

Extraction and Determination of Active Quinone from Spent Alumina used in
Hydrogen Peroxide Production



Eshetu Megersa Hordofa

A Thesis Submitted to the Department of Applied Chemistry,

School of Applied Natural Science.

In Partial Fulfillment of the Requirements for the Degree of Master of

Science in Applied Chemistry (Industrial Chemistry)

Office of Graduate Studies.

Adama Science and Technology University

January, 2024

Adama, Ethiopia

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DECLARATION

I hereby declare that this Master thesis entitled “Extraction and Determination of Active Quinone from Spent Alumina used in Hydrogen Peroxide Production.” is my original work. That is, it has not been submitted for the award of any academic degree, diploma or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

Eshetu Megersa Hordofa

Name of student

Signature

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Date

RECOMMENDATION

I, the advisor of this thesis, hereby certify that I have read the revised version of the thesis entitled “Extraction and Determination of Active Quinone from Spent Alumina used in Hydrogen Peroxide Production” prepared under my guidance by Eshetu Megersa Hordofa submitted in partial fulfillment of the requirements for the degree of Master of Science in Industrial Chemistry. Therefore, I recommend the submission of revised version of the thesis to the department following the applicable procedures.

Gemechu Deressa (PhD., Associate Professor)

Advisor

Signature

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Date

APPROVAL

I, the advisor of the thesis entitled “Extraction and Determination of Active Quinone from Spent Alumina used in Hydrogen Peroxide Production” and developed by Eshetu Megersa Hordofa, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Gemechu Deressa (PhD., Associate Professor)

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We, the undersigned, members of the Board of Examiners of the thesis by Eshetu Megersa Hordofa have read and evaluated the thesis entitled “Extraction and Determination of Active Quinone from Spent Alumina used in Hydrogen Peroxide Production” and examined the candidate during open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Industrial Chemistry.

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DEDICATION

This M.Sc. thesis is dedicated to my beloved families, especially to My mother Kebebu Dame, my brother Gosa Megersa and to my sister Chuchu Megersa, whose advice, support, prayers and love helped me all along the right way mademe who I am today. They will always be in my heart forever.

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Then I would like to express my sincere gratitude to Awash Melkassa Chemical Factory for providing all the necessary assistance and facilities to conduct my research work. I also express my genuine heartfelt gratitude to all workers of the factory, specially to Quality Control Laboratory staff members for their help on my work. I never forget great contribution.

I greatly acknowledge Ato Abera Tullu from Adami Tulu Pesticide Processing Share Company for GC characterization and Ato Amare Degu from Awash Melkassa Chemical Factory shift manager for his assistance in plotting TGA and DAT data in Origin software. Finally I would like to thank greatly, School of Applied Natural Science and Adama Science and Technology University for giving me the opportunity to join this postgraduate.

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LIST OF ACRONYMS AND ABBREVIATIONS

| | |
|----------|--------------------------------------|
| AHQ | Anthrahydroquinone |
| AO | Auto-oxidation |
| AQ | Anthraquinone |
| AT | 2-ethylanthrone |
| BPT | Boiling point temperature |
| A.M.C. F | Awash Melkassa Chemical Factory |
| DAT | 2-ethyl dianthrone |
| EAQ | 2-Ethyl anthraquinone |
| GC | Gas chromatography |
| gm | Gram |
| gpl | Gram per liter |
| kg | Kilogram |
| l | Liter |
| ml | Milliliter |
| mmol | Milimole |
| OAT | 2-ethyloxanthrone |
| OHAHQ | 2-ethyl octahydroanthrahydroquinone |
| OT | Orto-terphenyl |
| TBU | Tetra Butyl Urea |
| TGA | Thermo gravimetric analysis |
| THAHQ | Tetrahydroethylanthrahydroquinone |
| THAQ | Tetrahydroethylanthraquinone |
| THAQE | Tetrahydroethylanthraquinone epoxide |
| TOP | Trioctyl Phosphate |
| W | Weight |
| WS | Working solution |

ABSTRACT

Hydrogen peroxide was one of the major bleaching chemicals produced in Awash Melkassa Chemical Factory. The auto-oxidation anthraquinone process route utilizing the working solution as a working media used to produce hydrogen peroxide. However, continuous usage of working solution resulted in losing of active quinone and unable to produce the required products, due to adsorbed on the surface of deactivated Alumina with different types of byproducts during the regeneration of working solution. Thus, determine the amount of active quinone that contained on the surface of deactivated alumina by solvent extraction method was a subject of study. The organic on the surface of deactivated alumina washed by organic solvent. In Soxhlet solvent extraction, methanol, ethyl acetate and the mixture of methanol and ethyl acetate, acetonitrile and acetone were used to assess the removal of polar organic compounds contained in deactivated alumina. The highest organic removal efficiency was observed at 69.05% when mixture of methanol and ethyl acetate was used for extraction. The GC analysis also showed that the removal efficiency of organic compound (active quinone) contained in deactivated alumina by organic solvents from high to low was solvent mixture, methanol, Acetonitrile, Acetone, and Ethyl acetate respectively. Therefore, recovered active quinone could be used instead of fresh anthraquinone for working solution make up and as a Carrier for production of hydrogen peroxide.

Keywords: *Solvent extraction, Solvent evaporation, GC analysis, deactivated alumina, active quinone.*

CHAPTER ONE

1. INTRODUCTION

1.1 Background of the Study

Currently solid waste disposal has become a serious problem in Awash Melkassa Chemical Factory. The factory has produced aluminum sulphate, sulphuric acid and hydrogen peroxide products. In the production route of each product, the three main types of solid wastes namely kaolin filter cake, sulfur filter cake and spent alumina has been released to the environment. The adsorbed organic chemicals contained in this solid waste might create environmental pollutions if not handled properly. This solid waste is disposed and collected in some place as a landfill. After some time, the factory compound will be occupied by the disposed solid waste thereby covers large project expansion areas. The storage of industrial solid waste is now becoming one of the most neglected operational areas of the factory. There is very little knowledge for proper storage and handling of solid wastes in the factory. Thus, different solid waste types are found to be mixed waste and forming a pile against an open ground. If the storage of solid wastes continues like this, there will be uncontrollable pollution of the environment. Therefore, this solid waste and adsorbed organic chemicals contained in this solid waste should be stored and treated through regeneration containing combination of physical and chemical processes. Thus, waste treatment is required in order to protect and keep the environment free from contamination.

The hydrogen peroxide plant of Awash Melkassa Chemical Factory shown in figure 1, which had designed, installed and commissioned by Nuberg engineering PLC. The technology of Nuberg engineering uses AO process to produce hydrogen peroxide based on working solution. The working solution, which is a mixture of ethyl anthraquinone and solvents, is composed of a solute of 2-EAQ dissolved in a two polar solvents TBU and TOP, and a non-polar aromatic solvent called solvesso-150 or trimethyl benzene. The AO process generates

different types of byproducts because of the sequential hydrogenation and oxidation of EAQ. Of these byproducts, some are reversed to active quinones and some are absorbed by activated Alumina (Al_2O_3), which is used as a catalyst for dehydrogenation and de-epoxidation reactions, and as an adsorbent to remove the degradation products obtained from the working solution. However, after repeated cycling of the working solution, the alumina loses its activity and fails to maintain the hydrogen peroxide productivity of the working solution. This loss of activity is called deactivated alumina. Thus, deactivated alumina containing adsorbed byproducts or organic matters, is released to the environment as a solid waste. To recover the active sites of deactivated alumina and to determine the active quinone left in the degraded products, economically acceptable regeneration and recovering method is required. So that alumina and spent active quinone can be reused to restore effective hydrogen peroxide synthesizing capacity of the WS.

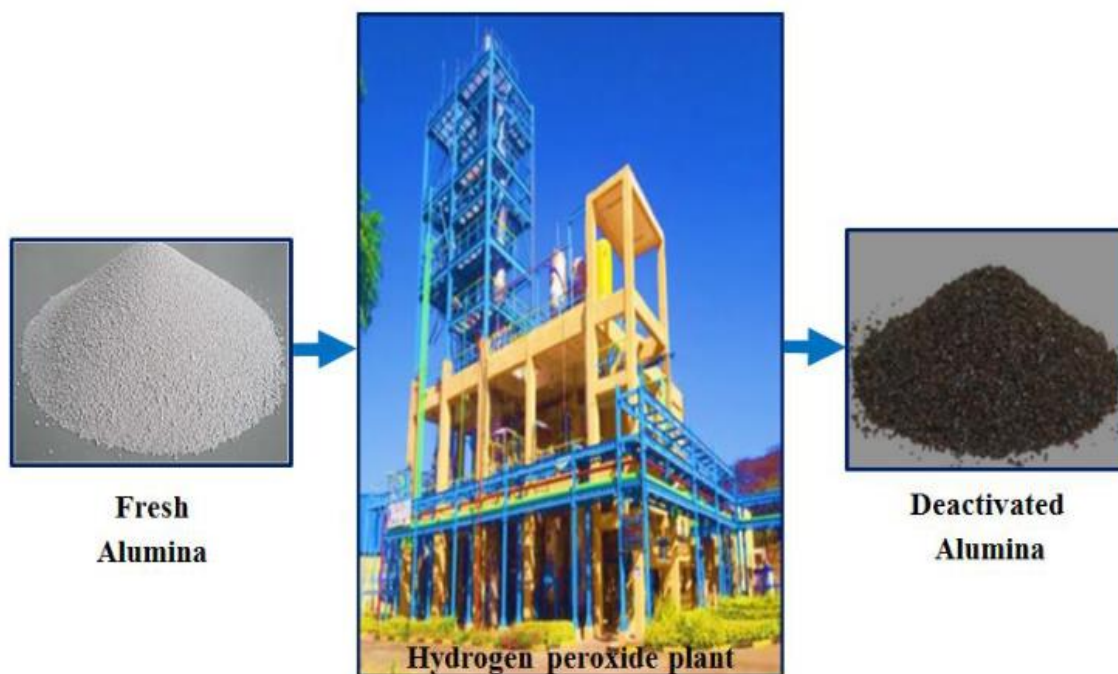


Figure 1.1: Solid waste disposal from hydrogen peroxide plant (A.M.C.F)

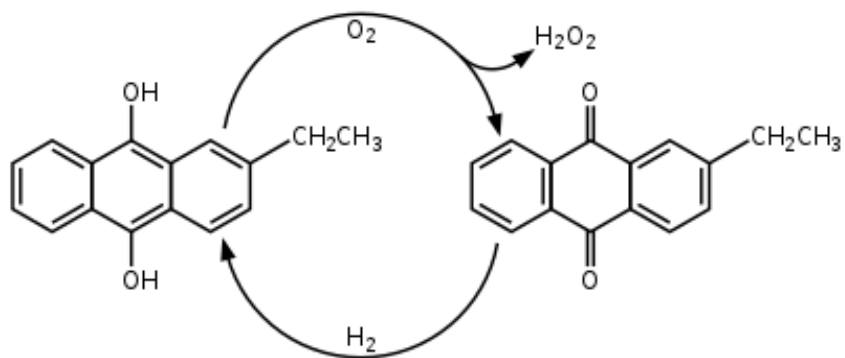


Figure 1.2: Schematic representation of successive hydrogenation and oxidation of Al anthraquinones (From Wikipedia, the free encyclopedia)

