this thesis is to treat SC particularly the removal of phenols from SC using ILs.

Chapter 3: Experimental Setup and Methodology

3.1. Materials

SC was obtained from ENOC (Emirates National Oil Company, UAE). All chemicals used were of analytical grade unless specified otherwise. Silver nitrate (99.9% metal basis) and acetone (reagent grade) were purchased from ACS (Alfa Aesar GmbH, Germany) and Merck (KGaA Germany), respectively. Double distilled water was generated using Aquatron A4000D Water Still, UK. pH adjustments were carried out using sulfuric acid.

3.2. Instrumentation

UV-VIS spectrophotometer (Model DR-5000, HACH, USA) at a wavelength of 345 nm and QP2010 Ultra Thermal Desorption-Gas Chromatography-Mass Spectrometry (TD-GC-MS: Shimadzu, Japan) were used for COD analysis and the identification of volatile and semi-volatile organic compounds present in the sample, respectively. Stuart vortex mixer at 2500 rpm, Centrifuge (HERMLE Labortechnik GmbH, Germany) at 3500 rpm and pH meter (3320, JENWAY Ltd., UK) were used for vigorous shaking, centrifuging and pH measurements. A hot plate stirrer (Model MSH-20D, DAIHAN Scientific Co. Ltd., Korea) was used for stirring and temperature control.

3.3. Methods

3.3.1. Preparation of tetrahexylammonium dihexylsulfosuccinate.

Tetrahexylammonium dihexylsulfosuccinate (IL1) was prepared in laboratory as described elsewhere [76]. Equimolar amounts of dihexylsulfosuccinate sodium salt solution (80% in H₂O w/w) and tetrahexylammonium bromide (99%) were mixed at a temperature of 50°C and stirring speed of 600 rpm for 20 minutes. The mixture was then separated using separatory funnel followed by washing the IL1 10 times with triple volumes of double distilled water each time. The concentration of NaBr was analyzed by dissolving the wash water with silver nitrate. After the complete removal of NaBr, IL1 was separated using separately funnel and centrifuged at 3500 rpm. The obtained clear and colorless viscous liquid was stored in glass containers at room temperature. The NMR spectroscopy results were found to be in good agreement with the results reported in literature [76]. The structure of reactants has been presented in Appendix A.1.

3.3.2. Preparation of trioctylmethyammonium salicylate.

Trioctylmethyammonium salicylate (IL2) was prepared in laboratory as described elsewhere [76]. Equimolar amounts of sodium salicylate (99%) and trioctylmethyammonium chloride (premixed in 400 ml of acetone) were mixed at room temperature and stirring speed of 600 rpm for five hours. The IL2-acetone mixture (liquid layer) was separated from the precipitate. The precipitate was allowed to settle and the liquid layer was withdrawn carefully. The liquid layer was subjected to rotary evaporator to evaporate acetone. The obtained IL2 was washed 10 times with triple volumes of double distilled water each time. After the water wash, the IL2 layer was separated and centrifuged at 3500 rpm. The obtained clear and light yellow viscous liquid was stored in glass containers at room temperature. The NMR spectroscopy results were found to be in good agreement with the results reported in literature [76]. The structure of reactants has been presented in Appendix A.1.

3.3.3. UV-Vis spectroscopy

3.3.3.1. Standard solutions of spent caustic. The SC had a COD value of 64166 mg/L with phenol concentration of 320 mg/L as provided by the supplier. The COD value of 64166 ± 3880 mg/L was also verified using EPA method 410.4. The SC samples was diluted to have an appropriate absorbance reading using UV-VIS photo spectrometer. Ten different concentrations ranging from 106.67 mg/L to 2 mg/L were prepared by dilution. These standard solutions were read on the UV at a wavelength of 345 nm.

3.3.3.2. Liquid- liquid extraction by ionic liquids. Three replicates of SC (no IL) were used for the sake of comparison, as blanks. ILs were added to SC of known concentration in specific phase ratio and stirred at 2500 rpm for 10 minutes at ambient temperature. Phase ratio is defined as ratio of volume of SC treated to the volume of IL used for liquid-liquid extraction. The mixture was then centrifuged for 5 minutes at 3500 rpm. The lower layer (treated SC) was then acquired and read on the UV. The same procedure is applied for mixtures with different phase ratio. For optimum time and pH determination, the above steps were repeated for different contact times and pH keeping other parameters at constant values, respectively.

3.3.4. Quantitative and qualitative analysis of pollutants in SC. Chemical oxygen demand (COD) was determined using EPA method 410.4. Quantitative and qualitative analysis of organic pollutants in SC were performed according to EPA-3510c and EPA-8270d.

3.3.5. Removal efficiencies and distribution coefficients. The overall distribution coefficient, D , was calculated from the following formula

$$R = \frac{[SC]_o - [SC]}{[SC]_o} * 100\% \quad (12)$$

$$D = P * \left(\frac{R}{100 - R} \right) \quad (13)$$

where, R , P , $[SC]_o$ and $[SC]$ represent the removal efficiency of the IL, volumetric ratio of SC to IL used, pollutants concentration in mg/L before and after treatment, respectively. The specific removal efficiency in case of GC-MS was calculated based on the initial and final peak areas of the corresponding impurities at the same instrumental conditions.

$$R_{GC-MS} = \frac{A_o - A}{A_o} * 100 \quad (14)$$

where, R_{GC-MS} , A_o and A represent the removal efficiency of the IL, the peak area of the impurity of the SC before and after treatment, respectively. The removal efficiency of specific pollutants was assessed qualitatively by peak area comparison before and after treatment as calculated from equation 3.

$$\text{Percentage Removal} = \sum_{i=1}^n R_{GC-MS} \quad (15)$$

where n corresponds to the number of compounds present in the SC.

Chapter 4: Results and Discussion

4.1. Spent Caustic UV-Spectra and Calibration Curve

Figure 4.1 represents the spectra of SC at varying concentrations. It is quite clear that the absorbance is increasing as the concentration of phenol in the SC is increasing.

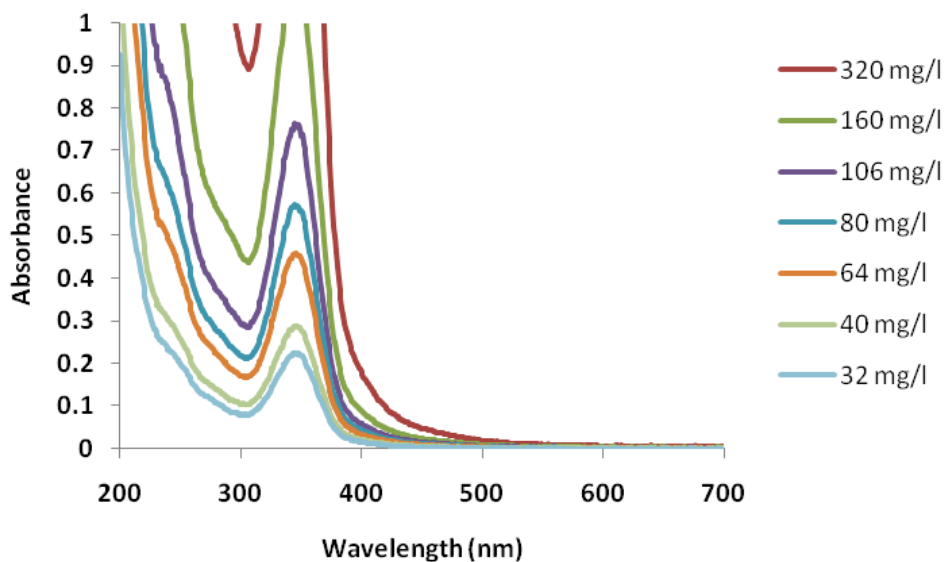


Figure 4.1: Spectra of SC at different COD concentrations

The calibration curve, Figure 4.2, shows the absorbance values of SC of varying concentrations. The peak appearing at 345 nm was considered and the calibration curve was calculated at this peak value of 345 nm. The calibration curve obtained by plotting the absorbance at 345 nm versus concentration of SC generated a linear curve with R^2 value of 0.999 that was used for precise and accurate calculations of concentrations of the mixture.

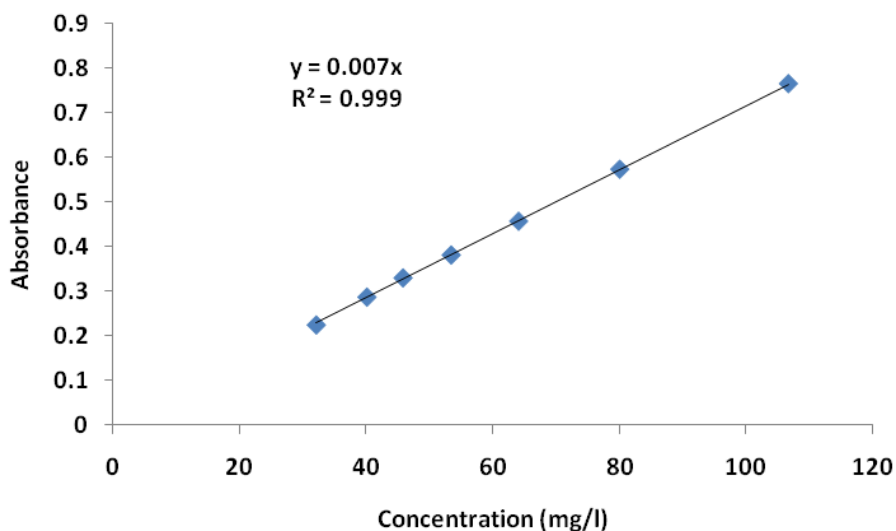


Figure 4.2: Calibration curve for concentration of SC

4.2. Ionic Liquid Selection

The selection of ionic liquid was based on the factors discussed in Section 2.6.1, the distribution coefficients of phenols and other aromatic compounds (as reported in literature) and the polarity of the ionic liquid. The solubility of IL1 and IL2 in water is $(8.6 \pm 0.2) \times 10^{-5} \text{ mol.L}^{-1}$ and $2.0 \pm 0.2 \times 10^{-4} \text{ mol.L}^{-1}$, respectively [76]. Thus the hydrophobicity of these ILs is several times greater than common ILs particularly imidazolium based ILs. These ILs have high affinity towards solute particularly phenols and their distribution coefficients of phenols is higher than other conventionally used ILs. Egorov et al. reported the use of these ILs to remove phenols and aromatic amines from aqueous solutions [76]. The distribution coefficients of respective pollutants by IL1 and IL2 were several times higher than the distribution coefficients of phenols and aromatic amines reported for other ILs. Distribution coefficients of the phenols and aromatic amines into IL1 and IL2 are shown in Appendix A.2. The thermal stability of these ILs, non-flammable nature and non-reactiveness to phenols in aqueous solutions is already established.

It is well known that the efficiency of liquid-liquid extraction is affected by the polarity of the solvent. The polarity of a solvent is an important characteristic that influences different types of interactions between the solute and the solvent molecules. Several experimental techniques, such as kinetic method, inverse gas chromatography, Dimroth-Reichardt's polarity $E_T(30)$ and refractive index measurement, are being utilized for the quantitative evaluation of polarity of compounds [76]. The Dimroth-Reichardt's polarity $E_T(30)$ of IL1 and IL2 along with few other solvents are presented in Appendix A.3. The $E_T(30)$ values of IL1 and IL2 are close to each other and vary from imidazolium-based ILs to some extent. The lower values of $E_T(30)$ these ILs clearly depicts these ILs to be less polar. The relatively lower values of $E_T(30)$ corresponds to higher extraction efficiency of solvents, in general [76]. This is in agreement to the results achieved in this study for the removal of pollutants such as phenols from SC as reported in Sections 4.3 – 4.10.

4.3. Effect of Phase Ratio

The effect of phase ratio (1 – 10) on the percent removal efficiency of pollutants from SC using IL1 and IL2 is illustrated in Figure 4.3. The operating conditions for liquid-liquid extraction in terms of contact time, pH, Initial COD concentration and stirring speed were 10 minutes, 13.0, 64166 mg/L and 2500 rpm, respectively. In LLE, various factors such as solubility of species, density of ILs, interfacial tension and

viscosity are known to affect the mass transfer between species. The removal efficiency of IL2 is observed to be higher than IL1 at the same parameters that can be due to lower viscosity of IL2 as compared to the viscosity of IL1. This lower viscosity of IL2 enhances the mixing efficiency leading to effective mass transfer of pollutants within the phases. It is evident from Figure 4.3 that the phase ratio of one is optimum for both ILs and thus was used in subsequent experimentation.

The removal efficiency of pollutants using IL1 and IL2 at high pH ranges is quite significant even at phase ratios of 10. At phase ratio 1 and pH of 13, the removal efficiency of pollutants using IL1 and IL2 were 76 and 86 percent, respectively. As the phase ratio increases, the removal efficiency decreases due to higher volumes of SC to be treated. However, the removal of pollutants from SC in to IL1 and IL2 was near to 40 percent even at a phase ratio of 20 and pH of 13.