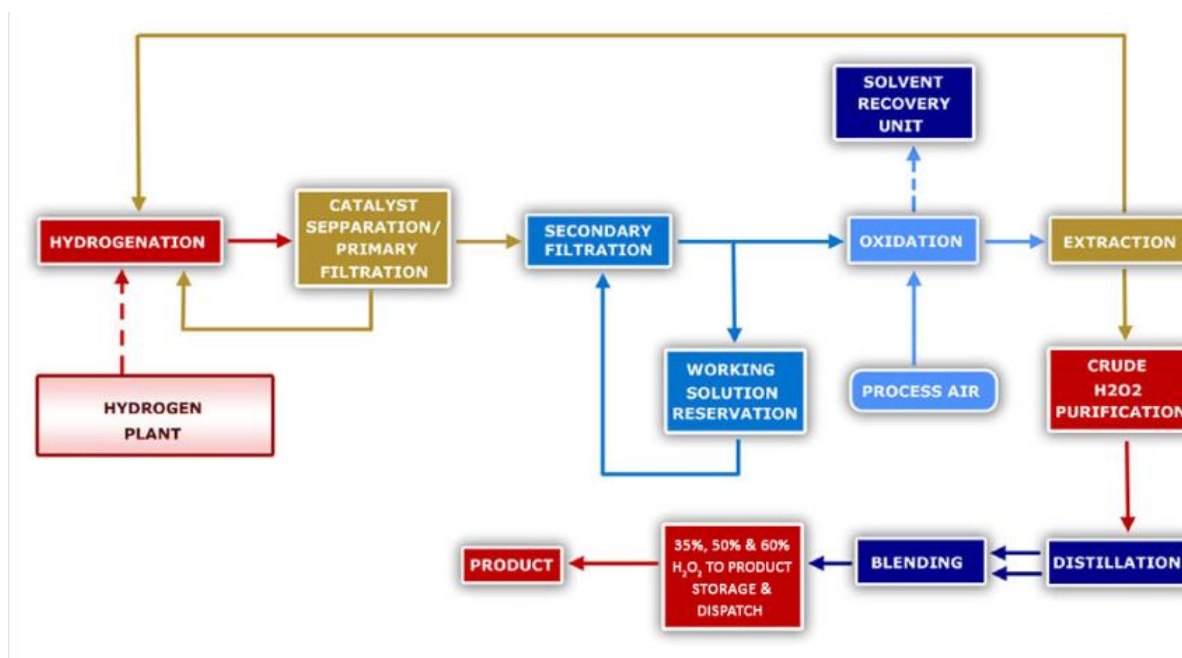


Figure 1.3: Hydrogen Peroxide Production Process Flow Diagram (w.w.w.Nubergindia.com)

Previous studies showed that Soxhlet extraction using different organic solvents followed by caustic treatment was the best regeneration method of spent alumina. In this research, the washing of deactivated alumina will be carried out through Soxhlet extraction to determine the spent active quinone. The organic polar solvent such as ethyl acetate methanol, acetone and acetonitrile which are best solvents for polar organic matter. Is used to extract organic matters

contained in deactivated alumina through Soxhlet extraction. The presence of active quinone in the degraded products of working solution can be determined by GC analysis.

1.2. Statement of the Problem

The solid wastes that can contain some adsorbed chemicals have been removed from the reversion beds of hydrogen peroxide plant. The solid activated alumina that was used as an adsorbent and a catalyst during working solution regeneration is being deactivated due to adsorption of organic degradation product typically OAHQ, OAT, AT, DAT and water. These degradation products result in the loss of active quinones that is capable to produce hydrogen peroxide, which are responsible for blocking the active sites of the alumina catalyst. Thus, the deactivated alumina that cannot be used for working solution regeneration in the next production process is discarded to the environment as landfills in the open ground thereby occupies future project expansion areas. This solid waste disposal causes not only landfills but also causes environmental pollution and health hazards. The environment can be polluted by gas emission caused by the fire of organic matters contained in deactivated alumina and this gas emission leads to health hazard. Therefore, it is necessary to reactivate spent alumina for working solution regeneration and purification and recovering the spent active quinone left in degradation products of WS for hydrogen peroxide production. So that, the environment will be free from gas emission and waste disposal. During the production of hydrogen peroxide in the working solution circulation, a one batch of 1850kg activated alumina contained in reversion bed is used for continuous working solution regeneration. This activated alumina is being deactivated while working continuously for 22 working days. Since the process of hydrogen peroxide production is continuous, the deactivated alumina contained in the reversion bed is replaced by fresh activated alumina. This deactivated alumina is removed from the reversion bed thereby discarded to the environment as a solid waste. More foreign currency is required for replacing this solid waste deactivated alumina. The purchasing cost of 1kg of fresh activated alumina and active anthraquinone (2-EAQ) are 90.27 and 90birr respectively, so that 1850kg activated alumina contained in one reversion bed will be about 167,000 birr per 22 working days. The annual consumption of fresh activated alumina in the hydrogen peroxide plant is about 27,750kg whereas the annual purchasing cost of this alumina

is about 2,505,000 birrs, but in the process the 2-EAQ is recyclable not discarded, except the one which can be losses through processes. This indicated that the Awash Melkassa chemical factory uses high amount of activated alumina annually. Therefore, it is necessary to regenerate deactivated alumina and recovering the spent active quinone in this factory to reduce waste disposal to the environment and foreign currency.

1.3. Research Questions

1. Can it be possible to extract adsorbed anthraquinone on the surface of deactivated alumina by using solvent extraction?
2. Is there active quinone found in the residue of solvent extraction, during the regeneration of deactivated alumina?
3. Can it be possible to determining the amount of active quinone contained in the residue of solvent extraction?
4. Is there the best method to recover the spent active quinone from the residue of solvent extraction?

1.4. Objective of the Study

1.4.1. General Object

The main objective of this study is to extract, determine and characterize the active quinone that contained on the surface of deactivated alumina, during the regeneration of deactivated alumina used in hydrogen peroxide production by using solvent extraction and GC analysis.

1.4.2. Specific Objectives

1. To extract anthraquinone that adsorbed on the surface of deactivated alumina by using solvent extraction (Methanol, Acetone, Acetonitrile, Ethyl acetate and Solvent mixture).
2. To determine active quinone found in residue of solvent extraction.

3. To do characterization for active quinone found in residue of solvent extraction by using GC.
4. To find the best method to recover the spent active quinone from the residue of solvent extraction.

1.5 Significance of the Study

This study helps the Awash Melkasa Chemical Factory, to reduce the loss (wastages) of an expensive active quinone through processing that used to produce hydrogen peroxide. This method of treatment assists to avoid subsequent reuse of fresh activequinoneand alumina for replacement and can be reducing the solid waste disposed to the environment that can be causes fire and health hazards problems. Large project expansion areas are also saved by this solid waste minimization. On the other hand, as both (Al_2O_3) and (2- EAQ) are not available in domestic market, and purchased from abroad, this research is addressed to minimize the purchasing and transportation cost of fresh activated alumina and quinone by treating spent deactivated alumina and quinone as often as desired. The outcome of this research can have a considerable effect on research and even on industrial activities as it serves as a basis for any scientific investigations of determining spent active quinone in residue of solvent extraction. It can also serve as background information for a researcher who wants to conduct further study on the topic under study and it provides information to prospects about various potential applications of active quinone for synthesizing hydrogen peroxide.

1.6 Scope of the Study

This study is limited to the area of hydrogen peroxide plant of Awash Melkassa Chemical Factory solid waste that is spent alumina. The research is bounded to remove organic compounds adsorbed on the surface of alumina by using solvent extraction and determine the active quinone left in the residue of solvent extract during the regeneration of deactivated alumina. Solvent extraction through Soxhlet apparatus is carried out by acetone, acetonitrile, ethyl acetate, methanol and a combination of methanol and ethyl acetate. The quantitative analysis of active quinone is determined by GC analysis. In this research, the presence of

active quinone in residue is determined by Gas Chromatography Measurement of Peak Area and Derivation of Sample Composition.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Anthraquinone autoxidation process

Hydrogen peroxide is produced worldwide by different routes. One of which route is auto-oxidation process (M Arshad *et al*, 2014). As it is the so called a green chemical (Hui Shang *et al*, 2011) product, it is widely used in the military industry, environmental protection, papermaking, textile bleaching, chemical synthesis, food processing, medical sterilization, and others. Commercially, hydrogen peroxide is produced using anthraquinone auto-oxidation process based on working solution in the presence of palladium catalyst. Fresh working solution is prepared by dissolving active anthraquinones in an organic solvent. Industrially, the synthesis of hydrogen peroxide via auto-oxidation process is carried out through the hydrogenation of ethyl anthraquinone into ethyl anthrahydroquinone and oxidation of anthrahydroquinone with atmospheric air (Kosydar *et al*, 2010)(Hui Shang *et al*, 2011)(Fuqing Li *et al*, 2010). (Peter W *et al*, 2013).

The industrial production of hydrogen peroxide by anthraquinone route is a cyclic process that involves four major steps: hydrogenation, oxidation, extraction and regeneration of the working solution (Fuqing Li *et al*, 2010)(Fuqing Li *et al*, 2014).from figure 1.4. During hydrogenation stage, EAQ is first dissolved in organic solvents and hydrogenated into EAHQ in the presence of palladium catalyst. Having reached working solution maturation, part of EAQ is converted to THEAQ. In this (cyclic form) have been used as a reaction carrier (Glenneberg *et al*, 2000). Most β and α process, EAQ and THEAQ (form of THEAQ α form of THEAQ is formed along with a small amount of β of the time (Dalbir S *et al*, 1987). Then EAHQ and THEAHQ are oxidized into EAQ and THEAQ producing hydrogen peroxide using air or oxygen atmosphere (M Arshad Majeed *et al.*, 2014)(Peter W *et al.*, 2013)(Dalbir *et al*, 1987). The hydrogen peroxide solution from the regenerated starting material, EAQ (organic phase) will then be separated by extraction with dematerialized water. Then hydrogen

peroxide is purified and concentrated, and the working solution is circulated back to the hydrogenation section (Fredrik Sandelin *et al*, 2006)(Fuqing Li *et al*,2010).

During working solution circulation in the catalytic hydrogenation step, the active anthraquinone is gradually converted to degradation products that are not capable to produce hydrogen peroxide (Nathan Dean Lee *et al*, 1969) (Peter W *et al*, 2013). If the temperature of hydrogenated and oxidized working solution is increased, the rates of formation of degradation products are increased. Moreover, the amount of degradation products increases sharply as the proportion of the working solution hydrogenated per pass through the system increased, which is called depth of hydrogenation (Nathan Dean Lee *et al*, 1969). Therefore, working solution regeneration through activated alumina and determining the active quinone left in residue is the key step in the anthraquinone process to avoid such degradation byproducts formed and spent active quinone along with the working solution.