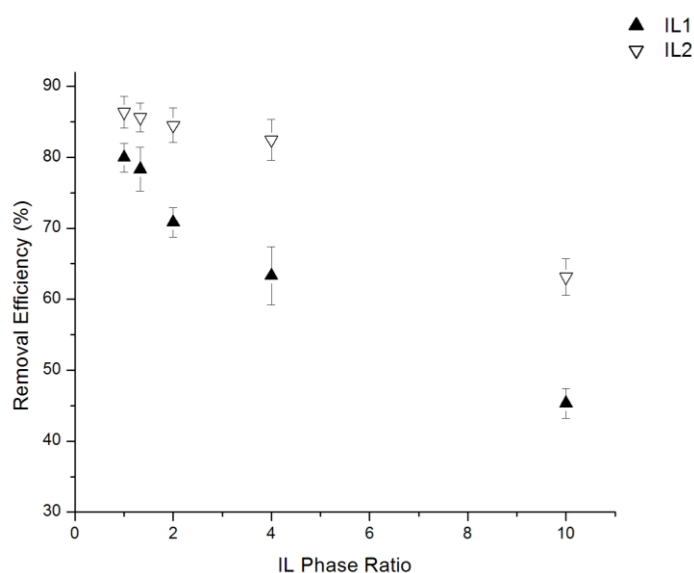


Figure 4.3: Effect of phase ratio on the removal percentage of pollutants from SC. Parameters: initial pH, stirring speed and contact time were 13, 2500 rpm and 10 minutes, respectively

4.4. Effect of Contact Time

Figure 4.4 depicts the removal efficiency of pollutants from SC as a function of contact time using IL1 and IL2. The LLE was carried out at optimum phase ratio of 1, pH of 13 and stirring speed of 2500 rpm while varying the contact time. The optimum time of less than 1 minute and 6 minutes was chosen for IL2 and IL1 as no appreciable increase in removal efficiency was observed after these optimum contact times, respectively. It is worth mentioning here that the contact time for the conventional SC

treatment processes is several hours for chemical treatment and even days in case of biological treatment facilities [2, 5, 7] while the processing time required for ILs is just few minutes.

The effect of scale-up on the contact time is quite obvious and pronounced in few cases due to the reduced surface to volume ratio and the limitations in intimate contact of phases between each other. This in turn increases the time necessary to achieve equilibrium in large-scale contactors or reactors. Hence, relatively large contact times will be observed to achieve equilibrium and transfer to pollutants to the IL phase as compared to bench-scale batch experiments.

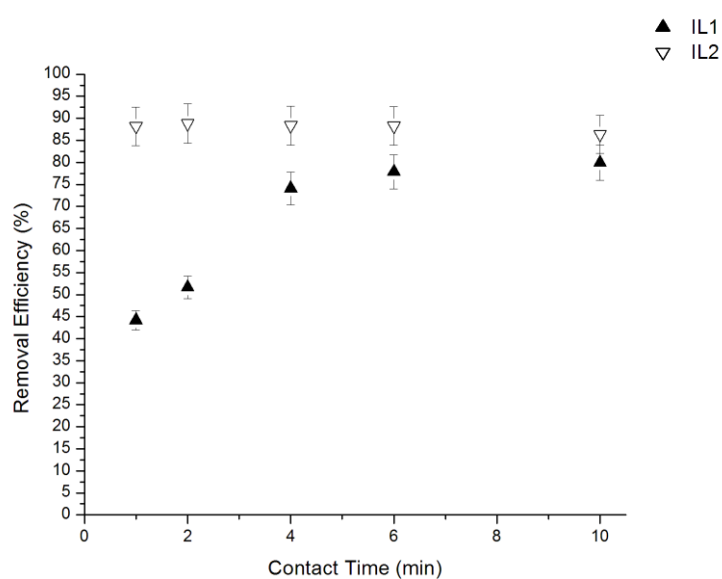


Figure 4.4: Effect of contact time on the removal percentage of pollutants from sc. Parameters: initial pH, stirring speed and phase ratio were 13, 2500 rpm and 1, respectively

It should be noted that the optimum contact time for SC treatment using other techniques is of several order of magnitudes larger than the bench-scale results of this study and the time required for ILs to achieve equilibrium can be anticipated to be relatively less even in large scale operations. Thus, this method has an added advantage of reduced processing times along with its simplified extraction procedure as compared to conventional complex processes requiring toxic chemicals and huge processing times for SC treatment.

4.5. Effect of pH

Figure 4.5 illustrates the effect of initial pH on the removal efficiency of pollutants from SC by using IL1 and IL2. The LLE was carried out in the pH range of 1.6 to 13 while keeping the other parameters at optimum conditions. It is obvious from Figure 4.5 that the LLE of pollutants from SC in ILs is highly pH dependent. The removal efficiencies of IL1 and IL2 increased from 76.5 and 85.3 to 99.9 percent as the initial pH was reduced from 12.9 to 1.76, respectively. The maximum removal efficiencies for both ILs were observed at acidic conditions. The results suggests that the removal efficiencies of pollutants such as phenols are highly favorable at acidic conditions [76, 86]. Similar trends have been reported in literature for phenol extraction using ILs [76, 86].

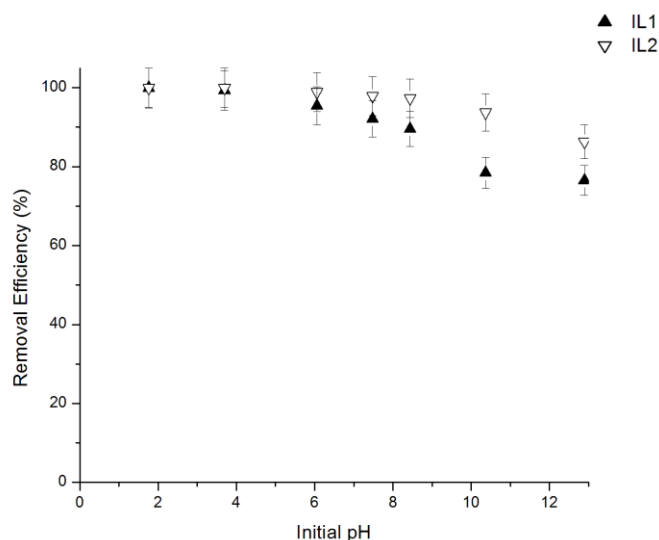


Figure 4.5: Effect of pH on the removal percentage of pollutants from SC. Parameters: phase ratio and stirring speed were 1 and 2500 rpm, respectively. The contact time for IL1 and IL2 was 4 minutes and 1 minute, respectively

Figure 4.6 reveals the effectiveness of these ILs in SC treatment at optimum conditions. At optimum conditions of phase ratio, time and pH, both ILs were able to remove majority of the pollutants from SC resulting in virtually clear water. The phenol concentration in treated wastewater (using IL2) was below the discharge limits as per environmental regulations for discharged bodies.

The behavior of IL1 and IL2 is quite remarkable in removing majority of the pollutants from SC at highly acidic pH. The removal efficiency of organic pollutants particularly phenols is highly pH dependent and tend to increase exponentially in acidic media [76]. The removal efficiency of imidazolium based ILs is higher in acidic media where the phenol is predominantly in their molecular form [76]. The distribution

coefficient for phenol tend to be negligible at pH values exceeding 12 in case of imidazolium based ILs.

The efficient transfer of phenols into these ILs points to the anion-exchange contribution to extraction. Egorov et al. discussed the contribution of anion-exchange to extraction at higher pH using 2,4-dinitrophenol as solute. The results of Egorov et al. confirms the anion-exchange mechanism contribution to extraction at $\text{pH} > \text{pK}_a$ (solute) [76].

The preferential portioning of aromatic amines and phenols may be attributed to the dispersive interactions of the solute particles with ILs cation. These dispersive interactions may be regarded as a driving force for mass transfer of phenol and aromatic compounds from aqueous phase to the IL phase [76].

4.6. Optimum Parameters

The optimum parameters for SC treatment by LLE using ILs in terms of phase ratio, time and pH were determined through experimentation, as described in Sections 4.2 – 4.4. The optimum pH and phase ratio for both IL was 1 and 1.6 respectively. The optimum time for SC treatment by LLE was less than one minute for IL2 and 6 minutes for IL1. At these optimum parameters, IL1 and IL2 were able to reduce the COD levels from 64166 ± 3880 mg/L to 54 ± 3.0 mg/L and 6.4 ± 1.8 mg/L spectroscopically. The standard deviations from the average values were calculated based on statistical analysis and the results from at least nine replicates.

The removal efficiency of both ILs is outstanding and this provides the foundation for studying the additional possibilities for SC treatment such as sequential batch contactors and use of IL for more than one extraction. The COD levels are within the discharge limits for industrial wastewaters. Conventional SC treatment plants require pre-treatment and post-treatment facilities to reduce the COD levels within the environmental regulations. It is noteworthy that this method does not require any pre-treatment or post-treatment technique and thus have high potential to reduce the SC treatment facility costs.

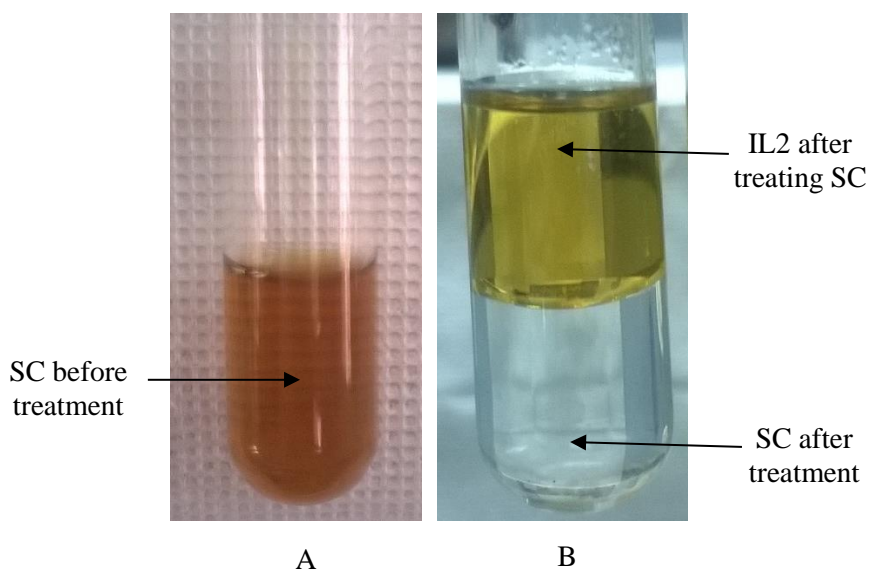


Figure 4.6: SC before treatment (A) and after treatment (B) with IL2. Parameters: Contact time: 1 min, stirring speed: 2500 rpm and pH of 1.7

4.7. Sequential Batch Contactors

LLE is a unique separation unit associated with the equilibrium concentration of solutes within two or more immiscible liquids. The complete transfer of pollutants from feed into the extractant (ILs) is, thus, limited by the relative solubility of these pollutants in both solvents and the equilibrium concentration. Mass transfer operations are mostly carried out in stages to enhance the mass transfer of species from one phase to another. In order to enhance the LLE of pollutants from SC into ILs, two types of sequential batch contactors were employed e.g. two sequential batch contactors and three sequential batch contactors. In case of two sequential batch contactors, the phase ratio of each IL was set at 2 keeping all other parameters at optimum conditions (Section 4.5). The optimum contact time was 1 minute and 4 minutes for IL1 and IL2, respectively. The pH and stirring speed was maintained at 1.76 and 2500 rpm, respectively. The results demonstrated that the first contactor removed majority of the pollutants from the SC. The removal efficiency of first contactor exceeded 95 percent while the second contactor removed virtually all remaining pollutants from SC for both ILs (Figure 4.7 – 4.8).

Three sequential batch contactors were employed at optimum conditions (Section 4.5) with phase ratio of 4. The results verify that increasing the stages or the number of batch contactor enhances the removal of pollutants from SC. First two

contactors jointly resulted in removal efficiencies exceeding 99 percent. The third contactor can be regarded as a polishing step as most of the pollutants were removed in first two contactors.

The sequential batch reactors were studied to ensure the potential of ionic liquids to be used in series or continuous mode operations. As the number of stages increases, the efficiency increases. This is in agreement to the literature as the mass transfer of solutes between different immiscible solvents is dependent on the mass transfer of solute within phases. The mass transfer efficiency is enhanced by increasing the number of stages. The efficiency in one batch is always limited due to the mass transfer limitations and the mass transfer driving force limitation. By increasing the number of batches the mass transfer rate and efficiency is increased due to enhanced mass transfer driving force at each stage.

4.8. Multiple Usage

The results, as described in Section 4.2 – 4.6, are encouraging to further analyze and determine the extraction effectiveness and the maximum concentration uptake by these ILs. These ILs were utilized several times to treat SC before these ILs reached their saturation limits. IL1 and IL2 were able to treat neat SC three times before they were saturated. In case of three sequential batch contactors, the first contactor and second contactors reached maximum capacity within three cycles while third contactor remained in service for more than 5 cycles. The removal efficiency of pollutants by IL1 and IL2 decreased to negligible amount in first two cycles. However, the extraction of pollutants from SC using LLE by ILs decreased exponentially as the ILs reached near to its respective saturation limits. These results points out towards the fact that it is prospective to utilize IL1 and IL2 more than once for SC treatment using LLE.