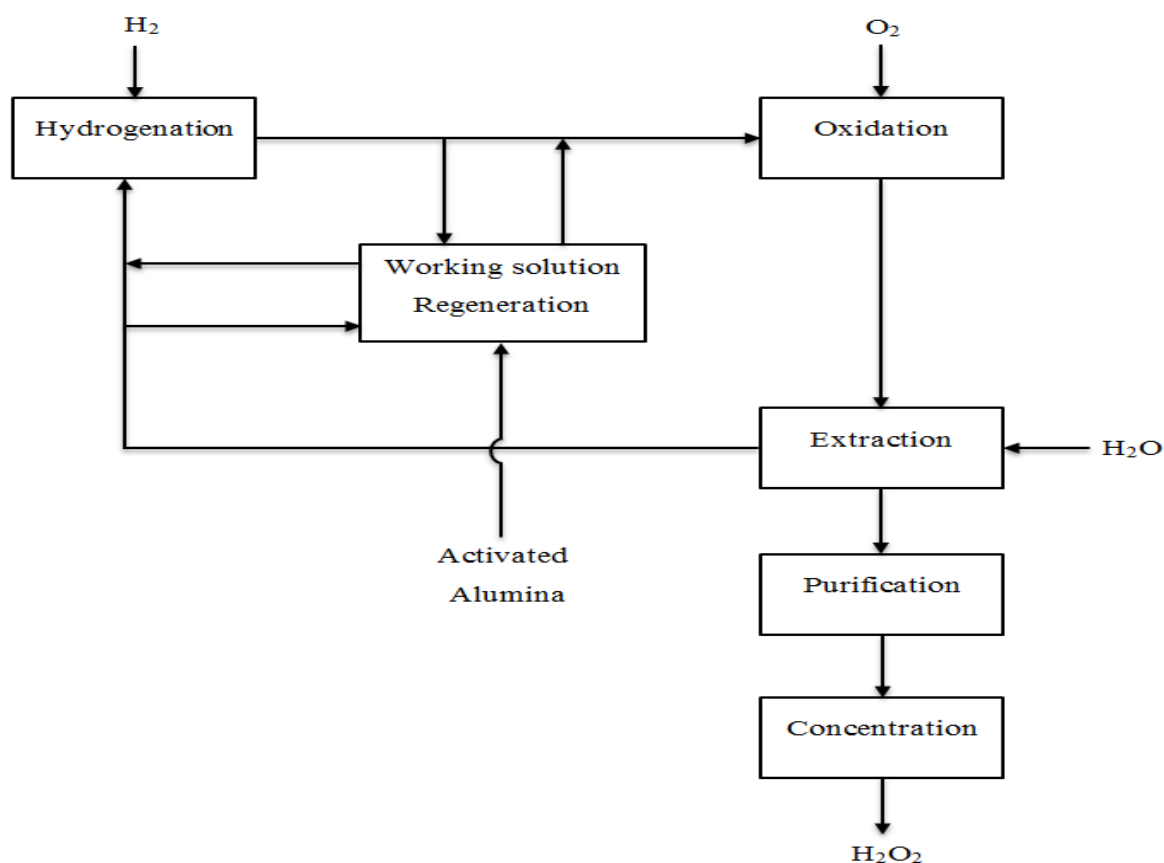


Figure 2.1: Schematic representation of H₂O₂ production process (Sandelin *et al.*, 2006)

2.2 Working Solution Composition and Quinone Solubility

Working solution is composed of a solute of ethyl anthraquinone dissolved in carrier solvents of tetra butyl urea, tri-octyl Phosphate and trimethyl Benzene (M Arshad *et al*, 2014). The solvents present in the working solution have the capability to dissolve all quinones and hydroquinone formed during hydrogenation and oxidation processes. In the working solution, quinones are readily dissolved in a non-polar organic aromatic solvent while hydroquinone is well dissolved in polar organic solvents since they have different solubility tendency (M Arshad *et al*, 2014). The solubility degree indicated that THEAQ has high solubility in reduced form and lower solubility in oxidized form or slower oxidation rate whereas EAQ has low solubility in reduced form and high solubility in oxidized form (Dalbir *et al*, 1987). The high solubility of THEAQ in reduced form showed that the rate of reduction reaction is faster than EAQ and less susceptible to side reaction causing loss of active quinone. The high oxidation rate and side reaction of EAQ result in higher quinone loss in the repeated cycle of working solution operation. Keeping the optimum molar ratio of EAQ and THEAQ provides the highest solubility of reduced EAHQ and THEAHQ, low byproduct formation and faster reaction rate. Therefore, the preferred optimum molar ratio of EAQ and THEAQ for solubility, rate of reduction reaction, and rate of oxidation reaction must be from 3:7 to 2:8 (Dalbir *et al.*, 1987) for efficient and economical production of hydrogen peroxide. In the working solution, the optimum ratio of THEAQ is maintained and reduced by reacting the oxidized working solution with activated alumina. In order to maximize the productivity of hydrogen peroxide, the preferred concentration of total quinones in the working solution must be 20-25 wt % as well (Dalbir *et al*, 1987).

The generation of byproducts in the side reaction is minimized not only through the quinone composition but also maintaining the degree of hydrogenation based on the total THEAQ. The allowable limit of hydrogenation degree must be from 70-100 mol%, preferably from 80-90 mol% of the total available THEAQ (Dalbir *et al*, 1987). If hydrogenation degree greater than 100 mol% of the total available THEAQ, EAQ might participate in the side reactions and result in degradation of active quinones. If hydrogenation degree becomes below 70 mol%, the hydrogen peroxide productivity becomes getting low.

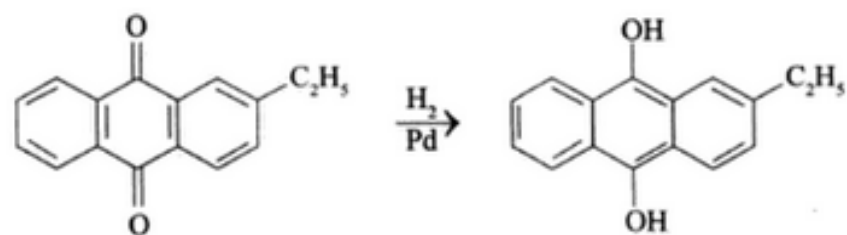
2.3. Formation of Degradation Products

In the cyclic production of hydrogen peroxide, unwanted EAQ degradation products (Fuqing Liet *al*, 2010)(Carl W *et al*,1959)(Aksela *et al*, 2005) are generated in every cycle of operation. The degradation of EAQ is mainly caused by the deep hydrogenation of its aromatic rings, hydrolysis of the C=O bonds and over-oxidation of THAQ (Fuqing Liet *al*, 2010)(Kosydaret *al*, 2010). The formation of degradation products generated during side reaction continued in the hydrogenation and oxidation stages include OHAHQ, OAT, H₂O,

AT, DAT and THAQE (M Arshad *et al*,2014)(Fuqing Liet *al* , 2010)(Aksela *et al*, 2005). The OHAHQ can be generated as a side reaction byproduct during hydrogenation of THAHQ. Theoretically, hydrogen peroxide can be generated from oxidized OHAHQ. However, the rate of oxidation is very slow and it does not form hydrogen peroxide at all. Therefore, OHAHQ can be viewed as degradation byproduct (Fuqing Li *et al*, 2010)(Aksela *et al*, 2005). During hydrogenation of anthraquinone, OAT is formed as a byproduct and further hydrogenation of OAT accelerates the formation of H₂O, AT and DAT which are inert and cannot be regenerated to active quinones. THAQE is a dominating byproduct appearing in the working solution, which is formed along with hydrogen peroxide in the oxidation step (Fredrik *et al*,2006). However, the accumulation of such degradation products from many repeated cycles of operation in the working solution will reduce the concentration of the effective anthraquinones the so-called AQ, AHQ, and THAQ. All of these degradation products represent a loss of active EAQ, which are not oxidized to form hydrogen peroxide (Drelinkiewicz *Aet al*, 2005)(Aksela *et al*, 2005). The degradation products which are unable to produce hydrogen peroxide are collectively known as inert (Wu *Qet al*, 2014)(Dalbir *Set al*, 1987)(M Arshad *etal*, 2014). When inert are accumulated over a critical level, they might cause increased total organic content in the quality of hydrogen peroxide, and the change in specific gravity and viscosity of the working solution. Indirectly such types of inert can disturb the catalyst filtration in hydrogenation and extraction process operations. The specific gravity of the working solution comprising inert ingredients, active quinones, and solvents at 30 °C shall have from 0.890-0.970, preferably from 0.910-0.940. The number of allowable limits of the inert ingredients in the working solution is from 3-20wt%, preferably 5-13wt % (Dalbir

Setal, 1987). Therefore, the working solution should be regenerated continuously to avoid the accumulation of such unwanted anthraquinone inert products as OHAHQ, THAQE, OAT, AT, DAT and H₂O (Aksela *et al*, 2005) (M Arshad *et al*, 2014)] and spent active quinone. The main reactions and side reactions in the hydrogenation and oxidation processes were shown in the following reaction mechanisms.

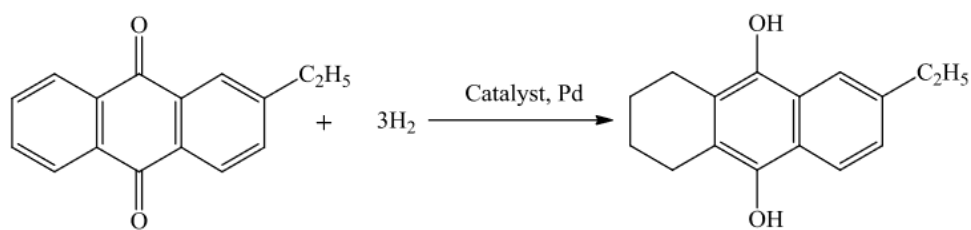
Reaction mechanism-1



2-Ethylanthraquinone

2-Ethylanthraquinol

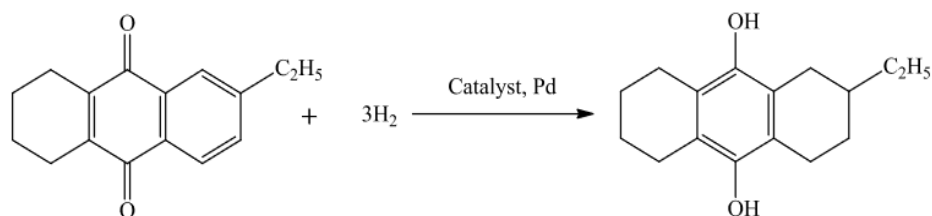
Reaction mechanism-2



2-Ethylanthraquinone

2-Ethylanthrahydroanthrahydroquinol

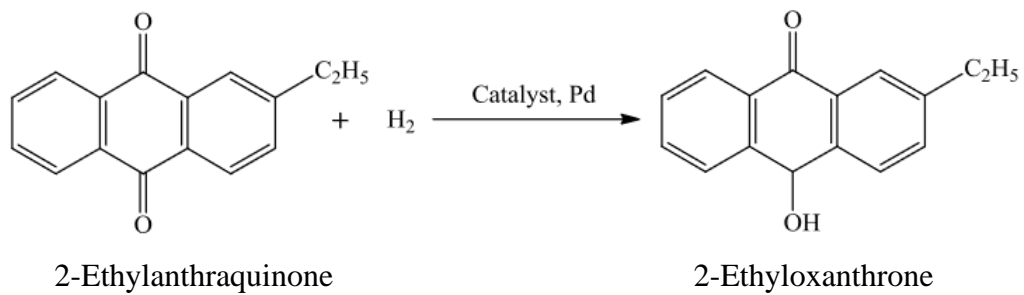
Reaction mechanism-3



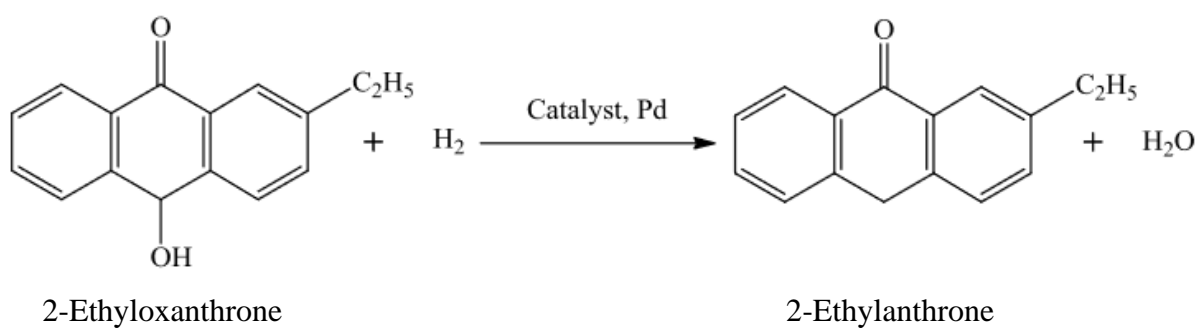
2-Ethyltetrahydroanthraquinone

2-Ethyloctahydroanthrahydroquinol

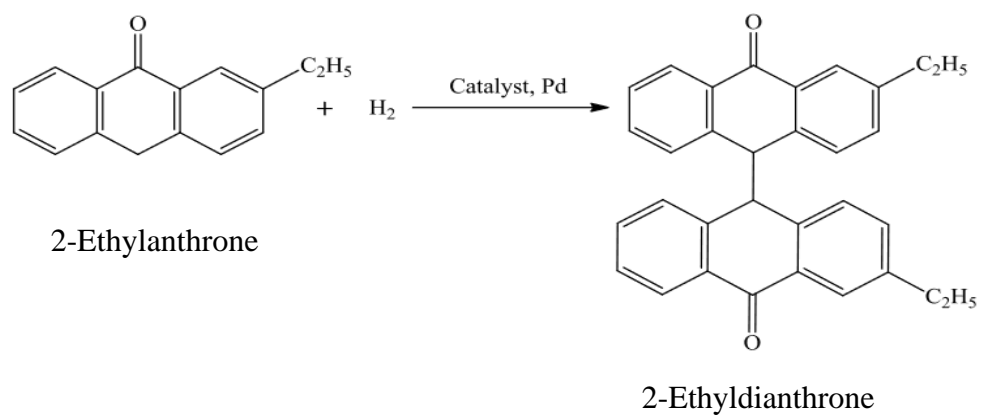
Reaction mechanism-4



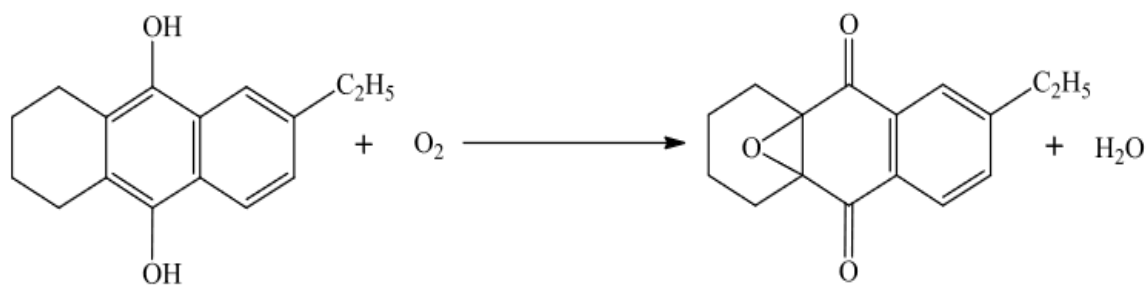
Reaction mechanism-5



Reaction mechanism-6



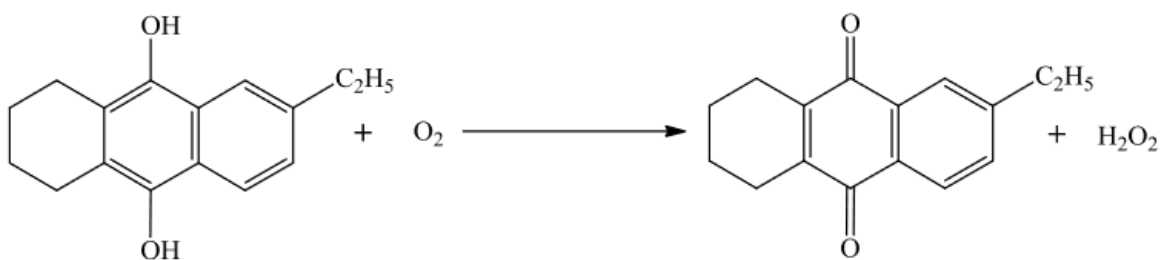
Reaction mechanism-7



2-Ethylhydroanthrahydroquinol

2-Ethylhydroanthraquinone epoxide

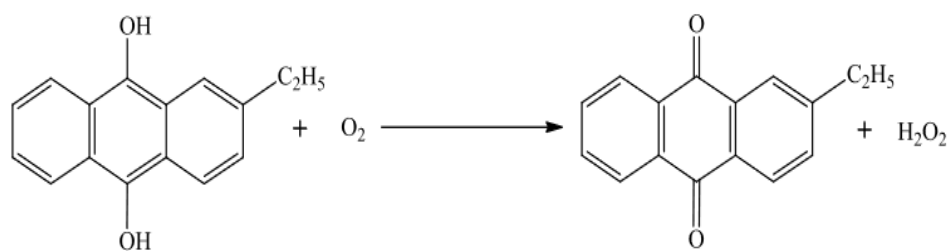
Reaction mechanism-8:



2-Ethylhydroanthrahydroquinol

2-Ethyltetrahydroanthraquinone

Reaction mechanism-9:



2-Ethylanthrahydroquinol

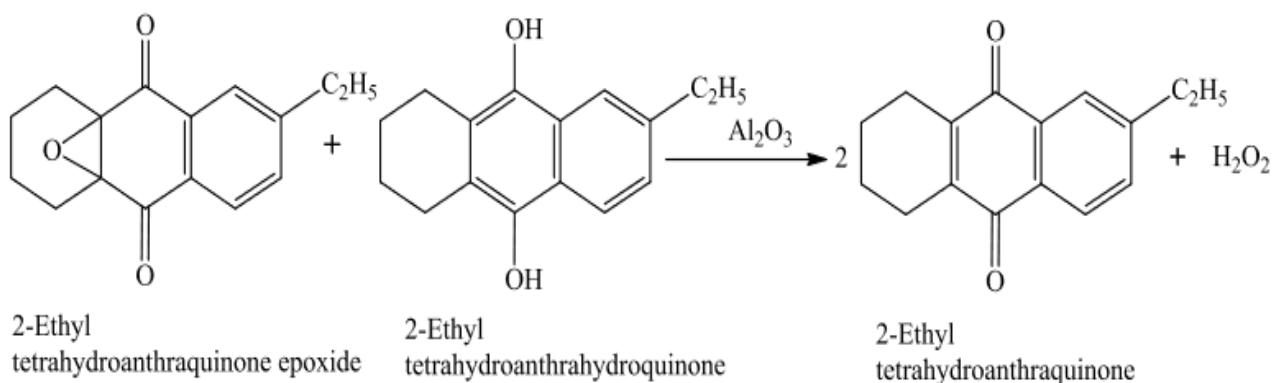
2-Ethylanthraquinone

Figure 2.2: Possible reaction mechanisms of AQ derivatives [Hess, 2000].

2.4. Regeneration of the Working Solution

The process of cyclic hydrogenation and oxidation of anthraquinone generates not only peroxide-producing anthrahydroquinones but also some by-products. These by-products of anthraquinone species can be converted back to useful quinones by the use of regeneration technique. Degraded working solution can be regenerated by caustic soda and activated alumina. Regeneration of working solution with aqueous caustic soda is accomplished by extracting the anthrahydroquinone from hydrogenated degraded working solution and recovering the solvent component of the resulting working solution (Carl W *et al*,1959). The aqueous extract containing the salt of anthrahydroquinones is oxidized at room temperature with oxygen to convert anthrahydroquinones to precipitated anthraquinones. In the industry, the working solution is regenerated by contacting the working solution with activated alumina (Svensson *et al*, 2002). (Fuqing Li *et al*,2014) at the temperature of 50-100°C (Fuqing Li *et al*, 2014) thereby converting the degradation products into effective anthraquinones. Working solution regeneration with activated alumina is accomplished by feeding a side-stream of working solution into a bed of dehydrogenation and de-epoxidation catalyst (Meshcheryakov EP *et al*, 2021). The degradation products of THAQE will be transformed into THAQ by reduction of THAHQ in the presence of basic activated alumina (Fuqing Li *et al*. 2014)(Aksela *et al*, 2005). The regeneration catalyst converts epoxidized anthraquinones and THAQs to their corresponding anthraquinones (Fuqing Li *et al*, 2010). As shown in the Following reaction mechanisms.

Reaction mechanism-1:



Reaction mechanism-2:

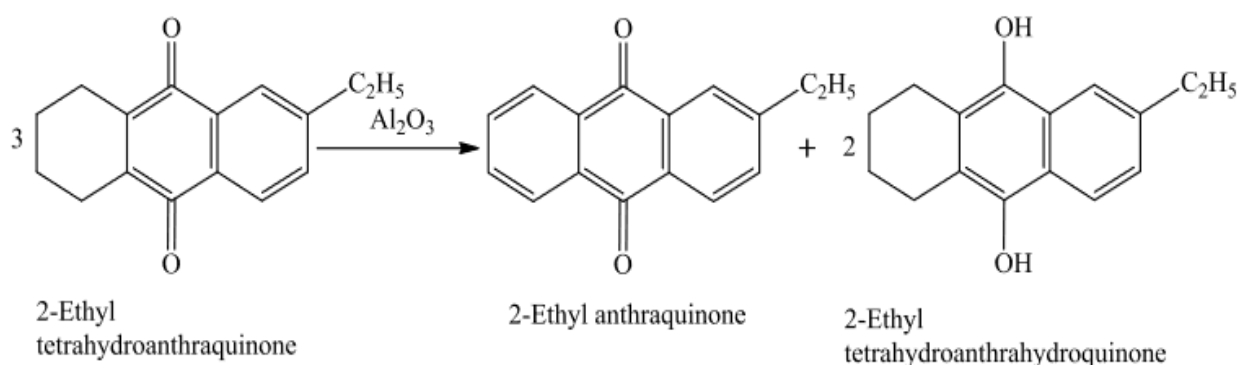


Figure 2.3: Converting epoxidized anthraquinones and THAQs to their corresponding anthraquinones by regeneration catalyst (FuqingLi *et al.*, 2010).

2.5 Activated Alumina

2.5.1. Phases of Alumina

Aluminum oxide or gamma alumina (γ -Al₂O₃) was the forms of alumina between the aluminum hydroxide (Al (OH)₃) and corundum or alpha alumina (α -Al₂O₃) (Rajamani, 2020). Activated alumina could be produced by the thermal decomposition of aluminum hydrates contained in bayerite, gibbsite and boehmite minerals (Rajamani, 2020). During thermal dehydration process of the aluminum hydrates, different types of transitional alumina could be formed. The thermal decomposition of boehmite in air at the temperature range of 300 to 500 °C had given the phase of γ -Al₂O₃ (gamma alumina). Further increased in temperatures, from 700 to 800 °C had given the phase of δ -Al₂O₃ and from 900 to 1000 °C had given the phase of θ -Al₂O₃ (Vasile *et al.*, 2021). The final anhydrous form of alumina obtained at 1100 °C was α -Al₂O₃ (corundum alumina) (Rajamani, 2020). The transitional gamma alumina had observed at the intermediate temperatures from 250 to 800 °C. Of which phases of alumina, gamma alumina (γ -Al₂O₃) was used as a catalyst and adsorbent in the hydrogen peroxide plant for working solution regeneration. The sequence of dehydration and transformation of alumina from bayerite, gibbsite and boehmite minerals at a given temperature were shown in the phase diagram of Figure 2.4.