4.9. Compositional Analysis using GC-MS

GC-MS profiles of industrial SC before and after treatment by IL1 and IL2 were investigated using EPA-3510c and EPA-8270d protocols. The treatment of SC was carried out at optimum conditions as per the parameters mentioned above (Section 4.5 – 4.6). Figure 4.7 and 4.8 (SC) represents the GC-MS profiles with the peaks and relative area of SC before treatment. GC-MS analysis revealed more than 120 peaks demonstrating the presence of several organic pollutants mostly identified as phenols and thiols in the SC under consideration. This emphasizes the complexity of this system

and the need to treat it in an environment friendly manner. The structure of representative and major pollutants present in SC has been presented in Appendix A.1. The major contaminants present in SC, before and after treatment, were identified using GC-MS analysis and the results are reported in Table 4.1. The results reveal the presence of major pollutants in the SC before treatment. From these 120 compounds present in the industrial SC, 5 major peaks were identified as thiol compounds, 36 peaks represent phenols and their derivatives while 10 peaks were identified as benzaldehyde compounds at different retention times.

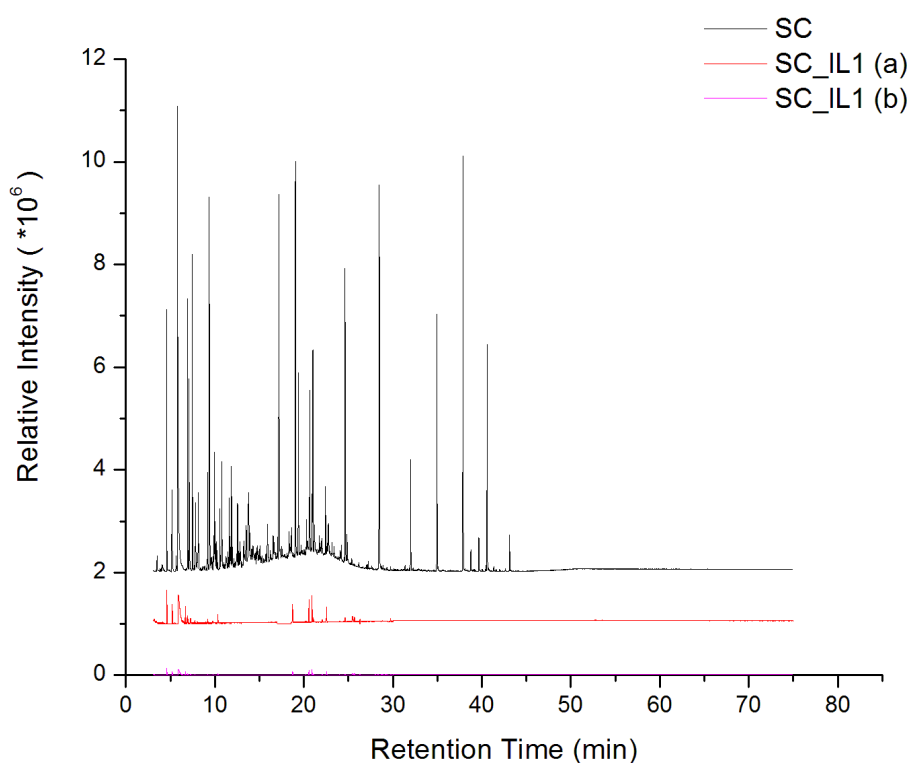


Figure 4.7: GC-MS profiles for SC (spent caustic without any treatment) and SC_IL1 (spent caustic after treatment with IL1) for (a) bench-scale batch experiment with phase ratio one (b) sequential batch contactor with phase ratio of 2. The LLE parameters in terms of time, pH and stirring speed were 6 min, 1.7 and 2500 rpm, respectively.

The presence of high concentrations of phenols and thiols was expected in SC and is in line with the SC received from the refinery. Figure 4.7 and 4.8 represent the peaks and relative areas of the pollutants present in industrial spent before and after treatment using IL1 and IL2 at optimum conditions for batch-bench scale and sequential batch experiments. The results in these figures demonstrate the complete transfer of the majority of pollutants from the aqueous phase (SC) to the IL phase (IL). The data summarized in Tables 4.1 demonstrate that most of the pollutants identified in the SC

were removed after treatment with IL1 and IL2. The overall removal efficiency of phenol by IL2 exceeded 99 percent. The thiols and benzaldehyde compounds were below the detection limit in the case of SC treated with IL2. The weighted removal efficiency of respective pollutant family was calculated to be exceeding 98 percent and 99 percent for IL1 and IL2 in case of bench-batch scale experiments (Table 4.2), respectively. Such results are in line with the experimental results discussed earlier using UV-VIS. Thus, this analysis indicates the complete removal of such hazardous pollutants from SC solution.

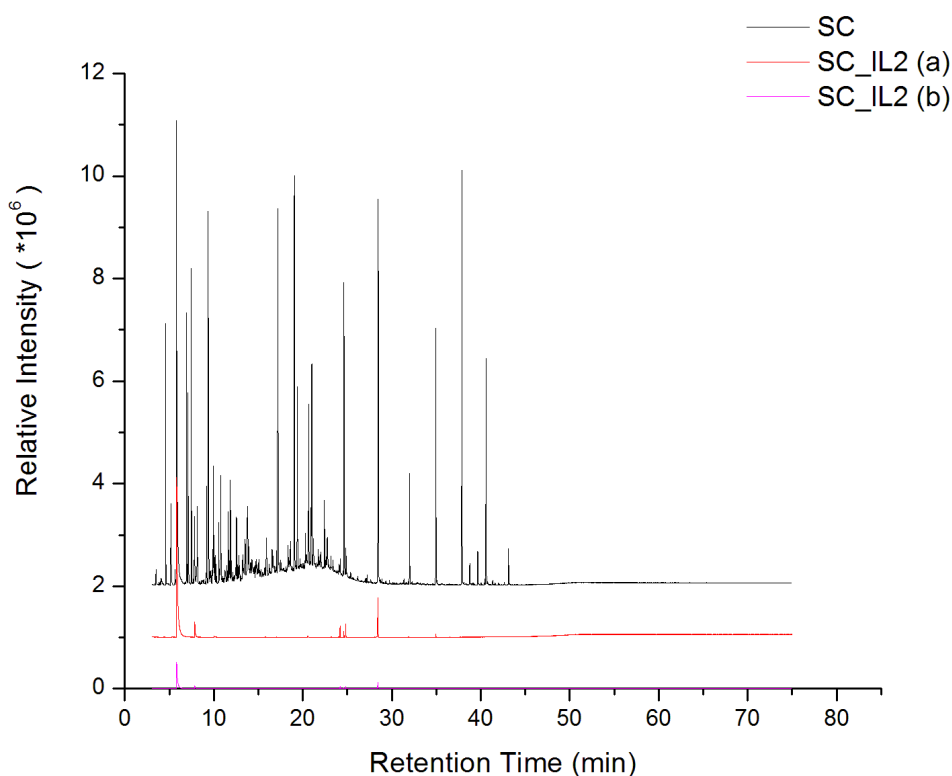


Figure 4.8: GC-MS profiles for SC (spent caustic without any treatment) and SC_IL2 (spent caustic after treatment with IL2) for (a) bench-scale batch experiment with phase ratio one (b) sequential batch contactor with phase ratio of 2. The LLE parameters in terms of phase ratio, time, pH and stirring speed were 1, 1 min, 1.7 and 2500 rpm, respectively

It is evident from Figure 4.7 and 4.8 that the removal efficiency of pollutants from SC by ILs was enhanced by the introduction of sequential batch contactors. Figure 4.7 and 4.8 represent the comparison of removal efficiencies of IL1 and IL2 in (a) bench-batch scale and (b) SBC studies by comparing the GC-MS profiles of SC treated with these ILs in both modes.

The sequential batch contactor details have been discussed in Section 4.6. It is evident from Figure 4.7 and 4.8 that the relative peak areas of pollutants were greatly

reduced to negligible amounts by use of two sequential batch contactors at optimum parameters and phase ratio of 2. The percentage removal efficiencies of pollutants from SC by IL1 exceeded 99.5 percent in case of thiols and 99.99 percent for phenols and benzaldehydes. The concentration levels for these hazardous pollutants were below detection limit in case of SC treated with IL2 in sequential batch mode. Detailed removal efficiencies of these ILs in case of bench-batch scale and sequential batch contactors experimentations are reported in Appendix A.4.

Table 4.1: Percentage removal of major impurities from SC as determined by GC-MS.

SC Component	Percentage Removal (% \pm 0.5%)			
	One Contactor		Two Contactors	
	Using IL1	Using IL2	Using IL1	Using IL2
Phenols	98.54	99.99	99.99	100.0
Thiols	88.59	100.0	99.59	100.0
Benzaldehyde	94.88	100.0	99.99	100.0

It is worth noting that both ILs were effective in removing pollutants. However, IL2 was more efficient in removing thiols and benzaldehyde from SC to below detectable limits.

As observed from Tables 4.1 and 4.2, IL2 was able to remove greater number of compounds from the SC as compared to IL1. However, it is worth noting that IL1 was able to remove some compounds from SC more effectively as compared to IL2. Overall, the removal efficiency of IL2 was higher than that of IL1, with a shorter contact time and demonstrated removal efficiencies exceeding 65 % even at IL:SC phase ratio of 1:10 as compared to below 50 percent efficiency of IL1 at phase ratio of 10 (Figure 4.3).

Table 4.3 represents the COD levels of SC before and after being treated by IL. The removal efficiency of organics based on the COD levels provides further confirmation of the results obtained in the GC-MS study.

Table 4.2: COD comparison of SC before and after treatment with respective IL

Using	COD Initial of SC	COD Final of TSC	Percentage Removal	COD Final of TSC	Percentage Removal
		One Contactor		Two Contactors	
IL1	64166 ± 3880	963 ± 81	98.50 ± 0.13	281 ± 43	99.56 ± 0.07
IL2	64166 ± 3880	481 ± 65	99.25 ± 0.10	63.0 ± 9.0	99.90 ± 0.01

The removal efficiencies of both ILs were determined using three different routes namely COD, UV-Vis spectrophotometry and GC-MS profiles. The differences in the relative peak areas of pollutants before and after treatment of SC by ILs represented the percentage removal of respective pollutants from SC. The results from all three methods are in sound agreement to each other thus pointing out towards the validity of this treatment method. In short, IL1 and IL2 were able to address the critical problem of SC treatment in environment benign simple method. The results indicate that the effluent after being treated with these ILs can be discharged to water bodies without any significant change in their physical or chemical nature and is of sufficient quality to comply with the environmental regulations governing effluent discharge standards.

4.10. Regeneration

Regeneration studies were carried out to determine the regeneration efficiency of IL1 and IL2 and the optimum parameters required for their regeneration. Till today, successful regeneration of IL1 and IL2 is elusive due to the lack of complete knowledge of their chemistry and regeneration parameters. Four different regeneration techniques could be suggested for effective regeneration of ILs such as : steam stripping, solvent extraction, high temperature regeneration and low temperature regeneration.

The steam stripping could be used to transfer the pollutants from IL phase to the vapor phase due to the mass transfer potential difference between the phases. However, this method carries limitation. It is not a feasible option because substantial amounts of steam will be required for regeneration.

In solvent extraction a volatile solvent is required to transfer the pollutant from the IL phase to the solvent phase. This method has limitations because of the selection of the volatile solvent. The use of a volatile solvent is again a major drawback. A second limitation arises in the cost of the selected solvent.

The freezing temperature of IL1 and IL2 is between 268 – 271 K and they are miscible with hexane, acetone and ethanol. The regeneration of ILs could be obtained by manipulating the freezing point. The used ILs were mixed with equal volumes of hexane and subjected to a temperature below 258 K. Reducing the temperature resulted in two phases, the solidified IL2 and the liquid phase (a mixture of pollutants and hexane). The results were not reproducible as the separation of liquid and solid phases depends on the chemistry and thermodynamic behavior of the mixture. The removal efficiency and the amount of pollutant transferred to the IL layer vary in each run resulting in changes in the phase behavior of the mixture. In-depth study of the mixture behavior is required to fully develop the technique.

The regeneration of IL1 and IL2 using elevated temperature was also tested. The behavior of ILs, SC and used ILs was studied using Thermal Gravimetric Analysis (TGA) and presented in Figure 4.9. These results dictate that the thermal process for regeneration of these ILs is not a feasible option. However, the TGA provided useful insight into the thermal behavior of these ILs before and after being utilized for SC treatment.

The TG curve of SC shows that the majority of the mass was either evaporated or decomposed before 423 K. It is worth noting that even at 1173 K, the mass fraction of the SC sample was still retained, which indicated that not all components of SC were decomposed at 1173 K. This is in line with the literature as higher temperature and pressure conditions are required for the complete oxidation of pollutants in SC [5, 10]. The TG curves of IL1 and IL2 show that ILs decompose at 513 K and 483 K, respectively and are thermally stable before these temperatures. It is apparent from Figure 4.9 that the used IL1 and IL2 decompose completely at 973 K and 993 K, respectively. However, the majority of the pollutants were decomposed with IL2 at 580 K. This suggests that IL2 could behave like a catalyst by decomposing the SC pollutants at lower temperatures than usual [5, 10]. Secondly, there might be some chemical interaction between the IL2 and the pollutants that could be effective at elevated temperatures. This needs to be further analyzed. The suggestion of any chemical interaction between pollutant and ILs is purely indicative rather than conclusive.

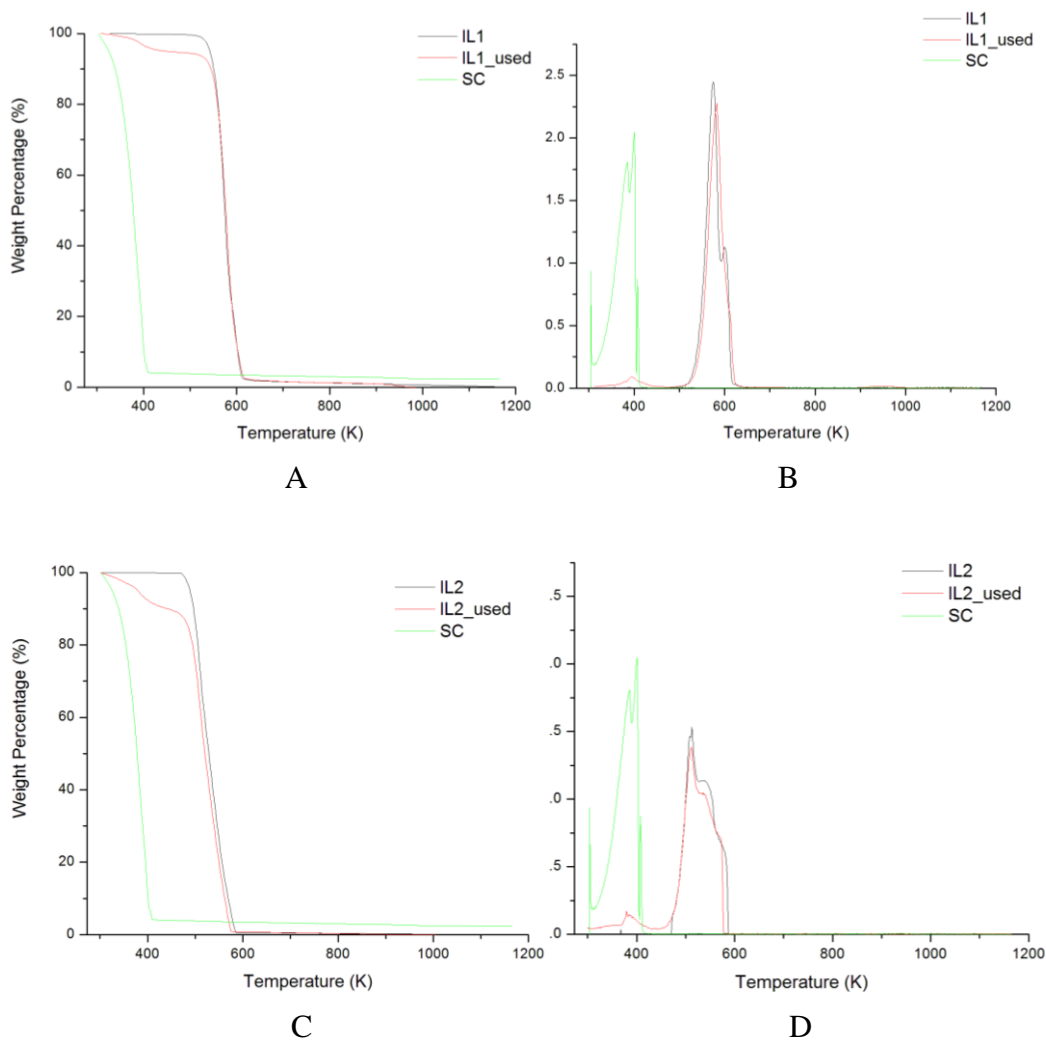


Figure 4.9: TGA of SC, ILs and used ILs. Parameters: Phase ratio of 1, contact time of 1 minute (IL2) and 4 minutes (IL1), pH: 1.75

4.11. Process Intensification and Recommendations

The high distribution coefficient and sequential batch contactor results at low pH suggest that a detailed study of the removal efficiency of pollutants from SC using ILs at low pH is needed and hints at the potential of the ILs to be used in continuous extraction operation.

The reduction in COD levels of SC using IL1 and IL2 was studied at pH 1.75 and 1.55 with a phase ratios between 1 to 20. Figure 4.10 illustrates that these ILs were able to reduce considerable amount of COD even with a phase ratio of 20 and a pH of 1.55. The IL2 was superior to IL1 in terms of removal efficiency of pollutants from SC. However, according to the Egorov et al., IL1 is superior to L2 [76]. This might be due to sample characteristic such as high concentration, chemistry and the distribution coefficients of pollutants between ILs and water. Furthermore, SC is a multicomponent

system while the results reported by Egorov et al. for the use of IL1 and IL2 for phenol and aromatic compounds removal was for single pollutant in water system [76].

LLE of any system is dependent on a variety of factors including, but not limited to, the interfacial area, rate of mass transfer, viscosity, and the affinity of extractant for solute. The extraction efficiency is increased by either increasing the interfacial area or reducing the mass transfer resistance. The mass transfer resistance could be reduced by increasing temperature that reduces the fluid viscosity causing an improvement in the mass transfer between the phases. Interfacial area can be increased by decreasing the droplet size. Very small droplet size can create emulsions, generating difficulties in emulsion separations afterwards. Therefore, an optimum droplet size is required in the SC treatment process. The removal efficiency and distribution coefficient for pollutants from SC using IL1 and IL2 has been summarized in Table 4.3. The results were utilized to determine the number of stages for continuous flow systems.

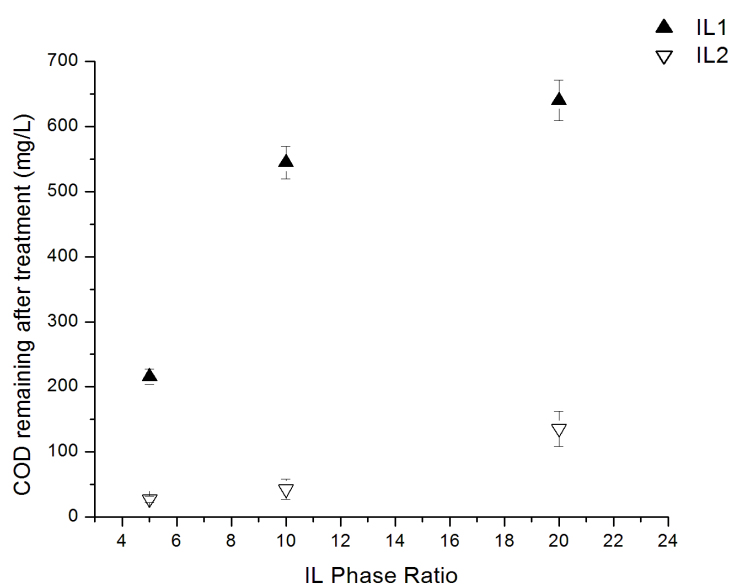


Figure 4.10: COD remaining after SC treatment using IL1 and IL2 at different phase ratios. Parameters: pH = 1.55 and contact time: 1 minute (IL2), 4 minutes (IL1)

Table 4.3: COD comparison of SC before and after treatment with respective IL. Parameters: pH = 1.55, contact time = 1 minute (IL2), 4 minutes (IL1), mixing speed = 2500 rpm

Using	COD Initial of SC	COD Final of TSC	Percentage Removal	D	COD Final of TSC	Percentage Removal	D
		Phase ratio = 10			Phase ratio = 20		
IL1	64166 ± 3880	544 ± 20	99.15 ± 0.03	1166	640 ± 25	99.00 ± 0.04	1980
IL2	64166 ± 3880	42.7 ± 7.7	99.93 ± 0.02	14275	135 ± 22	99.79 ± 0.04	9503

The continuous extraction column is preferred over mixer settlers or batch process because of the short equilibrium contact time. The number of stages required for decreasing the pollutant levels to the permissible discharge limits has been calculated using Kremser Method for dilute systems [87]. The pollutant concentration in the SC is nearly 64 g/L which makes up to 6.4 percent by weight of the solution. Taking this assumption to be valid for preliminary assessment, the number of stages required were calculated [87]. In addition, the value of distribution coefficients (D) was calculated using equation (13) based on UV-Vis spectroscopic readings. The values of these distribution coefficients are in a good agreement with the values of distribution coefficients for phenols and aromatic compounds for these ILs [76].

Using the assumption of linear equilibrium and Kremser method for dilute systems [87], the equilibrium form can be written as

$$y_i = m_i x_i + b_i \quad (16)$$

and the number of stages can be determined using following equation

$$N = \frac{\ln\left[\left(1 - \frac{mE}{R_f}\right)\left(\frac{y_{N+1} - y_1^*}{y_1 - y_1^*}\right) + \frac{mE}{R_f}\right]}{\ln\left(\frac{R_f}{mE}\right)} \quad (17)$$

where m_i is the slope and is equal to the distribution coefficient, R_f is the raffinate (SC) flowrate, E is the flowrate of the Extractant (ILs), Y_i and x_i refer to the extract fraction of solute and raffinate fraction of solute leaving stage i , respectively. N is the number

of stages required for removal. The quantity mE/R_f is referred to as extraction factor, E_f . Y_1^* is given by the following equation

$$y_1^* = mx_o + b \quad (18)$$

The values of theoretical number of stages in 99.9 percent removal efficiency and the extraction factor for both IL2 have been summarized in Table 4.4.

Table 4.4: Number of stages required for percentage removal exceeding 99.99 % with respective IL. Parameters: pH = 1.55, contact time = 1 minute (IL2), 4 minutes (IL1), mixing speed = 2500 rpm

Using	D	Extraction Factor	No of Stages	D	Extraction Factor	No of Stages
	Phase ratio = 10			Phase ratio = 20		
IL1	1166	116.6	<2	1980	99.0	<2
IL2	14275	1427	<2	9503	475	<2

It can be concluded from this preliminary analysis that higher phase ratio could be used to reduce the volume of IL used for SC treatment. This will increase the number of stages, however it will significantly increase the economic feasibility of this process.

4.12. Suggestions and Recommendations

Spent caustic treatment is an industrial waste generated by petrochemical industries due to processes such as scrubbing of gasoline, light petroleum gas, kerosene and diesel. In general, diluted spent caustic is used to remove pollutants from these hydrocarbon streams thus increasing the quality of these fuels. However, this result in the production of wastewater stream known as spent caustic containing toxic contaminants such as, but not limited to, phenols, mercaptans, thiols and their derivatives.

Treatment of spent caustic is arduous task due to its complex characteristics such as high pH, high COD levels, high toxicity, high corrosivity and is known as one of the most difficult and toxic wastewater to be treated and disposed of. The composition of spent caustic is dependent on the process, hydrocarbon feed, purity of feed and the maturity of the oil fields. Thus, the composition of spent caustic varies

from time to time. For example, in a typical oil company the COD level variations within one month were recorded to be between 52000 and 78000 mg/L. The enhanced complexity of SC treatment is quite obvious from these details. Important conventional methods include incineration, wet air oxidation, neutralization and chemical oxidation. These mostly require use of toxic chemicals, high capital cost, high temperature and pressure conditions. These methods are neither economical no environment friendly.

To address all these problems and treat spent caustic wastewater in economically and environment friendly way, a simple liquid-liquid extraction technique for SC treatment using ILs is proposed. This technique is environment friendly, unique and operates at normal temperature and pressure conditions. Figure 4.11 shows the simplified block diagram of this proposed model.

In this technique, the spent caustic from the process is sent to the mixer or liquid-liquid extraction unit. Ionic liquid as extractant is added continuously. The required contact time is less than 1 minute after which these streams are sent to the separation unit. The separation is based on density difference of ionic liquid and the wastewater stream.

The treated wastewater could be discharged directly to the water bodies as the COD levels and other contaminants are either completely removed or their concentration levels are well below the discharge limits as set by the environmental agencies. Note that the process does not require the use of any post-treatment systems such as biological treatment plants. This completes the first phase.

What happens with the ionic liquid is the second phase. The ionic liquid is utilized more than twice to pre-treat the incoming spent caustic stream to minimize the fresh ionic liquid addition requirements. After complete exhaustion of ionic liquid, it could be sent to the combustion chamber where it will decompose along with the majority of the pollutants at 523 K -580 K and atmospheric pressure. It is worth noting that the temperature conditions in traditional incineration unit is quite high, typically 1123 K. These pollutants decompose at much lower temperature due to the presence of ionic liquid. This decreases the energy requirements and safety concerns of this technique. Though the decomposition of ILs does not feel viable due to their commercial prices, however preparation of these ILs from their respective precursors can yield suitable economic feasibility. Detailed economic study is essential to substantiate this procedure for SC treatment at industrial scale.

The CO₂ and H₂ or H₂O produced in the combustion chamber could be captured and converted to methane using bi-functional adsorption-catalysis. This is an area of particular research interest. Some research is being carried out at the various research institutes. The methane could be the raw material for the synthesis of these ionic liquids thus completing the cycle. The excess methane produced could be used to meet or lower the energy requirements of the combustion chamber.