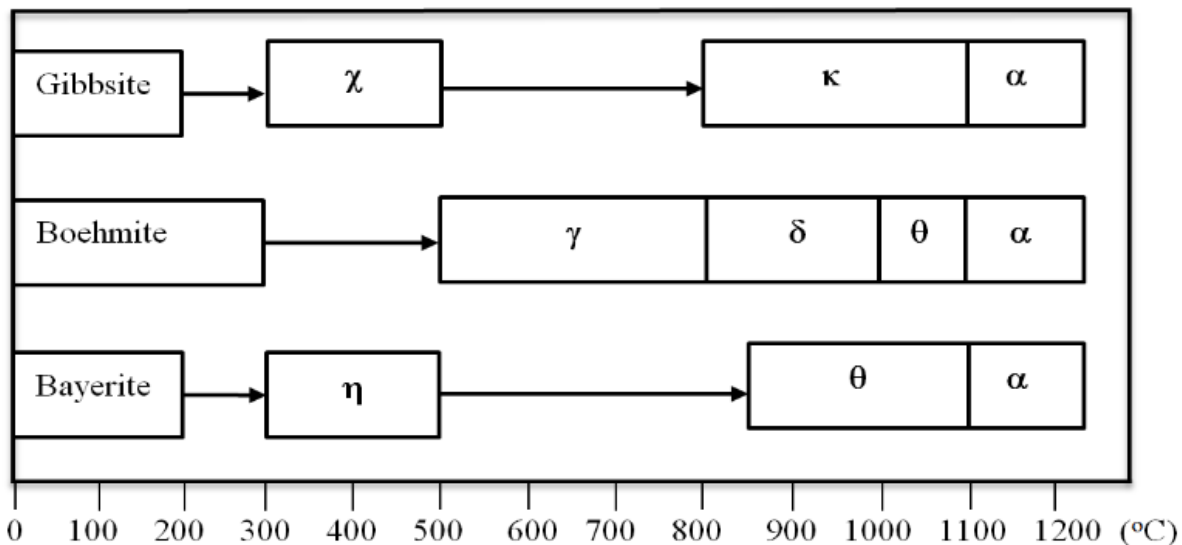


Figure 2.4: Phase diagrams of bayerite, boehmite and gibbsite minerals (Rajamani, 2020)

2.5.2 Acid Sites of Activated Alumina

Activated alumina was made from a combination of aluminum, oxygen and hydroxyl groups to form acidic and basic types of Bronsted and Lewis sites (Meshcheryakov *et al.*, 2021; Rajamani, 2020). The hydroxyl groups were the acid and basic types of Bronsted sites. A comparative study of the Bronsted acidity and basicity of hydroxyl groups showed that the alumina hydroxyls were more basic than acidic (Meshcheryakov *et al.*, 2021). Oxygen atoms were strong basic sites whereas aluminum ions were strong Lewis sites. There were two basic Lewis sites identified in alumina, which were strong and weak sites. Strong Lewis sites were associated with the bridging oxygen atoms of Al-O-Al whereas weak Lewis sites were associated with oxygen atoms of hydroxyl groups. The catalytic activity of alumina was related to strong Lewis's acid sites, which could accept electron pair by coordination bond and were represented by small number of low coordinated surface of Al³⁺ ions. The adsorption and catalytic properties of alumina had directly related to the surface activity, which could be controlled by the hydroxyl ion concentration. The surface of activated alumina had electron-acceptor and electron-donator sites, which could reduce or oxidize the adsorbed molecules. For example, Quinones and hydroquinone's present in the working solution were non-ionic Proton donors and proton acceptors (Rajamani, 2020). The presence of hydrogen bonding with

oxygen atoms in the quinones and hydroquinone made it to adsorb strongly on the surface of alumina. However, hydrocarbons were not a non-ionic proton donors and proton acceptors and were adsorb weakly on the surface of alumina.

During thermal and chemical conversion process of alumina, dehydrogenation and dehydroxylation of the surface of alumina led to the coordination of unsaturated Lewis's base of O^{2-} atoms and Lewis's acid of Al^{3+} ion (Meshcheryakov *et al.*, 2021). The Bronsted acid sites of the bridge and terminal hydroxyl groups were appeared on the surface of the alumina. The dehydration of two neighboring hydroxyl groups led to the formation of water molecule. The water was then released while the Lewis acid (Al^{3+}) and Lewis's base (O^{2-}) sites remain on the surface of alumina. After calcinations at temperatures above $470^{\circ}C$, strong acidity was formed on the surface of alumina. Further increased in temperatures up to $700^{\circ}C$, the number of Lewis sites increased with the decreased in the content of hydroxyl group. Thus, the acidity of activated alumina was determined by the proton sites of Lewis acid sites rather than Bronsted acid sites. During dehydration of activated alumina, there was a simultaneous formation of Lewis acid sites and Bronsted acid sites as shown in Figure 2.5.

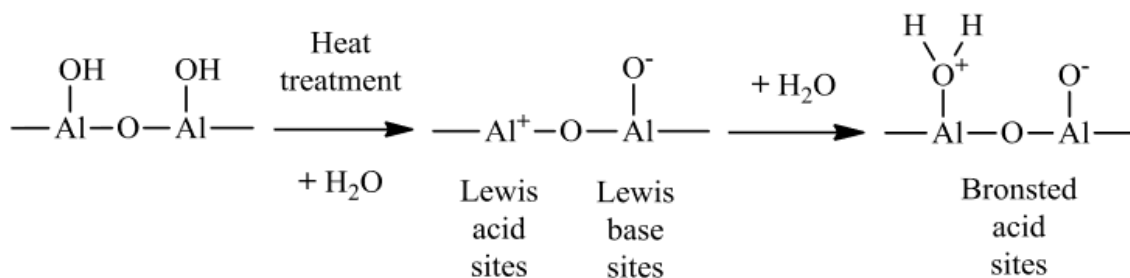


Figure 2.5: Different acid sites of activated alumina (Rajamani, 2020)

The surface of activated alumina could be modified by adding alkaline cations such as Na^+ (Meshcheryakov *et al.*, 2021) in order to control the change in active sites and increase the Adsorption efficiency. When the surface of alumina was modified by low content of Na^+ , the total surface basicity increased whereas Lewis and Bronsted acid sites also increased. When the surface of alumina was modified by high content of Na^+ , the strength and concentration of weak base sites increased and the strength of Lewis acid sites decreased while the

concentration of coordinated unsaturated Al^{3+} cations on the surface decreased. Hence, strong Lewis base sites had formed due to the binding of oxygen atoms with that of sodium.

2.5.3 Properties of activated alumina

Activated alumina had typically high surface area, high adsorption capacity (Rabia *et al.*, 2018), good chemical resistance, high abrasion resistance and high drying efficiency (Rajamani, 2020). The adsorption mechanism of activated alumina was determined by its surface property of active sites and hydroxyl radicals (Meshcheryakov *et al.*, 2021). The surface property had played a big role in the catalytic reactions that taken place at the inner surface of the catalyst (Rajamani, 2020). The two distinct adsorption mechanisms carried out in activated alumina were physical and chemical adsorptions (Rabia *et al.*, 2018). In physical adsorption mechanism, electron exchange had not carried out between the solid adsorbent and the liquid adsorbate. A non-specific and reversible process of physical adsorption made it to permit regeneration process. The characteristic features of physical adsorption were Vander Waals forces, dipole interactions, and hydrogen bonding. In chemical adsorption mechanism, there was change of chemical and electronic properties of the solid adsorbent. A specific and irreversible process of chemical adsorption made it difficult for regeneration process. The characteristic features of chemical adsorption were directly related to surface reactions caused by covalent and ionic bonds that made the chemical link between the solid adsorbent and liquid adsorbate. Covalent bond was a weak chemical adsorption whereas ionic bond was a strong chemical adsorption such as hydrogen radical in phenol. Therefore, adsorption of hydrogenation degradation byproducts on the surface of alumina, which formed from subsequent reduction of the working solution, was a type of chemical adsorption. On the other hand, the adsorption of water on the surface of alumina was a type of physical and chemical adsorption (Meshcheryakov *et al.*, 2021). Water adsorption had undergone three processes. The first process was chemisorptions by dissociative adsorption of water molecules that formed the first layer on the active sites. The second process was physical adsorption by hydrogen bonds that formed multilayer on the active sites. The third and final process was capillary condensation in catalyst pores.

2.5.4 Application of Activated alumina in Hydrogen peroxide Plant

During the production of hydrogen peroxide, unwanted degradation products have generated in every cycle of operation. The accumulation of such degradation products resulted in low concentration of effective anthraquinones in the working solution. Thus, working solution should be regenerated by contacting the working solution with the activated alumina containing alkali metals, alkaline-earth metals or rare earth elements (Li *et al.*, 2014). The preferred particle size and specific surface area of activated alumina that used for working solution regeneration was not more than 3.5 mm and not less than 50 m²/gm respectively. High adsorption capacity of activated alumina made it suitable for removing organic compounds such as surfactants, pesticides, dyes, and aromatic molecules (Rabia *et al.*, 2018). Activated alumina as a solid catalyst and adsorbent in the hydrogen peroxide anthraquinone production route had been used for working solution regeneration. During working solution regeneration, activated alumina as a porous adsorbent (Yang *et al.*, 2012) was used for adsorbing the inert impurities formed in the working solution. It was prevented to absorb the hydrogenation degradation products, reduce the consumption of ethylanthraquinone and stabilize working solution components by maintaining the proportion of THAQ at a constant level. The solid catalyst could convert the hydrogenation degradation products to useful anthraquinones due to its high regeneration capacity. During consecutive hydrogenation and oxidation steps, unwanted byproducts produced from the side reaction of active quinones had accumulated with the working solution. In order to convert inactive quinones like THAQE to active quinones and to remove other impurities, some of the working solution was regenerated before or after reduction reaction. The regenerating working solution allowed to pass through the reversion bed of alumina was 10 to 20 % (Yang *et al.*, 2012) of the total reacted working solution. The working solution regeneration was carried out continuously at optimum temperature of 60 to 80 °C.

2.5.5 Regeneration of Spent Alumina

Upon time, the alumina is being deactivated and unable to regenerate THAQE due to the blockage of active sites occupied by surface adsorption of highly polar inert. These inert impurities such as OHAHQ, OAT, AT, DAT, H₂O (Fuqing Li *et al.*, 2014) and others are

responsible for adhering on the surface of alumina via the acid sites and the hydroxyl-groups, (Gandhi, 2020) which made the alumina to be deactivated. Schematic presentation of deactivated alumina catalyst containing degraded quinone byproducts is shown in the following figure.



Figure 2.6: Schematic presentation of deactivated alumina

Catalyst deactivation is caused by the loss of catalytic activity, which is a problem of great industrial concern in the catalytic processes (Svensson, 2002). If catalyst activity declined to a critical level, four alternative ways are placed to make decision. The first alternative is regeneration and reuse of the catalyst, the second alternative is using the catalyst for another application, the third alternative is reclaimed and recycle important and expensive component of catalyst, the fourth alternative is discarding the catalyst. Among those alternatives, the first alternative that is regeneration and reuses the catalyst is always preferred.