The first phase of this method has been completed successfully showing excellent results with percent removal efficiencies exceeding 99.99 for phenols, thiols and mercaptans. This in itself is unique as no method gives that much removal efficiency for phenols particularly. Furthermore, this method does not require pre-treatment and post-treatment facilities and thus enhances the overall economic feasibility of this technique. This technique even in this raw or first phase outnumbers the advantages of various other methods and once developed can revolutionize the petroleum industry.

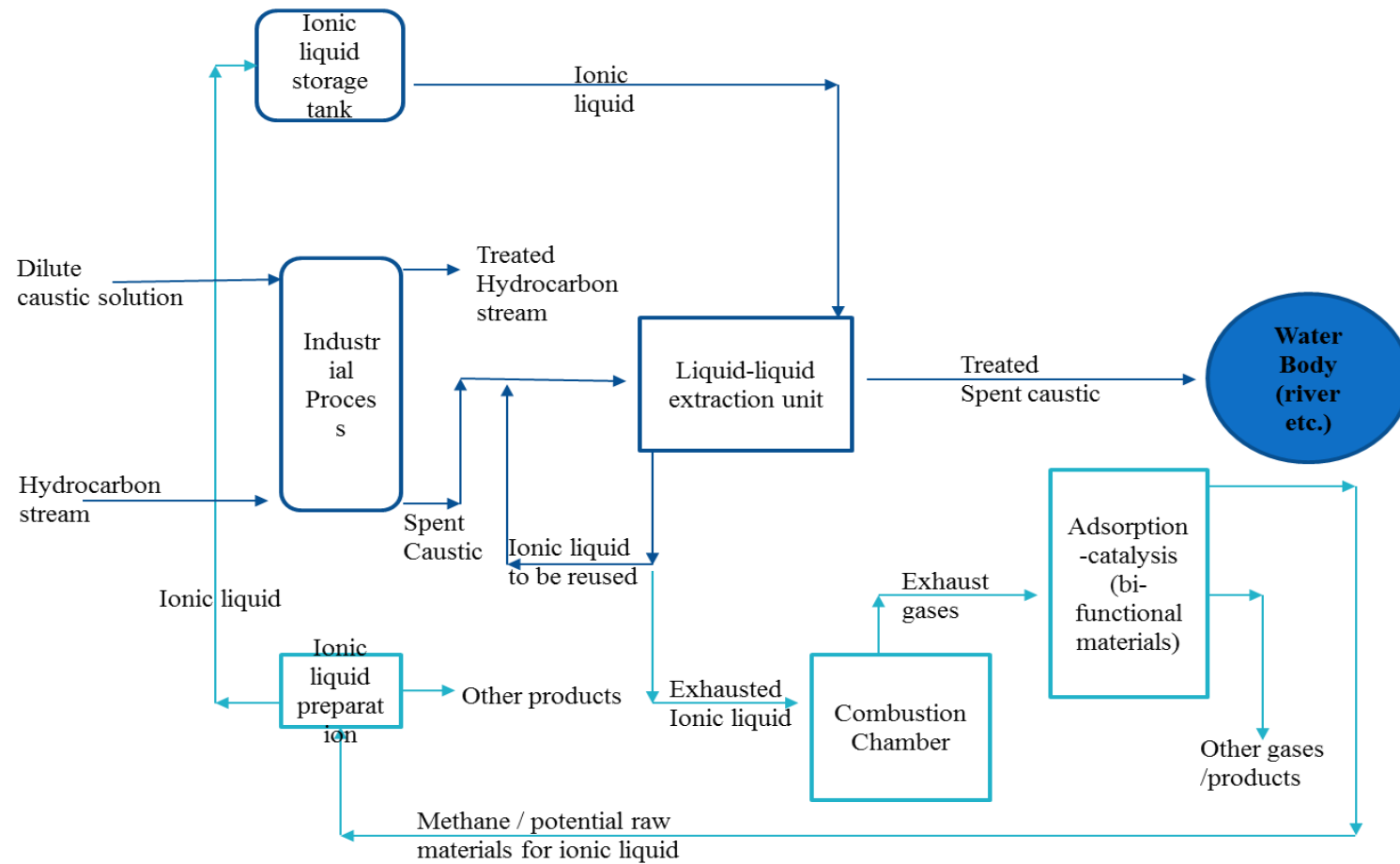


Figure 4.11: Non-conventional Spent Caustic Treatment Technique

Chapter 5: Conclusions

Two hydrophobic room temperature ILs, tetrahexylammonium dihexylsulfosuccinate (IL1) and trioctylmethylammonium salicylate (IL2), were employed as extraction solvents for pollutant removal, such as phenols and thiols, from industrial spent caustic (SC) wastewater in bench-scale batch contactor and sequential batch contactors. The chemical oxygen demand concentrations and compositional analysis of SC wastewater was carried out using standard COD method and GC-MS spectroscopy, respectively. The GC-MS spectroscopy using EPA-3510c and EPA-8270d protocols revealed that the SC consists of more than 120 compounds, majority of which were identified as phenols, thiols, benzaldehydes and their derivatives. Liquid-liquid extraction technique (LLE) using IL1 and IL2 was employed successfully for pollutants extraction from SC. The optimum parameters of LLE in terms of phase ratio and pH were determined to be 1 and 1.7 for both ILs in batch-bench scale studies. The optimum contact time for IL1 and IL2 was determined to be six minutes and less than 1 minute, respectively. At optimum conditions, the removal efficiency of phenols exceeded 99.9 percent and 99.8 percent in case of IL2 and IL1, respectively. Thiols and benzaldehydes were below detection limit in case of wastewater treated with IL2. The COD concentration levels was reduced from 64166 mg/L to 963 mg/L and 481 mg/L in case of IL1 and IL2 resulting in virtually clear water after treatment. In case of sequential batch contactors, the removal efficiency of both ILs exceeded 99.9 percent for two contactors. The COD concentration levels were reduced from 64166 mg/L to 63 mg/L in case of IL1. The treated SC was of sufficient quality to comply with the environmental wastewater discharge standards. These remarkable results of pollutants level reduction in just few minutes at ambient temperature and pressure conditions represent the outstanding potential of ILs for SC treatment. Furthermore the inherent properties of ILs such as negligible vapor pressure, high thermal stability and environment friendly nature along with their potentials in wastewater treatment emphasizes their possible utilization as green solvents and alternative to existing complex SC treatment techniques. In short, this work identifies a novel simple LLE process that employs environment friendly solvents with processing times less than 6 minutes in contrast to conventional complex techniques that require hazardous chemicals, large retention times and drastic conditions of temperatures and pressures

for SC treatment. Further experimentation and pilot scale studies are required to fully determine the feasibility of this method at commercial scale.

References

- [1] P. R. Gogate and A. B. Pandit, "A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions," *Advances in Environmental Research*, vol. 8, no. 3–4, pp. 501-551, 2004.
- [2] K. Bryan, C. Felch, and C. Maugans, "Wet air oxidation treatment of spent caustic in petroleum refineries," presented at the National Petroleum Refiner's Association Conference, Phoenix, AZ, 2010.
- [3] J. Ketu, "Treatment and disposal of spent caustic at TEMA oil refinery (TOR)," M.Sc. thesis, Department of Materials Engineering, Kwame Nkrumah University of Science and Technology, Kumasi, South Ghana, 2013.
- [4] "What Are Spent Caustics". Available: <http://www.spentcaustic.com/whataresp.html>. [accessed: 9 April 2016]
- [5] G. Veerabhadraiah, N. Mallika, and S. Jindal. Spent caustic management: Remediation review," 2011. Available: <http://www.hydrocarbonprocessing.com/Article/2925664/Spent-caustic-management-Remediation-review.html>. [accessed: 9 April 2016]
- [6] J. G. Speight, *The Chemistry and Technology of Coal*, 2nd ed. NY, USA: Marcel Dekker Inc. New York, 1995
- [7] R. L. Stephensen and J. B. Blackburn Jr., *The Industrial Wastewater Systems Handbook*. Boca Raton, USA: Lewis Publishers, 1998.
- [8] A. Kolhatkar and K. L. Sublette, "Biotreatment of refinery spent sulfidic caustic by specialized cultures and acclimated activated sludge," *Applied Biochemistry and Biotechnology*, vol. 57, no. 1, pp. 945-957, 1996.
- [9] J. A. Conner, R. R. Beitle, K. Duncan, R. Kolhatkar, and K. L. Sublette, "Biotreatment of refinery spent-sulfidic caustic using an enrichment culture immobilized in a novel support matrix," (in eng), *Appl Biochem Biotechnol*, vol. 84-86, pp. 707-19, 2000.
- [10] R. Alnaizy, "Economic analysis for wet oxidation processes for the treatment of mixed refinery spent caustic," *Environmental Progress*, vol. 27, no. 3, pp. 295-301, 2008.
- [11] S. Z. Masoomian, "Apparatus for treating and regenerating spent caustic," US Patent 5368726 A, November 29, 1994.
- [12] R. A. Meyers, *Handbook of Petroleum Refining Processes*, 4 ed. NY, USA: McGraw-Hill, 2016.
- [13] A. Samadiashar, "Study on basic methods of spent caustic treatment," 2012. Available: http://www.sid.ir/en/VEWSSID/s_pdf/155E20120105.pdf. [accessed: 9 April 2016]
- [14] R. Forbess, B. Kumfer, and S. Olsen, "Wet air oxidation treatment of spent caustic in ethylene plants and petroleum refineries," SIEMENS, Available: <http://www.sawea.org/pdf/2009/Session%20F/Wet%20Air%20Oxidation%20>

- Treatment% 20of% 20Spent% 20Caustic% 20in% 20Ethylene% 20Plants% 20and% 20Petroleum% 20Refineries.pdf. [accessed: 9 April 2016]
- [15] A. Olmos, P. Olguin, C. Fajardo, E. Razo, and O. Monroy, "Physicochemical Characterization of Spent Caustic from the OXIMER Process and Sour Waters from Mexican Oil Refineries," *Energy & Fuels*, vol. 18, no. 2, pp. 302-304, 2004.
- [16] "Spent caustic (from normal alpha olefins unit)," 2010. Available: http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3019333/pdf/11606_2010_Article_1527.pdf. [accessed: 9 April 2016]
- [17] USEPA, "EPA Hazardous waste codes". Available: <http://www.des.umd.edu/hw/rest/manual/codes.html>. [accessed: 9 April 2016]
- [18] USEPA, "Petroleum refining effluent guidelines". Available: <https://www.epa.gov/eg/petroleum-refining-effluent-guidelines>. [accessed: 9 April 2016]
- [19] "Hydrogen sulphide management mitigation options in petroleum refining, storage and transportation," *Baker Hughes*, 2014. Available: <http://www.bakerhughes.com/news-and-media/resources/white-papers/hydrogen-whitepaper-060210>. [accessed: 9 April 2016]
- [20] H. M. Ramadan, "Characterization and treatment of spent caustic," M.Sc. thesis, Environmental Engineering, Qatar University, 2013.
- [21] L. Oliviero, J. Barbier Jr, and D. Duprez, "Wet Air Oxidation of nitrogen-containing organic compounds and ammonia in aqueous media," *Applied Catalysis B: Environmental*, vol. 40, no. 3, pp. 163-184, 2003.
- [22] K.-H. Kim and S.-K. Ihm, "Heterogeneous catalytic wet air oxidation of refractory organic pollutants in industrial wastewaters: A review," *Journal of Hazardous Materials*, vol. 186, no. 1, pp. 16-34, 2011.
- [23] C. E. Ellis, "Wet air oxidation of refinery spent caustic," *Environmental Progress*, vol. 17, no. 1, pp. 28-30, 1998.
- [24] F. Arena, C. Italiano, A. Raneri, and C. Saja, "Mechanistic and kinetic insights into the wet air oxidation of phenol with oxygen (CWAO) by homogeneous and heterogeneous transition-metal catalysts," *Applied Catalysis B: Environmental*, vol. 99, no. 1-2, pp. 321-328, 2010.
- [25] S. T. Kolaczowski, P. Plucinski, F. J. Beltran, F. J. Rivas, and D. B. McLurgh, "Wet air oxidation: a review of process technologies and aspects in reactor design," *Chemical Engineering Journal*, vol. 73, no. 2, pp. 143-160, 1999.
- [26] W. Zhu, Y. Bin, Z. Li, Z. Jiang, and T. Yin, "Application of catalytic wet air oxidation for the treatment of H-acid manufacturing process wastewater," *Water Research*, vol. 36, no. 8, pp. 1947-1954, 2002.
- [27] V. K. Sharma *et al.*, "Destruction of microcystins by conventional and advanced oxidation processes: A review," *Separation and Purification Technology*, vol. 91, pp. 3-17, 2012.

- [28] J. M. Poyatos, M. M. Muño, M. C. Almecija, J. C. Torres, E. Hontoria, and F. Osorio, "Advanced Oxidation Processes for Wastewater Treatment: State of the Art," *Water, Air, and Soil Pollution*, vol. 205, no. 1, pp. 187-204, 2009.
- [29] R. Munter, "Advanced oxidation processes—current status and prospects," *Proc. Estonian Acad. Sci. Chem*, vol. 50, no. 2, pp. 59-80, 2001.
- [30] P. Cañizares, R. Paz, C. Sáez, and M. A. Rodrigo, "Costs of the electrochemical oxidation of wastewaters: A comparison with ozonation and Fenton oxidation processes," *Journal of Environmental Management*, vol. 90, no. 1, pp. 410-420, 2009.
- [31] R. Andreozzi, V. Caprio, A. Insola, and R. Marotta, "Advanced oxidation processes (AOP) for water purification and recovery," *Catalysis Today*, vol. 53, no. 1, pp. 51-59, 1999.
- [32] A. G. Chakinala, P. R. Gogate, A. E. Burgess, and D. H. Bremner, "Treatment of industrial wastewater effluents using hydrodynamic cavitation and the advanced Fenton process," *Ultrasonics Sonochemistry*, vol. 15, no. 1, pp. 49-54, 2008.
- [33] P. R. Gogate and A. B. Pandit, "A review of imperative technologies for wastewater treatment II: hybrid methods," *Advances in Environmental Research*, vol. 8, no. 3-4, pp. 553-597, 2004.
- [34] H. K. Shon, S. Vigneswaran, and S. A. Snyder, "Effluent Organic Matter (EfOM) in Wastewater: Constituents, Effects, and Treatment," *Critical Reviews in Environmental Science and Technology*, vol. 36, no. 4, pp. 327-374, 2006.
- [35] S. Sharma, J. Ruparelia, and M. L. Patel, "A general review on Advanced Oxidation Processes for waste water treatment," *Nirma University International Conference*, Ahmedabad, Gujarat, 2011.
- [36] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, and R. Sanchirico, "Advanced oxidation processes for the treatment of mineral oil-contaminated wastewaters," *Water Research*, vol. 34, no. 2, pp. 620-628, 2000.
- [37] C. Gottschalk, J. A. Libra, and A. Saupe, "Application of Ozone in Combined Processes," in *Ozonation of Water and Waste Water*: Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 267-343.
- [38] F. Hernandez and G. Geissler, "Photooxidative treatment of sulfurous water for its potabilization," (in eng), *Photochem Photobiol*, vol. 81, no. 3, pp. 636-40, 2005.
- [39] W. H. Glaze, J.-W. Kang, and D. H. Chapin, "The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation," *Ozone: Science & Engineering*, vol. 9, no. 4, pp. 335-352, 1987.
- [40] I. A. Alaton, I. A. Balcioglu, and D. W. Bahnemann, "Advanced oxidation of a reactive dye bath effluent: comparison of O₃, H₂O₂/UV-C and TiO₂/UV-A processes," *Water Research*, vol. 36, no. 5, pp. 1143-1154, 2002.

- [41] T. Yonar, G. K. Yonar, K. Kestioglu, and N. Azbar, "Decolorisation of textile effluent using homogeneous photochemical oxidation processes," *Coloration Technology*, vol. 121, no. 5, pp. 258-264, 2005.
- [42] T. J. Mason and J. P. Lorimer, "Sonochemistry in Environmental Protection and Remediation," in *Applied Sonochemistry: Wiley-VCH Verlag GmbH & Co. KGaA*, 2003, pp. 131-156.
- [43] H. Shemer and N. Narkis, "Trihalomethanes aqueous solutions sono-oxidation," *Water Research*, vol. 39, no. 12, pp. 2704-2710, 2005.
- [44] C. G. Joseph, G. Li Puma, A. Bono, and D. Krishnaiah, "Sonophotocatalysis in advanced oxidation process: A short review," *Ultrasonics Sonochemistry*, vol. 16, no. 5, pp. 583-589, 2009.
- [45] S. H. Bossmann, E. Oliveros, S. Sabine Göb, S. Siegart, E. P. Dahlen, L. Payawan, Jr., M. Straub, M. Wörner, and A. M. Braun, "New Evidence against Hydroxyl Radicals as Reactive Intermediates in the Thermal and Photochemically Enhanced Fenton Reactions," *The Journal of Physical Chemistry A*, vol. 102, no. 28, pp. 5542-5550, 1998.
- [46] C. Walling, "Intermediates in the Reactions of Fenton Type Reagents," *Accounts of Chemical Research*, vol. 31, no. 4, pp. 155-157, 1998.
- [47] J. J. Pignatello, D. Liu, and P. Huston, "Evidence for an Additional Oxidant in the Photoassisted Fenton Reaction," *Environmental Science & Technology*, vol. 33, no. 11, pp. 1832-1839, 1999.
- [48] F. K. Nesheiwat and A. G. Swanson, "Clean contaminated sites using Fenton's reagent," *Chemical Engineering Progress*, vol. 96, no. 4, pp. 47-52, 2000.
- [49] P. Wasserscheid and W. Keim, "Ionic liquids - New "solutions" for transition metal catalysis," *Angewandte Chemie-International Edition*, vol. 39, no. 21, pp. 3772-3789, 2000.
- [50] J. Saji, "Studies on liquid-liquid extraction separation of valuable metals from titania wastes," PhD thesis, Faculty of sciences, Cochin university of science and technology, Kerala, India, 2002.
- [51] M. Aguilar Sanjuán and J. L. Cortina, *Solvent Extraction and Liquid Membranes : Fundamentals and Applications in New Materials*. Boca Raton, USA: CRC Press, 2008.
- [52] J. D. Thornton, "Extraction, liquid-liquid," *Thermopedia*, 2011. Available: <http://www.thermopedia.com/content/752/>. [accessed: 9 April 2016]
- [53] J. Koch and G. Shivelor, "Design Principles for Liquid-Liquid Extraction," *CEP Magazine*, 2015. Available: <https://www.aiche.org/resources/publications/cep/2015/november/design-principles-liquid-liquid-extraction>. [accessed: 9 April 2016]
- [54] V. S. Kislik, *Solvent Extraction : Classical and Novel Approaches*, 1st ed., Amsterdam, USA : Elsevier, 2011.
- [55] M. Soniya and G. Muthuraman, "Comparative study between liquid-liquid extraction and bulk liquid membrane for the removal and recovery of

- methylene blue from wastewater," *Journal of Industrial and Engineering Chemistry*, vol. 30, pp. 266-273, 2015.
- [56] A. Y. Zahrim and N. Hilal, "Treatment of highly concentrated dye solution by coagulation/flocculation–sand filtration and nanofiltration," *Water Resources and Industry*, vol. 3, pp. 23-34, 2013.
- [57] A. Bahadori, *Essentials of Oil and Gas Utilities : Process Design, Equipment, and Operations*, Amsterdam, USA : Elsevier, 2016.
- [58] B. Santos, J. G. Crespo, M. A. Santos, and S. Velizarov, "Oil refinery hazardous effluents minimization by membrane filtration: An on-site pilot plant study," (in eng), *J Environ Manage*, vol. 181, pp. 762-769, 2016.
- [59] A. Hawari, H. Ramadan, I. Abu-Reesh, and M. Ouederni, "A comparative study of the treatment of ethylene plant spent caustic by neutralization and classical and advanced oxidation," *Journal of Environmental Management*, vol. 151, pp. 105-112, 2015.
- [60] Z. Li, M. Wu, Z. Jiao, B. Bao, and S. Lu, "Extraction of phenol from wastewater by N-octanoylpyrrolidine," *Journal of Hazardous Materials*, vol. 114, no. 1–3, pp. 111-114, 2004.
- [61] H. Li *et al.*, "(Liquid + liquid) extraction of phenols from aqueous solutions with cineole," *The Journal of Chemical Thermodynamics*, vol. 107, pp. 95-103, 2017.
- [62] K. Farhod Chasib, "Extraction of Phenolic Pollutants (Phenol and p-Chlorophenol) from Industrial Wastewater," *Journal of Chemical & Engineering Data*, vol. 58, no. 6, pp. 1549-1564, 2013.
- [63] Y. Lei, Y. Chen, X. Li, Y. Qian, S. Yang, and C. Yang, "Liquid–Liquid Equilibria for the Ternary System 2-Methoxy-2-methylpropane + Phenol + Water," *Journal of Chemical & Engineering Data*, vol. 58, no. 6, pp. 1874-1878, 2013.
- [64] C. Yang, Y. Qian, J. Guo, and J. Chen, "Liquid–Liquid Equilibria for the Ternary System Methyl Isobutyl Ketone + 1,2-Benzenediol + Water," *Journal of Chemical & Engineering Data*, vol. 59, no. 11, pp. 3663-3667, 2014.
- [65] R. Lv, Z. Wang, L. Li, and Y. Chen, "Liquid–liquid equilibria in the ternary systems water + cresols + methyl butyl ketone at 298.2 and 313.2 K: Experimental data and correlation," *Fluid Phase Equilibria*, vol. 404, pp. 89-95, 2015.
- [66] D. Liu, L. Li, R. Lv, and Y. Chen, "Liquid–Liquid Equilibria for the Ternary System Mesityl Oxide + Phenol + Water at 298.15, 313.15, and 323.15 K," *Journal of Chemical & Engineering Data*, vol. 61, no. 7, pp. 2493-2498, 2016.
- [67] J.-f. Liu, G.-b. Jiang, Y.-g. Chi, Y.-q. Cai, Q.-x. Zhou, and J.-T. Hu, "Use of Ionic Liquids for Liquid-Phase Microextraction of Polycyclic Aromatic Hydrocarbons," *Analytical Chemistry*, vol. 75, no. 21, pp. 5870-5876, 2003.
- [68] V. Pino, J. L. Anderson, J. H. Ayala, V. González, and A. M. Afonso, "The ionic liquid 1-hexadecyl-3-methylimidazolium bromide as novel extracting system for polycyclic aromatic hydrocarbons contained in sediments using

- focused microwave-assisted extraction," *Journal of Chromatography A*, vol. 1182, no. 2, pp. 145-152, 2008.
- [69] Q. Zhou, H. Bai, G. Xie, and J. Xiao, "Temperature-controlled ionic liquid dispersive liquid phase micro-extraction," *Journal of Chromatography A*, vol. 1177, no. 1, pp. 43-49, 2008.
- [70] Y. Mochizuki and K. Sugawara, "Removal of Organic Sulfur from Hydrocarbon Resources Using Ionic Liquids," *Energy & Fuels*, vol. 22, no. 5, pp. 3303-3307, 2008.
- [71] M. L. Dietz and D. C. Stepinski, "Anion concentration-dependent partitioning mechanism in the extraction of uranium into room-temperature ionic liquids," *Talanta*, vol. 75, no. 2, pp. 598-603, 2008.
- [72] G. Wytze Meindersma, A. Podt, and A. B. de Haan, "Selection of ionic liquids for the extraction of aromatic hydrocarbons from aromatic/aliphatic mixtures," *Fuel Processing Technology*, vol. 87, no. 1, pp. 59-70, 2005.
- [73] K. Nakashima, F. Kubota, T. Maruyama, and M. Goto, "Ionic liquids as a novel solvent for lanthanide extraction," (in eng), *Anal Sci*, vol. 19, no. 8, pp. 1097-8, 2003.
- [74] M. Li, C. U. Pittman, Jr., and T. Li, "Extraction of polyunsaturated fatty acid methyl esters by imidazolium-based ionic liquids containing silver tetrafluoroborate - Extraction equilibrium studies," (in eng), *Talanta*, vol. 78, no. 4-5, pp. 1364-70, 2009.
- [75] J. Abulhassani, J. L. Manzoori, and M. Amjadi, "Hollow fiber based-liquid phase microextraction using ionic liquid solvent for preconcentration of lead and nickel from environmental and biological samples prior to determination by electrothermal atomic absorption spectrometry," (in eng), *J Hazard Mater*, vol. 176, no. 1-3, pp. 481-6, 2010.
- [76] V. M. Egorov, S. V. Smirnova, and I. V. Pletnev, "Highly efficient extraction of phenols and aromatic amines into novel ionic liquids incorporating quaternary ammonium cation," *Separation and Purification Technology*, vol. 63, no. 3, pp. 710-715, 2008.
- [77] J. Fan, Y. Fan, Y. Pei, K. Wu, J. Wang, and M. Fan, "Solvent extraction of selected endocrine-disrupting phenols using ionic liquids," *Separation and Purification Technology*, vol. 61, no. 3, pp. 324-331, 2008.
- [78] K. S. Khachatryan, S. V. Smirnova, I. I. Torocheshnikova, N. V. Shvedene, A. A. Formanovsky, and I. V. Pletnev, "Solvent extraction and extraction-voltammetric determination of phenols using room temperature ionic liquid," *Analytical and Bioanalytical Chemistry*, vol. 381, no. 2, pp. 464-470, 2004.
- [79] F. Huang *et al.*, "Surfactant-based ionic liquids for extraction of phenolic compounds combined with rapid quantification using capillary electrophoresis," *Electrophoresis*, vol. 35, no. 17, pp. 2463-2469, 2014.
- [80] G. Inoue, Y. Shimoyama, F. Su, S. Takada, Y. Iwai, and Y. Arai, "Measurement and Correlation of Partition Coefficients for Phenolic Compounds in the 1-Butyl-3-methylimidazolium Hexafluorophosphate/Water