The release and poor handling of deactivated alumina in Awash Melkassa Chemical Factory can be viewed as a solid waste. In the near future, high quantity of solid waste will be released into the environment that results in public health and environmental problems. Furthermore,

the solid waste leads to the loss of valuable materials in the waste composition (Mostafa Mahinroosta and Ali Allahverdi, 2018]). If this solid waste disposal cannot be controllable, flammable gasses can be freely released in ambient air that results in fire hazard. Therefore, many researchers are trying to find a solution or method to recover valuable organic compounds and reduce the release of solid wastes and gases to the environment. There are three well known methods proposed to remove such organic compounds and regenerate the alumina thereby avoiding the solid waste disposal into the environment. These methods are calcinations with caustic treatment, solvent extraction with caustic treatment, and solvent extraction with caustic solutions containing active oxygen.

2.5.5.1 Calcinations with Caustic treatment

In this method, regeneration was carried out by roasting the alumina at about 300-400 °C until the adsorbed organic and carbonaceous matter has been removed (Browning, 1974). Then contacting the roasted alumina with Na₂O contained in an aqueous sodium hydroxide solution. Again roasting the caustic-treated alumina at about 300-400 °C until the reaction of the remaining Na₂O and the alumina were completed. This processing method required high-energy input that could alter the crystalline structure of the alumina. This structural change of alumina caused a higher risk of losing the alumina durability.

2.5.5.2 Soxhlet Solvent extraction with Caustic treatment

Solvent extraction through Soxhlet apparatus is used to remove the adsorbed organics and carbonaceous matters. Since alumina is highly polar in nature due to the presence of both positive and negative species, the preferred compatible extraction solvents will be highly polar in nature. The extracting polar solvents are expected to have low boiling point, flash point, auto-ignition temperature, liquid and vapor density in order to minimize the risk of fire and explosion while extraction (Gandhi, 2020). The compatible organic polar solvents used to extract organic matters contained in alumina are acetone, methanol, ethyl acetate and acetonitrile. They have a good history on extracting polar compounds from the solid matrix of

deactivated alumina. The solvents acetone and methanol are suitable for removing all polar compounds while ethyl acetate is suitable for removing phenolic compounds. The presence of red-brown color in the solvent during extraction is an indication of extracted organic compounds. Color is an indication of solvents extraction power such that a darker color indicates the presence of large concentration of organics. The extraction power of ethyl acetate, methanol, acetonitrile and acetone increased from high to low order respectively.

2.6 Application of Anthraquinone

Utilized in the manufacture of hydrogen peroxide, colorings, in the fabric and pulp diligence, and as araspberry repellent. Anthraquinones (9, 10- dioxoanthracenes) constitute an important class of natural and synthetic composites with a wide range of operations. Besides their application as Colorings, anthraquinone derivations have been used since centuries for medical operations, for illustration, as laxatives and antimicrobial and ante-inflammatory agents. Current remedial suggestions include constipation, arthritis, multiple sclerosis, and cancer. Also, biologically activeanthraquinones deduced from Reactive Blue 2 have been employed as precious tool composites for biochemical and pharmacological studies. They may serve as super eminent structures for the development of unborn medicines.

(<https://pubmed.ncbi.nlm.nih.gov/27111664/>)

CHAPTER THREE

3. MATERIALS/EQUIPMENT AND METHOD

3.1 Materials

The materials used for determining the active quinone contained on the surface of deactivated alumina were Soxhlet apparatus, rotary, evaporator, oven dryer, 100ml volumetric flask, 1 μ l syringe, 5 μ l syringe, 100 μ l syringe, 10ml volumetric flask, Analytical balance, 100ml Glass flask, electric heating mantle. Analytical grade Soxhlet extraction solvents were obtained from Awash Melkassa Chemical Factory with purity, as methanol 99.5%, ethyl acetate 99.95%, acetone 99.5% and acetonitrile 99.5%. The solid waste of spent alumina was obtained from Awash Melkassa Chemical Factory.

3.2. Methods

3.2.1. Sample preparation and Analysis

The spent deactivated alumina sample was collected from the hydrogen peroxide plant solid waste of Awash Melkassa Chemical Factory. The total amount of solid sample required for Experimental work is about 150gm. Extraction process through Soxhlet extraction was done for 5 different experiments. For one experiment, the waste of 30gm solid sample with 30ml of extracting solvent (Fuqing Li *et al*, 2010) was used for Soxhlet extraction. Extraction solvents such as acetone, acetonitrile, methanol and ethyl acetate were obtained from Awash Melkassa Chemical Factory. 150ml total solvents are required for five experiments such that 30ml acetone, 30ml acetonitrile, 30ml methanol, 30ml ethyl acetate and a combination of 15ml methanol and 15ml Ethyl acetate was used for each experiment. But in this study 600gm solid sample and 600ml of solvents and combination of 100ml methanol and 100ml ethyl acetate were used for each experiment. After Soxhlet extraction; the solvent and extracted organic matters were separated by using rotary evaporator, then the solid residue was dried in oven at 110 °C for 2 hours. The dried sample was weighed and dissolved by using solvent-150. From prepared sample appropriate amount was prepared for GC and TGA analysis. The active

quinone contained in residue was determined by using standard WS, which can be prepared by mixing by percent of solvesso-150 (75%), TBU (21%), TOP (4%),EAQ (0.6gm), H₄EAQ (1gm), Cyclohexane (1ml) and OT (2gm/ml) and analyzed by using GC. Finally, the quantity of active quinone was determined by using Nuberg Engineering calculation sheet (excel) based on the GC peak area.

3.2.2 Soxhlet solvent extraction

Soxhlet solvent extraction was carried out using Soxhlet apparatus that consisted of thimble, distillation flask, and condenser and Soxhlet unit. The organic compounds or quinones contained in spent alumina were extracted by using ethyl acetate, methanol, acetonitrile, acetone, and solvent mixture (ethyl acetate and methanol) (Dulo *et al.*, 2021; Rajamani, 2020). The polar nature of these organic solvents used to dissolve and extract polar organic compounds. Since all solvents were colorless in nature, the presence of colored organics removed from spent alumina was easily seen in the mixture. For 15 gm of spent alumina sample, 200 ml of extracting organic solvent was used for each Soxhlet solvent extraction experiment (Rajamani,2020), which implied that excess solvent was used for small quantity of solid sample. However, in this research, 200 ml of extracting solvent was used enough for each 200gmof spent alumina sample used for Soxhlet extraction experiment. Equal proportion of the solid sample with the extracting solvent was used because the extracting solvent could soak the solid sample above the solid surface. The solvent ratio used for ethyl acetate to methanol was 1:1. The Soxhlet solvent extraction experiments that conducted at a given temperature were shown in table 3.1.

Table 3.1: Solvent volume and sample weight for Soxhlet extraction experiment

| Trial Number | Types of Solvent | Solvent Volume (ml) | Sample Weight (gm) | Boiling point (°C) | Set point (°C) |
|--------------|-------------------------|---------------------|--------------------|--------------------|----------------|
| 1 | Acetone | 200 | 200 | 56 | 85 |
| 2 | Acetonitrile | 200 | 200 | 82 | 120 |
| 3 | Methanol | 200 | 200 | 65 | 100 |
| 4 | Ethyl acetate | 200 | 200 | 77 | 100 |
| 5 | Ethyl acetate& methanol | 200 | 200 | 65&77 | 100 |

1 BPT stand for boiling point temperature of the solvents.

2SPT stand for set point temperature of the solvents.

During solvent extraction, the heating mantle was allowed to heat the mixture contained in distillation flask above the boiling point of the solvent. Putting the temperature above the boiling point was used to reduce the time taken to extract the organics and to increase the solvent circulation. The solvent extraction was continued for three hours and at the end of extraction, there was no color change observed around the thimble or the color of solvent in the thimble was similar to that of the original solvent. After complete extraction, the solvent and extracted organic matters were separated by using rotary evaporator. The extracted organics obtained from rotary evaporator were oven dried at 110 °C for 2hours. The experimental set up of Soxhlet solvent extraction was shown in Figure 3.1.



Figure 3.1: Experimental set up of Soxhlet solvent extraction (Dreamstime.com <https://www.dreamstime.com/soxhlet...>)

From figure 3.2 Visibility of layers in Soxhlet extraction acetone solvent there is a two layer at the bottom of thimble dark color and uniform slightly reddish color above in the thimble which shows the carbon and quinone extraction respectively on the surface of spent alumina and also shows the extracted organic matter settled at the bottom of solid sample found in the thimble.



Figure 3.2: Visibility of layers in soxhlet extraction acetone solvent (A.M.C.F)

3.2.3 Characterization of the extracted quinone

3.2.3.1 Gas chromatography

GC analysis was an analytical technique used to determine the chemical composition of various organic components of the working solution that was extracted on the surface of spent alumina. The concentrations of the working solution components were analyzed by using Agilent Technologies 7890A GC System and then the conversion of THAQE to THAQ and

EAQ were determined. The GC instrument was equipped with flame ionization detector, which had a column length 60 meters and internal diameter 0.25 mm coiled to fit inside the instrument. The sample of each extracted working solution of volume 5 μ l was introduced into the GC column via the automated injection port using a micro liter syringe. These samples were moved by high purity carrier gas nitrogen having a flow rate of 1.0028 ml/min through the oven-heated column. The oven temperature was programmed from 35 °C to 280 °C at a rate of 3°C/min where the various components of the working solution mixture were separated and eluted at 55.5 minutes. These components were reached the detector at different retention times thereby the detector generated an electric signal in which the output signal was recorded by a computer. The retention time was a measure of how long from the time of injection it took the component to exit the column. Once all components of the working solution mixture elute from the column and detected, a retention time versus peak height called chromatogram was produced in the computer.

The GC of known reference working solution components was used to compare with the GC of unknown sample components. Since the GC parameters and column were identical for each sample run, the identity of unknown sample had the same retention time as the reference chromatogram. Thus, the chromatograms output of retention time was matched likely that the unknown and known samples were identical compounds. The lowest boiling point of the working solution components eluted from the GC column had provided the peak with the lowest retention time. On the other hand, the highest boiling point of the working solution components eluted from the GC column had provided the peak with the highest retention time. The known reference working solution components were cyclohexane, solvesso-150, TBU, orto-terphenyl, THAQE, THAQ, EAQ and TOP. Of these components, cyclohexane was the solvent used to dilute orto-terphenyl whereas orto-terphenyl was used as internal standard for working solution components determination. Thus, cyclohexane that provided best elution was not included in the total peak area calculation. Since the concentration of activequinone was calculated from the total peak area of chromatogram by using excel calculation sheet (from GC operation manual).

3.2.2.2 Thermo gravimetric analysis

TGA analysis was a thermo-analytical technique used to determine the thermal analysis of Soxhlet solvent treated alumina samples as well as fresh and spent alumina samples. The TGA analysis of spent and fresh alumina was used to compare their weight loss with Soxhlet solvent treated alumina. HCT-1 BJHENEVEN (ATAT 1000, China) was used to analyze the samples using nitrogen flow rate of 20 ml/min and a sample weight of 10 mg. TGA measured the change in weight of the sample in relation to change in temperature and provided qualitative and quantitative information about the weight loss and purity of the given sample. The temperature was adjusted between 25 to 900 °C with a heating rate of 20°C/min and the decomposition of the sample weight (%) against temperature (°C) was recorded.

CHAPTER FOUR

4. RESULT AND DISCUSSION

In this chapter, the results obtained from the recovering active quinone process using Soxhlet extraction on the surface of spent alumina were discussed in detail. The characterization results also were explained briefly.

4.1 Soxhlet solvent extraction

In this extraction, five experiments were conducted through Soxhlet apparatus by using ethyl acetate, methanol, acetone, acetonitrile and mixture solvents (methanol and ethyl acetate), to extract organic compounds contained in spent alumina. The extraction of organic compounds as quinones and carbon deposits were started when the solvent and alumina were heated up above the boiling point of solvents. The extracted organic compound around the thimble was visible as a reddish color. After each cycle of operation, the solvent with extracts were separated using rotary evaporator. The solute extract containing desorbed quinones was obtained at the bottom of distillation flask while the vaporized solvent was recycled for further extraction.

The total number of solvent cycles observed during Soxhlet extraction at a given set point temperature and extraction time were tabulated in Table 4.1. The number of solvent cycles for each solvent extraction was dependent on the color of extracted organics that observed around the thimble. These solvent cycles were used to distinguish the end of extraction efficiency of the organic solvents. The set point temperature of the solvent was placed above the boiling point for each solvent used in order to check the cycle of vaporized solvent. The extraction times for all solvent extraction experiment were allowed to complete within 3 hours because there was no color observed that represent extractable organics around the thimble. However, the complete extraction time with no color change observed at 2 hours, 3 hours, 2.5 hours, 3 hours and 2.5 hours for acetone, acetonitrile, ethyl acetate, methanol and solvent mixture

respectively. Based on the polarity of the solvents, methanol was the most polar followed by acetonitrile and ethyl acetate but acetone was the least polar. Thus, acetone had low extraction potential whereas methanol had high extraction potential. The number of cycles and extraction times for acetonitrile and ethyl acetate were higher than acetone due to the presence of high extraction potential.

Table 4.1: Soxhlet extraction solvent cycles

| Trial number | Types of solvent | SPT (°C) | Extraction time (hour) | Number of cycles |
|--------------|--------------------------|----------|------------------------|------------------|
| 1 | Acetone | 85 | 2 | 5 |
| 2 | Acetonitrile | 120 | 3 | 7 |
| 3 | Ethyl acetate | 100 | 2.5 | 6 |
| 4 | Methanol | 100 | 3 | 5 |
| 5 | Ethyl acetate & Methanol | 100 | 2.5 | 5 |

The color of extracted organics showed that solvent extraction conducted with acetone, Acetonitrile and methanol gave a homogeneous reddish color while solvent extraction Conducted with ethyl acetate gave a slight darker homogeneous color. The observation of reddish and darker color was due to the presence of low and high concentration of quinone Organics extracted from spent alumina respectively. On the other hand, solvent extraction Conducted by the mixture or a combination of methanol and ethyl acetate showed two color Layers such that the orange color at the top and the darker color at the bottom. The orange Color in the solvent mixture indicated the presence of quinone whereas the darker color in the solvent mixture indicated the presence of carbon deposits formed by the precipitation of complex compound. Depending on the color observation, the order of solvent extraction efficiency from high to low were obtained by ethyl acetate-methanol mixture, ethyl acetate, methanol, acetonitrile and acetone respectively such that the better solvent for extraction was the solvent mixture. However, the color observation alone not indicated a definite conclusion that made to select better solvent for extraction (Rajamani, 2020). The color observation of

desorbed quinones and carbon deposits obtained from Soxhlet solvent extraction were shown in Figure 4.1.

The acetonitrile, methanol, mixture of ethyl acetate and methanol treated alumina samples showed high bleached color observation while acetone treated alumina sample showed low bleached color observation after drying as shown in Figure 4.2. From this observation, a definite conclusion was not made in order to compare the solvents extraction efficiency (Rajamani, 2020).

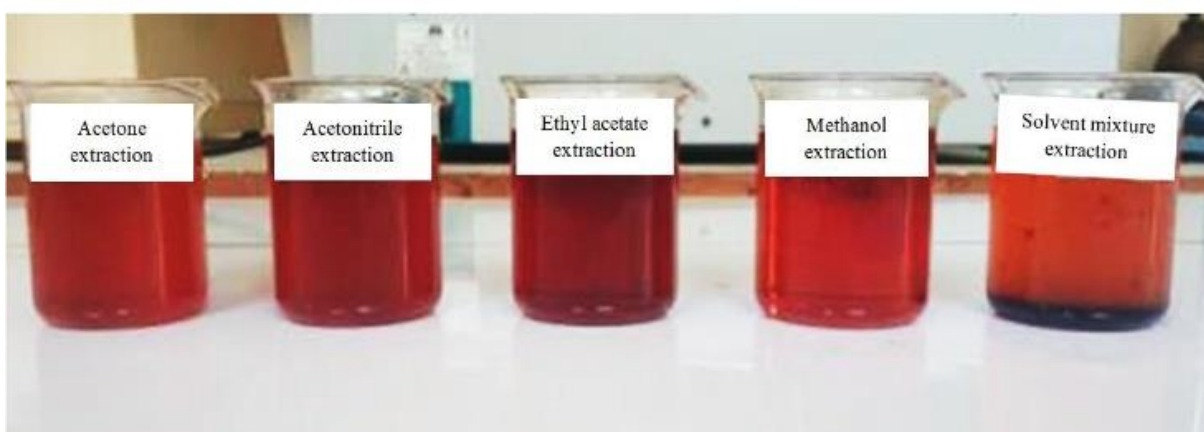


Figure 4.1: Soxhlet solvent extraction color observation



Figure 4.2: Soxhlet extraction solvent treated alumina

Solvent treated alumina samples were oven dried at a temperature of 110 °C for 2 hours in order to avoid the absorbed solvents and prepare the solid sample for caustic treatment. The acetonitrile, methanol, mixture of ethyl acetate and methanol treated alumina samples showed high bleached color observation while acetone treated alumina sample showed low bleached color observation after drying as shown in Figure 4.3. From this observation, a definite conclusion was not made in order to compare the solvents extraction efficiency (Rajamani, 2020).

4.1.1 Solvent-adsorbate mixture separation

The quantity of organic compounds removed from spent alumina during Soxhlet extraction within the bounded limit of 3 hours was obtained by separating the extracting solvent from the mixture using rotary evaporator. The removed organic compounds from spent alumina were collectively known as residue/adsorbate after oven dried at 110 °C for 2 hours. The dried residue of acetone, acetonitrile, ethyl acetate, methanol and mixture solvents extraction were shown in Figure 4.3. The color of acetone and methanol extraction residue was shown orange color whereas the color of acetonitrile and ethyl acetate extraction was shown black and dark color respectively. However, the color of mixture solvent extraction residue was shown two layers of dark and white colors. The darker color was the indication of carbon deposits whereas the white color was the indication of heavy organic solvents.



Figure 4.3: The dried residue of Acetone (A), Acetonitrile (B), Ethyl acetate (C), and Methanol (D) and Solvent mixture (E) extraction obtained after separation.

As shown from Table 4.2, the quantity of adsorbate removed increasing in the order of solvent extraction efficiency as solvent mixture, methanol, ethyl acetate, acetonitrile and acetone respectively. Depending on the degree of solvent extraction, the highest residue removal efficiency of 69.05% was obtained using a combination of methanol and ethyl acetate extraction. The highest percentage residue removal obtained by this solvent mixture was caused by the dissolving potential of different polar components at the sometime. Therefore, the solvent mixture was found as the best solvent for extracting organics contained in spent alumina which was the same finding as the color observation of solvent-adsorbate mixture in Soxhlet solvent extraction.

The Soxhlet solvent treated alumina was thermally analyzed using TGA (Figure 4.4) in order to determine the total organics adsorbed/removed on its surface. The TGA curve showed that the total mass of organics removed from spent alumina was 44.2 gm. Thus, the percentage of residue or adsorbate weight could be compared to the total mass of organics obtained from the TGA curve. The percentage removal of residue or adsorbate that separated from the solvent mixture was set forth in Table 4.2.

Table 4.2 Solvent –adsorbate mixture separation

| Extracting solvent | Extracted organics volume (ml) | Flask empty weight (gm) | Flask with residue weight (gm) | Net Residue weight (gm) | Dried net Residue weight (gm) | Dried residue removal (%) |
|--------------------|--------------------------------|-------------------------|--------------------------------|-------------------------|-------------------------------|---------------------------|
| Acetone | 180 | 155 | 164.01 | 9.010 | 9.005 | 20.37 |
| Acetonitrile | 185 | 155 | 169.99 | 14.99 | 14.86 | 33.62 |
| Methanol | 190 | 155 | 171.24 | 16.24 | 16.13 | 36.49 |
| Ethyl acetate | 180 | 155 | 170.33 | 15.33 | 15.24 | 34.48 |
| Mixture solvent | 188 | 155 | 185.72 | 30.72 | 30.52 | 69.05 |

4.1.2 Thermo gravimetric analysis

In addition to color observation and solvent-adsorbate mixture separation, further investigation of Soxhlet solvent treated alumina with TGA was required to compare the solvent extraction efficiency. The thermal stability of Soxhlet solvent treated alumina, fresh alumina and spent alumina samples were indicated by the decomposition of the sample weight (%) against temperature (°C) as shown in Figure 16. The degradation temperature of all alumina samples had easily seen in the DTG profile of Figure 4.4 (A), which showed multiple small and large endothermic peaks. The multiple small weight loss of adsorbed organics was observed in the small multiple endothermic peaks that corresponded with multiple degradation temperature. However, the maximum degradation temperature with the maximum weight loss of adsorbed organics for each sample had shown from large endothermic peaks. Thus, the maximum degradation temperature of acetone treated alumina, acetonitrile treated alumina, ethyl acetate treated alumina, methanol treated alumina, mixture solvent treated alumina, and fresh alumina and spent alumina were observed at 527.4 °C, 523.9 °C, 535.9 °C, 531.5 °C, 524.5 °C, 534.8 °C and 408.3 °C respectively.

The simple presentation for the percentage weight loss of Soxhlet solvent treated alumina, fresh alumina and spent alumina samples had shown in the TGA curve of Figure 4.5 (B). In this curve, the percentage weight loss of acetone treated alumina, acetonitrile treated alumina, ethyl acetate treated alumina, methanol treated alumina, mixture treated alumina spent alumina and fresh alumina were 17.5%, 14.8%, 15.9%, 13.7%, 11.4%, 22.1% and 6.4% respectively.