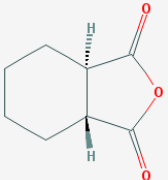
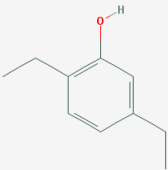
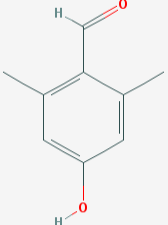
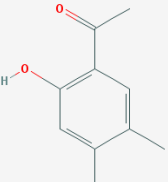
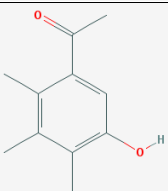
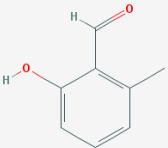
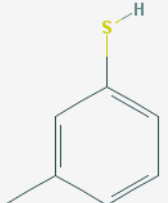
- Two-Phase System," *Journal of Chemical & Engineering Data*, vol. 52, no. 1, pp. 98-101, 2007.
- [81] N. Deng, M. Li, L. Zhao, C. Lu, S. L. de Rooy, and I. M. Warner, "Highly efficient extraction of phenolic compounds by use of magnetic room temperature ionic liquids for environmental remediation," *Journal of Hazardous Materials*, vol. 192, no. 3, pp. 1350-1357, 2011.
- [82] A. Balasubramanian and S. Venkatesan, "Removal of phenolic compounds from aqueous solutions by emulsion liquid membrane containing Ionic Liquid [BMIM]⁺[PF6]⁻ in Tributyl phosphate," *Desalination*, vol. 289, pp. 27-34, 2012.
- [83] H. Parham and S. Saeed, "Ultrasound-assisted solid phase extraction of nitro- and chloro-(phenols) using magnetic iron oxide nanoparticles and Aliquat 336 ionic liquid," *Journal of Chromatography A*, vol. 1336, pp. 34-42, 2014.
- [84] H. Q. Ni, J. Dong, J. J. Shi, and W. Wang, "Ionic liquid as extraction agent for detection of volatile phenols in wastewater and its regeneration," (in eng), *J Sep Sci*, vol. 33, no. 9, pp. 1356-9, 2010.
- [85] R. I. Canales and J. F. Brennecke, "Comparison of Ionic Liquids to Conventional Organic Solvents for Extraction of Aromatics from Aliphatics," *Journal of Chemical & Engineering Data*, vol. 61, no. 5, pp. 1685-1699, 2016.
- [86] N. Deng, M. Li, L. Zhao, C. Lu, S. L. de Rooy, and I. M. Warner, "Highly efficient extraction of phenolic compounds by use of magnetic room temperature ionic liquids for environmental remediation," (in eng), *J Hazard Mater*, vol. 192, no. 3, pp. 1350-7, 2011.
- [87] P. C. Wankat, *Separation Process Engineering Includes Mass Transfer Analysis*, 3rd ed. NY, USA: Prentic Hall, 2012.
- [88] 1,3-Isobenzofurandione, hexahydro-, trans-. Available: https://pubchem.ncbi.nlm.nih.gov/compound/trans-Hexahydroisobenzofuran-1_3-dione#section=2D-Structure. [accessed: 9 April 2016]
- [89] 2,5-Diethylphenol. Available: https://pubchem.ncbi.nlm.nih.gov/compound/2_5-Diethylphenol#section=Top. [accessed: 9 April 2016]
- [90] 2,6-Dimethyl-4-hydroxybenzaldehyde. Available: https://pubchem.ncbi.nlm.nih.gov/compound/2_6-Dimethyl-4-hydroxybenzaldehyde#section=Top. [accessed: 9 April 2016]
- [91] 2'-Hydroxy-4',5'-dimethylacetophenone. Available: <http://www.chemspider.com/Chemical-Structure.106314.html>. [accessed: 9 April 2016]
- [92] 5'-Hydroxy-2',3',4'-trimethylacetophenone. Available: <http://www.chemspider.com/Chemical-Structure.518169.html>. [accessed: 9 April 2016]

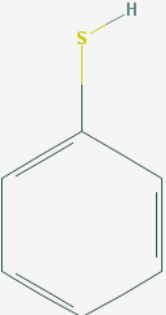

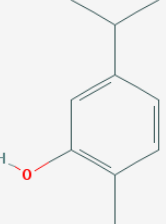
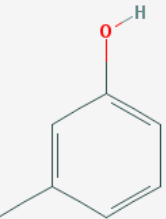
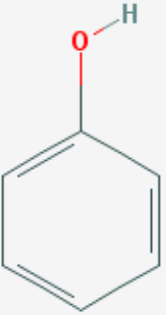
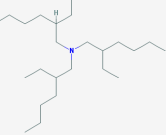
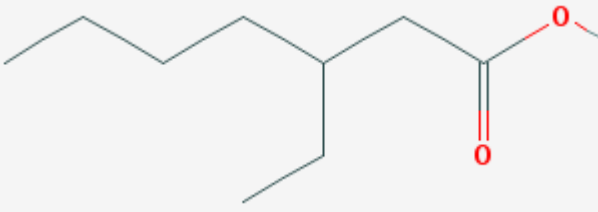
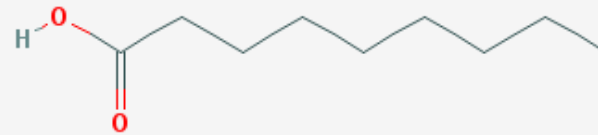
- [93] Benzaldehyde, 2-hydroxy-6-methyl-. Available:
<https://pubchem.ncbi.nlm.nih.gov/compound/2-Hydroxy-6-methylbenzaldehyde#section=Top>. [accessed: 9 April 2016]
- [94] Benzenethiol, 3-methyl-. Available:
<https://pubchem.ncbi.nlm.nih.gov/compound/3-Methylbenzenethiol#section=Top>. [accessed: 9 April 2016]
- [95] Benzenethiol. Available:
<https://pubchem.ncbi.nlm.nih.gov/compound/Benzenethiol#section=Top>. [accessed: 9 April 2016]
- [96] Hexathiane. Available:
<https://pubchem.ncbi.nlm.nih.gov/compound/139602#section=Top>.
- [97] Phenol, 2-methyl-5-(1-methylethyl)-. Available:
<https://pubchem.ncbi.nlm.nih.gov/compound/carvacrol#section=Top>. [accessed: 9 April 2016]
- [98] Phenol, 3-methyl-. Available:
<https://pubchem.ncbi.nlm.nih.gov/compound/342#section=Top>. [accessed: 9 April 2016]
- [99] Phenol. Available:
<https://pubchem.ncbi.nlm.nih.gov/compound/phenol#section=Top>. [accessed: 9 April 2016]
- [100] Tris(2-ethylhexyl)amine. Available:
https://pubchem.ncbi.nlm.nih.gov/compound/Tris_2-ethylhexyl_amine#section=Top. [accessed: 9 April 2016]
- [101] 3-Ethylheptanoic acid. Available:
https://pubchem.ncbi.nlm.nih.gov/compound/3-Ethylheptanoic_acid#section=Top. [accessed: 9 April 2016]
- [102] Undecanoic acid. Available:
https://pubchem.ncbi.nlm.nih.gov/compound/undecanoic_acid#section=Top. [accessed: 9 April 2016]
- [103] 1-Octanamine, N-methyl-N-octyl-. Available:
<https://pubchem.ncbi.nlm.nih.gov/compound/78202#section=Top>. [accessed: 9 April 2016]
- [104] 1-octanol. Available: <https://pubchem.ncbi.nlm.nih.gov/compound/1-octanol#section=2D-Structure>. [accessed: 9 April 2016]
- [105] 1-Pentadecanamine, N,N-dimethyl-. Available:
<https://pubchem.ncbi.nlm.nih.gov/compound/87232#section=Top>. [accessed: 9 April 2016]

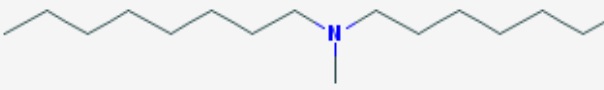
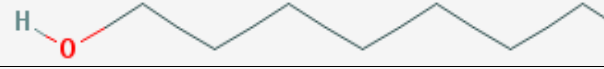

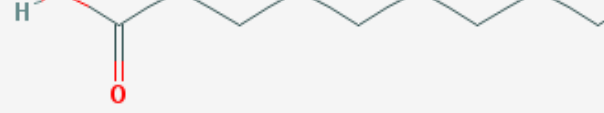
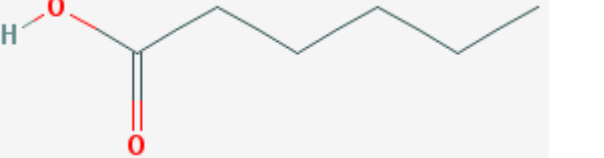
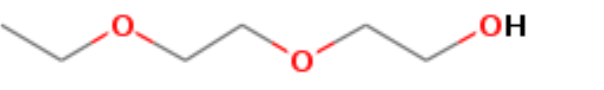
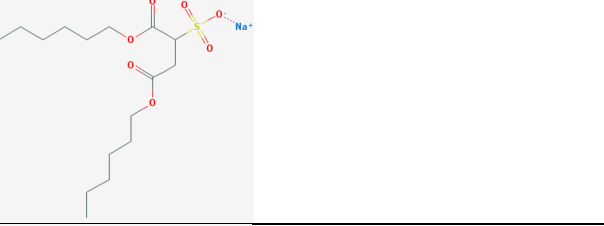
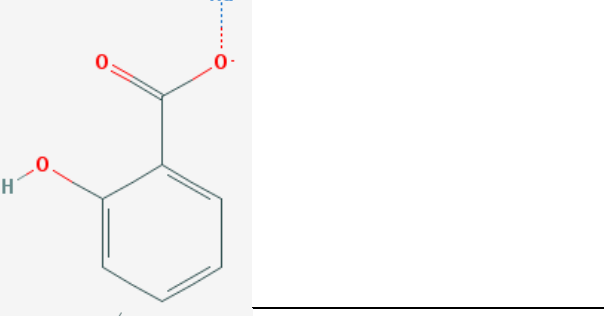
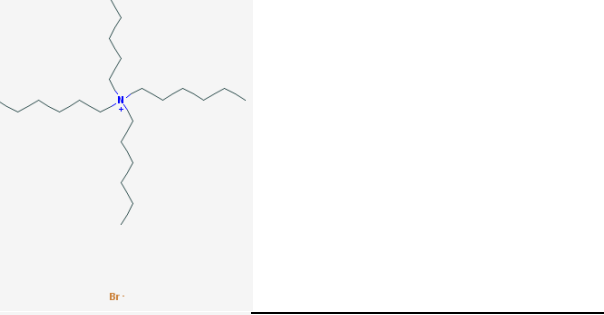
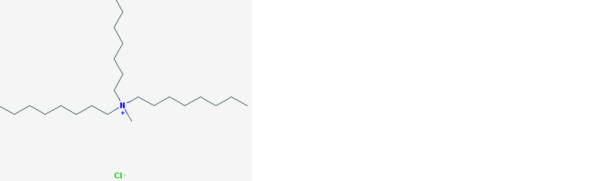
- [106] n-Decanoic acid. Available:
https://pubchem.ncbi.nlm.nih.gov/compound/Decanoic_acid. [accessed: 9 April 2016]
- [107] Hexanoic acid. Available:
https://pubchem.ncbi.nlm.nih.gov/compound/hexanoic_acid#section=Top. [accessed: 9 April 2016]
- [108] Ethanol, 2-(2-ethoxyethoxy)-. Available:
<http://webbook.nist.gov/cgi/cbook.cgi?ID=111-90-0>. [accessed: 9 April 2016]
- [109] Dihexylsulfosuccinate sodium salt solution. Available:
https://pubchem.ncbi.nlm.nih.gov/compound/Dihexyl_sodium_sulfosuccinate#section=Top. [accessed: 9 April 2016]
- [110] Sodium salicylate. Available:
<https://pubchem.ncbi.nlm.nih.gov/compound/16760658#section=2D-Structure>. [accessed: 9 April 2016]
- [111] Tetrahexylammonium bromide. Available: <https://pubchem.ncbi.nlm.nih.gov/compound/78026#section=Top>. [accessed: 9 April 2016]
- [112] Trioctylmethylammonium chloride. Available: <https://pubchem.ncbi.nlm.nih.gov/compound/21218#section=Top>. [accessed: 9 April 2016]
- [113] K. A. Fletcher et al., "Behavior of the solvatochromic probes Reichardt's dye, pyrene, dansylamide, Nile Red and 1-pyrenecarbaldehyde within the room-temperature ionic liquid bmimPF₆", *Green Chemistry*, vol. 3, pp. 210-215, 2001
- [114] "Solvatochromic Studies of Ionic Liquid/Organic Mixtures", *The Journal of Physical Chemistry B*, vol. 111, issue 1, pp. 131-138, 2007
- [115] C. Reichardt, "Polarity of ionic liquids determined empirically by means of solvatochromic pyridinium N-phenolate betaine dyes", *Green Chemistry*, vol. 7, pp. 339-351, 2005

Appendix

A.1 Structure of Compounds

Compound	Structure	Reference
1,3-Isobenzofurandione, hexahydro-, trans-		[88]
2,5-Diethylphenol		[89]
2,6-Dimethyl-4-hydroxybenzaldehyde		[90]
2'-Hydroxy-4',5'-dimethylacetophenone		[91]
5'-Hydroxy-2',3',4'-trimethylacetophenone		[92]
Benzaldehyde, 2-hydroxy-6-methyl-		[93]
Benzenethiol, 3-methyl-		[94]

Benzenethiol		[95]
Hexathiane		[96]
Phenol, 2-methyl-5-(1-methylethyl)-		[97]
Phenol, 3-methyl-(chem)		[98]
phenol		[99]
Tris(2-ethylhexyl)amine		[100]
3-Ethylheptanoic acid		[101]
Undecanoic acid		[102]

1-Octanamine, N-methyl-N-octyl-		[103]
1-octanol		[104]
1-Pentadecanamine, N,N-dimethyl-		[105]
n-Decanoic acid		[106]
Hexanoic acid		[107]
Ethanol, 2-(2-ethoxyethoxy)-		[108]
dihexylsulfosuccinate sodium salt solution		[109]
sodium salicylate		[110]
tetrahexylammonium bromide		[111]
Trioctylmethyl ammonium chloride		[112]

A.2 Distribution Coefficients of Phenols and Aromatic Compounds for ILs

Solute	IL1	IL2	Reference
Phenol	2.5	2.1	[76]
4-Nitrophenol	3.6	3.4	[76]
2,4-Dinitrophenol	4.1	3.5	[76]
2,6-Dinitrophenol	4.0	3.6	[76]
2,4,6-Trinitrophenol	3.9	3.8	[76]
1-Naphthol	3.8	3.4	[76]
2-Naphthol	3.7	3.2	[76]
Aniline	1.9	1.8	[76]
3-Nitroaniline	2.3	2.3	[76]
p-Toluidine	2.0	2.0	[76]
Tryptamine	3.5	2.6	[76]

A.3 $E_T(30)$ values for solvents

Solvent	ET (30) (KJ.mol ⁻¹)	Ref
BMIMPF ₆	219.6	[113]
Ethanol	219.2	[113]
HMIMTf ₂ N	216.7	[114]
IL2	201.7	[76]
IL1	194.5	[76]
Acetonitrile	190.0	[76]
THABzO	183.7	[115]
Acetone	176.6	[76]
Chloroform	171.5	[76]
Dichloromethane	170.7	[113]

A.4 Major Compounds present in industrial SC before and after treatment using GC-MS spectroscopy by the procedure EPA-3510c and EPA-8270d

Ret. Time	Name	formula	Removal Percentage using					
			One contactor		Two Contactors		Three Contactors	
			IL1	IL2	IL1	IL2	IL1	IL2
4.566	Benzenethiol	C ₆ H ₆ S	87.10	100.0	97.42	100	99.99	100.0
5.156	Phenol	C ₆ H ₆ O	76.08	100.0	94.04	100.0	95.44	100.0
5.823	Ethanol, 2-(2-ethoxyethoxy)-	C ₆ H ₁₄ O ₃	93.82	63.76	93.91	94.45	99.99	95.48
6.901	Phenol, 3-methyl-	C ₇ H ₈ O	93.62	100.0	96.91	100.0	97.87	100.0
7.071	Benzenethiol, 3-methyl-	C ₇ H ₈ S	95.87	100.0	97.94	100.0	95.12	100.0
7.138	Benzenethiol, 2-methyl-	C ₇ H ₈ S	95.05	100.0	98.35	100.0	98.89	100.0
7.442	Phenol, 3-methyl-	C ₇ H ₈ O	100.0	100.0	100.0	100.0	100.0	100.0
7.856	1-Octanol	C ₈ H ₁₈ O	100.0	75.15	100.0	100.0	100.0	100.0

8.136	Phenol, 2,3-dimethyl-	C ₈ H ₁₀ O	100.0	100.0	100.0	100.0	100.0	100.0
9.167	Phenol, 2-ethyl-	C ₈ H ₁₀ O	100.0	100.0	100.0	100.0	100.0	100.0
9.357	Phenol, 2,3-dimethyl-	C ₈ H ₁₀ O	100.0	100.0	100.0	100.0	100.0	100.0
9.927	Phenol, 4-ethyl-	C ₈ H ₁₀ O	100.0	100.0	100.0	100.0	100.0	100.0
10.132	Phenol, 2,3-dimethyl-	C ₈ H ₁₀ O	100.0	100.0	100.0	100.0	100.0	100.0
10.258	Phenol, 4-(1-methylethyl)-	C ₉ H ₁₂ O	100.0	100.0	100.0	100.0	100.0	100.0
10.548	Phenol, 2,3-dimethyl-	C ₈ H ₁₀ O	100.0	100.0	100.0	100.0	100.0	100.0
10.772	Phenol, 2,3,6-trimethyl-	C ₉ H ₁₂ O	100.0	100.0	100.0	100.0	100.0	100.0
11.472	Phenol, 2,3,6-trimethyl-	C ₉ H ₁₂ O	100.0	100.0	100.0	100.0	100.0	100.0
11.615	Phenol, 2-ethyl-5-methyl-	C ₉ H ₁₂ O	100.0	100.0	100.0	100.0	100.0	100.0
11.703	Phenol, 4-(1-methylethyl)-	C ₉ H ₁₂ O	100.0	100.0	100.0	100.0	100.0	100.0
11.854	Phenol, 2-ethyl-5-methyl-	C ₉ H ₁₂ O	100.0	100.0	100.0	100.0	100.0	100.0
11.965	Phenol, 2,3,6-trimethyl-	C ₉ H ₁₂ O	100.0	100.0	100.0	100.0	100.0	100.0
12.546	Phenol, 2,3,6-trimethyl-	C ₉ H ₁₂ O	100.0	100.0	100.0	100.0	100.0	100.0

12.690	Phenol, 2,3,6-trimethyl-	C ₉ H ₁₂ O	100.0	100.0	100.0	100.0	100.0	100.0
12.829	Phenol, 2-ethyl-4,5-dimethyl-	C ₁₀ H ₁₄ O	100.0	100.0	100.0	100.0	100.0	100.0
12.893	Phenol, 3-(1-methylethyl)-	C ₉ H ₁₂ O	100.0	100.0	100.0	100.0	100.0	100.0
13.238	Phenol, 2-methyl-5-(1-methylethyl)-	C ₁₀ H ₁₄ O	100.0	100.0	100.0	100.0	100.0	100.0
13.915	Phenol, 2-ethyl-4,5-dimethyl-	C ₁₀ H ₁₄ O	100.0	100.0	100.0	100.0	100.0	100.0
14.671	Phenol, 2,3,4,6-tetramethyl-	C ₁₀ H ₁₄ O	100.0	100.0	100.0	100.0	100.0	100.0
14.747	Phenol, 2-ethyl-4,5-dimethyl-	C ₁₀ H ₁₄ O	100.0	100.0	100.0	100.0	100.0	100.0
14.835	2,5-Diethylphenol	C ₁₀ H ₁₄ O	100.0	100.0	100.0	100.0	100.0	100.0
14.989	4-Methyl-1-phenyl-1,2-dithiapentane	C ₁₀ H ₁₄ S ₂	100.0	100.0	100.0	100.0	100.0	100.0
16.544	Benzaldehyde, 2-hydroxy-6-methyl-	C ₈ H ₈ O ₂	100.0	100.0	100.0	100.0	100.0	100.0
17.204	2,6-Dimethyl-4-hydroxybenzaldehyde	C ₉ H ₁₀ O ₂	86.55	100.0	96.31	100.0	97.55	100.0
17.437	p-Nonyloxybenzaldehyde	C ₁₆ H ₂₄ O ₂	100.0	100.0	100.0	100.0	100.0	100.0
18.226	2-Naphthalenethiol	C ₁₀ H ₈ S	100.0	100.0	100.0	100.0	100.0	100.0
18.424	1,4-Benzenediol, 2,3,5-trimethyl-	C ₉ H ₁₂ O ₂	100.0	100.0	100.0	100.0	100.0	100.0

18.519	4-Hydroxy-2-methylacetophenone	C ₉ H ₁₀ O ₂	100.0	100.0	100.0	100.0	100.0	100.0
18.600	2-Methoxy-4-vinylphenol	C ₉ H ₁₀ O ₂	100.0	100.0	100.0	100.0	100.0	100.0
18.835	2,6-Dimethyl-4-hydroxybenzaldehyde	C ₉ H ₁₀ O ₂	100.0	100.0	100.0	100.0	100.0	100.0
19.050	2,3-Dimethyl-para-anisaldehyde	C ₁₀ H ₁₂ O ₂	100.0	100.0	100.0	100.0	100.0	100.0
19.377	2'-Hydroxy-4',5'-dimethylacetophenone	C ₁₀ H ₁₂ O ₂	85.78	100.0	96.45	100.0	97.48	100.0
19.676	1-Pentadecanamine, N,N-dimethyl-	C ₁₇ H ₃₇ N	100.0	100.0	100.0	100.0	100.0	100.0
20.273	5'-Hydroxy-2',3',4'-trimethylacetophenone	C ₁₁ H ₁₄ O ₂	100.0	100.0	100.0	100.0	100.0	100.0
20.384	2,5-Dimethyl-para-anisaldehyde	C ₁₀ H ₁₂ O ₂	100.0	100.0	100.0	100.0	100.0	100.0
20.450	Carbonothioic acid, O,O-diphenyl ester	C ₁₃ H ₁₀ O ₂ S	100.0	100.0	100.0	100.0	100.0	100.0
20.653	Phenol, 3,5-bis(1-methylethyl)-	C ₁₂ H ₁₈ O	100.0	100.0	100.0	100.0	100.0	100.0
20.923	Benzeneacetaldehyde, 2-methoxy-.alpha.,5-dimethyl-	C ₁₁ H ₁₄ O ₂	100.0	100.0	100.0	100.0	100.0	100.0
21.003	5'-Hydroxy-2',3',4'-trimethylacetophenone	C ₁₁ H ₁₄ O ₂	100.0	100.0	100.0	100.0	100.0	100.0
21.832	2,6-Dimethyl-4-hydroxybenzaldehyde	C ₉ H ₁₀ O ₂	100.0	100.0	100.0	100.0	100.0	100.0
21.998	Phenol, 2-(1-methyl-2-buthenyl)-4-methoxy-	C ₁₂ H ₁₆ O ₂	100.0	100.0	100.0	100.0	100.0	100.0

22.311	Aminoformic acid, N-n-hexyl-, 2,6-diisopropylphenyl(ester)	C ₁₉ H ₃₁ NO ₂	100.0	100.0	100.0	100.0	100.0	100.0
24.053	Phenol, 2,4-bis(1,1-dimethylethyl)-	C ₁₄ H ₂₂ O	100.0	100.0	100.0	100.0	100.0	100.0
24.616	1-Octanamine, N-methyl-N-octyl-	C ₁₇ H ₃₇ N	100.0	98.40	100.0	100.0	100.0	100.0
24.841	1-Hexanamine, N,N-diethyl-	C ₁₈ H ₃₉ N	100.0	100.0	100.0	100.0	100.0	100.0
28.435	Cyclic Octaatomic sulfur	S ₈	100.0	90.31	100.0	98.99	100.0	99.25
28.435	Tris(2-ethylhexyl)amine	C ₂₄ H ₅₁ N	100.0	98.88	100.0	100.0	100.0	100.0
31.994	Methylamine, N,N-bis(N.-decyl)-	C ₂₁ H ₄₅ N	100.0	100.0	100.0	100.0	100.0	100.0
37.872	1-Octanamine, N,N-dioctyl-	C ₂₄ H ₅₁ N	100.0	100.0	100.0	100.0	100.0	100.0
37.88	Ethyamine, N,N-dinonyl-2-(2-thiophenyl)- ¹	C ₂₄ H ₄₅ NS	100.0	99.89	100.0	100.0	100.0	100.0
38.759	Benzaldehyde, 3-[(3,5-dimethylphenoxy)methyl]-4-methoxy-	C ₁₇ H ₁₈ O ₃	100.0	100.0	100.0	100.0	100.0	100.0
39.656	Benzaldehyde, 4-methoxy-3-(4-propylphenoxy)methyl-	C ₁₈ H ₂₀ O ₃	100.0	100.0	100.0	100.0	100.0	100.0
43.107	1-Decanamine, N,N-didecyl-	C ₃₀ H ₆₃ N	100.0	100.0	100.0	100.0	100.0	100.0

Vita

Muhammad Ashraf Sabri received his B.Sc. degree in Chemical Engineering with Honors from University of Engineering and Technology (Lahore, Pakistan) in 2011 and was awarded with a Gold Medal for his outstanding academic performance. During his undergraduate studies, he was an active and unparalleled member of several societies.

Mr. Sabri joined MNS – University of Engineering and Technology (Multan, Pakistan) as a Lecturer at the department of chemical engineering in 2012. He held many managerial positions, apart from academic, at this institute including the post of Incharge Sports (2012-2015). Owing to his interest in research and higher education, he joined American University of Sharjah in 2015, where he is currently enrolled as an MSChE student.

Mr. Sabri's research interests include, but are not limited to, nanotechnology, environmental remediation, wastewater treatment, energy and chemicals from biomass. He has published three paper in renowned journals and presented a paper in Fifth International Conference on Water, Energy and Environment (ICWEE/5) in 2017.