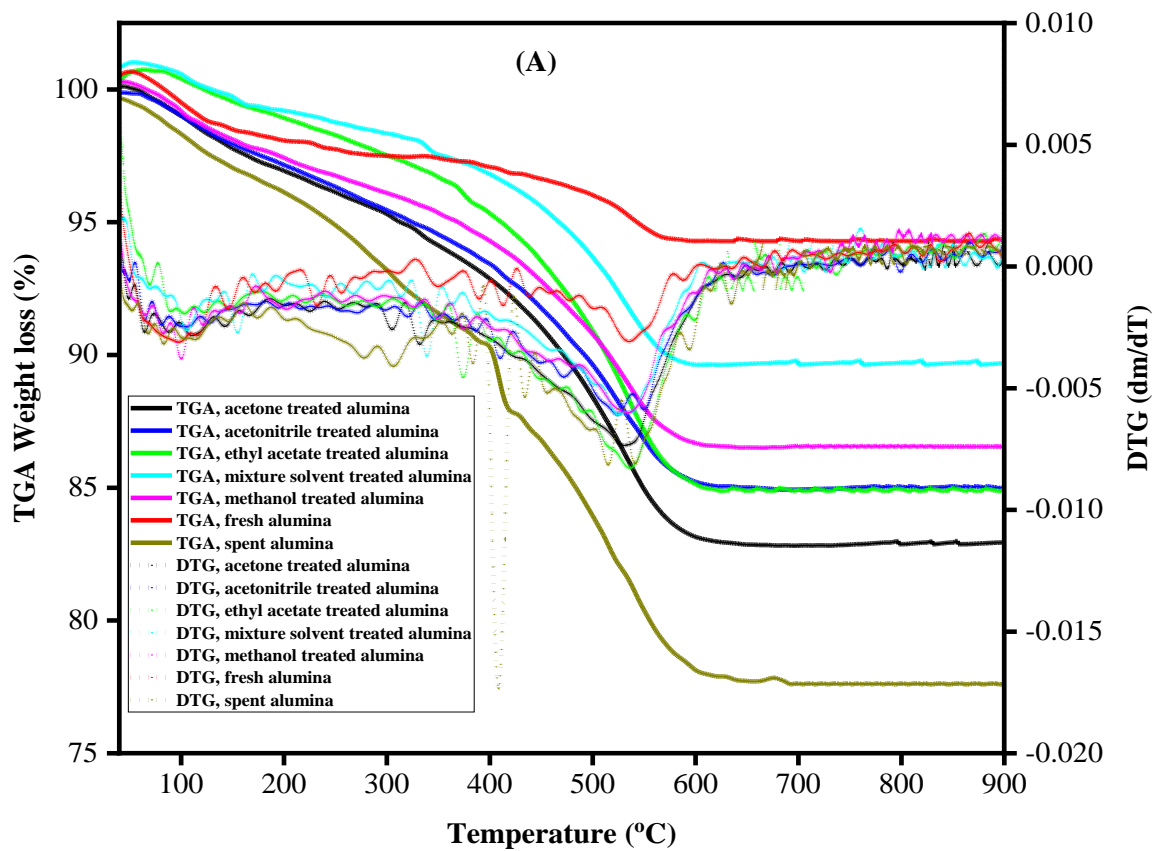


Figure 4.4: (A): TGA and DTG profiles for solvent treated, fresh and spent alumina

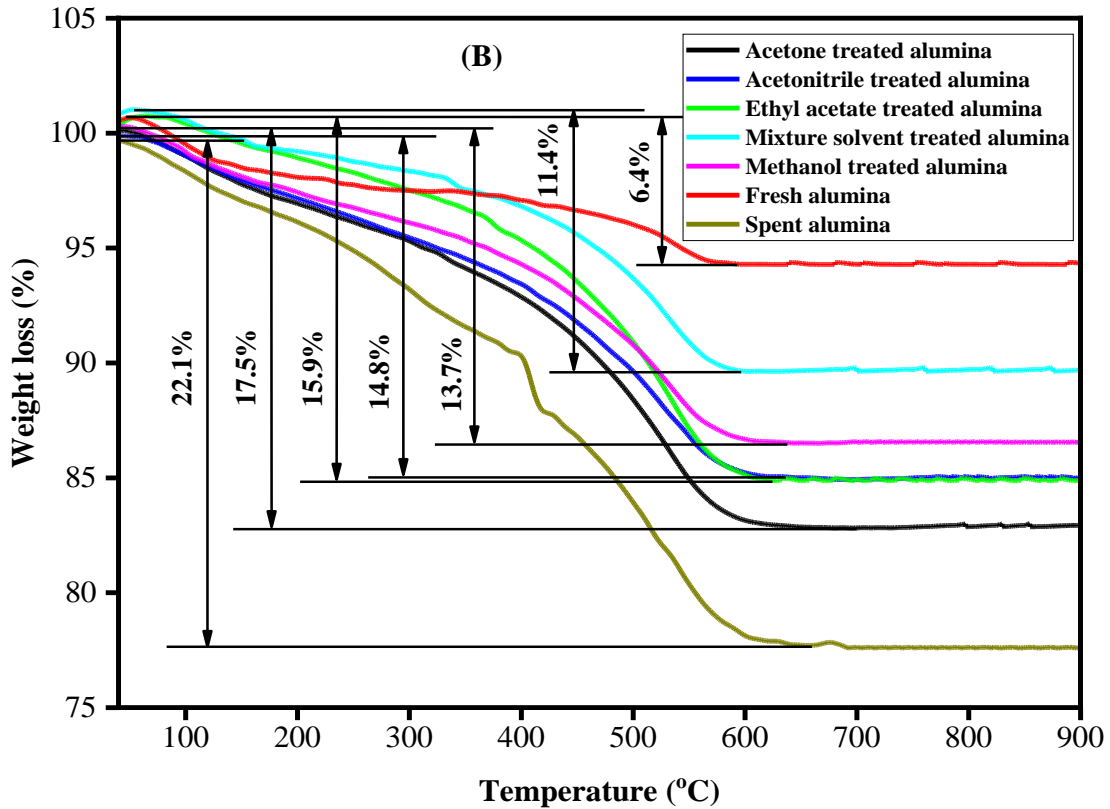


Figure 4.5 :(B): Weight loss in TGA curves for solvent treated, fresh and spent alumina

The TGA curve showed that the weight loss of solvent treated alumina samples were in-between the weight loss of fresh and spent alumina samples. Relative to the weight loss of spent alumina, the percentage weight loss for acetone treated alumina, acetonitrile treated alumina, ethyl acetate treated alumina, methanol treated alumina and mixture solvent treated alumina were reduced by 4.6%, 7.3%, 6.2%, 8.4%, 10.7% respectively. The higher percentage weight loss reduced from spent alumina in the TGA curve corresponded with the lower weight of adsorbed organics present during solvent extraction. In this case, the TGA curve of mixture solvent treated alumina had shown the lower weight loss of adsorbed organics. Thus, the higher solvent extraction efficiency was obtained by using mixture of ethyl acetate and methanol solvents. Therefore, the solvent mixture was selected as the best solvent for Soxhlet solvent extraction.

4.2 Gas Chromatography

GC was used to show the sample Composition and amount active quinone left in the residue of solvent extraction. The GC chromatogram was obtained and drawn with the help of the software Origin lab. As shown from table 1,2,3,4 and 5 respectively working solution GC result calibration sheet, the Solvent mixture extraction gives higher amount of active quinone (630.3 μ g/ml or 59.5gpl), Methanol extraction (630 μ g/ml or 58.8gpl), Acetonitrile extraction (523.23 μ g/ml or 34.2gpl), Ethyl acetate extraction (443.63 μ g/ml or 41.7gpl) and Acetone extraction (114.63 μ g/ml or 32.4gpl). This indicated that the solvent mixture has a good extraction efficiency of active quinone from organic compound adsorbed on the surface of deactivated alumina during the regeneration of working solution, when compared to with other organic solvents which were used in extraction process, in another way depending on the obtained results the total extraction efficiency of organic compound on the surface of spent alumina and active quinone extraction efficiency organic solvents are different, that means the order were different. The value measured by μ g/ml indicated that, the amount (concentration) of active quinone found in an adsorbate organic compound removed from spent alumina, whereas the value measured by gpl indicated that amount of active qinone found in plant working solution which was used as references during the GC analysis. This indicated that, there are losses of high amount of active quinone during the regeneration of working solution in hydrogen peroxide plant of AMC. So, during the regeneration of deactivated alumina the active quinone also must be recovered and used for makeup of working solution again for processing hydrogen peroxide rather than buying new Ethylanthraquinone for replacement.

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Currently spent alumina disposal to the environment in the Awash Melkassa Chemical factory became a big problem. Spent alumina had collected on the open ground and exposed to direct sun light. This might create environmental pollution and health hazard that caused by the fire of adsorbed organics contained in spent alumina. This solid waste and adsorbed organic (active quinone) on the surface of it, not only brought about environmental pollution but also requested high foreign currency for replacement. Therefore, spent alumina and active quinone should be regenerated and recovered to minimize the waste and foreign currency so that it can reuse for working solution regeneration and processing of hydrogen peroxide.

In this study, Organic on the surface of spent alumina was washed to recover active quinone using Soxhlet solvent extraction. The Soxhlet extraction was conducted by acetone, acetonitrile, ethyl acetate, methanol and a combination of ethyl acetate and methanol solvents. Among these extracting solvents, the extraction conducted by a combination of ethyl acetate and methanol solvents had shown higher extraction performance. Moreover, based on the TGA analysis, the minimum weight loss of 11.4% was obtained which indicated that the solvent mixture of ethyl acetate and methanol could efficiently remove the adsorbed organics. Depending on the degree of solvent extraction, the highest residue removal efficiency of 69.05% was obtained using a combination of methanol and ethyl acetate extraction. Solvent mixture extraction provides higher amount of active quinone. This indicated that the solvent mixture has a good extraction efficiency of active quinone from organic compound adsorbed on the surface of deactivated alumina during the regeneration of working solution when compared to with other organic solvents which were used in extraction process. Therefore, recovered active quinone could be used as fresh ethylanthraquinone for working solution make up during hydrogen peroxide production.

5.2 Recommendation

This research was conducted to recover the active quinone on the surface of spent alumina using Soxhlet solvent extraction. However, the active quinone (organic compounds) adsorbed on spent alumina were not completely removed during extraction process. Hence, there was some difference relative to fresh and deactivated alumina in terms of color. Therefore, finding other treatment methods can be recommended.

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<https://doi.org/10.1021/acs.jpcc.5b01325>

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APPENDICES

Table 1 (A) Working solution GC result calibration sheet for Solvent mixture extraction

| A | StandardWS(Sol,75%,,TBU21%,TOP4%,EAQ60gpl,H4EAQ100gpl) | | | | Date | 27/03/2023 | Time | 12:30pm | |
|-------|--|-----------|-----------------|---------|---------------|------------|-------|---------|--------------|
| S.No. | Component | Peak Area | Injected sample | | % without O.T | O.T.factor | AxB | Result | |
| | | | Conc.ug/ml | % | A | B | | gpl | Sol. Ratio,% |
| 1 | Solvesso150 | 3892.813 | 10676.4 | 74.1914 | 75.24 | 0.487001 | 36.64 | | 70.5 |
| 2 | TBU | 1007.3775 | 2762.8 | 19.1992 | 19.47 | 0.700001 | 13.63 | | 26.2 |
| 3 | TOP | 44.06654 | 120.9 | 0.84 | 0.85 | 2.000 | 1.70 | | 3.3 |
| 4 | OT | 72.92373 | 200 | 1.39 | 0 | 0 | 0.00 | 0.0 | |
| 5 | THAQE | 0 | 0.0 | 0.00 | 0.00 | 1.270 | 0.00 | 0.0 | |
| 6 | THAQ | 0 | 0.0 | 0.00 | 0.00 | 0.961 | 0.00 | 0.0 | |
| 7 | EAQ | 229.80824 | 630.3 | 4.38 | 4.44 | 0.74009 | 3.29 | 59.5 | |
| 8 | Total | | 14390.3 | 100 | 100 | 0.55 | | 59.5 | 100 |

Table 2 (B) Working solution GC result calibration sheet for Ethyl acetate extraction

| A | StandardWS(Sol,75%,,TBU21%,TOP4%,EAQ60gpl,H4EAQ100gpl) | | | | Date | 27/03/2023 | Time | 12:30pm | |
|-------|--|-----------|-----------------|--------|---------------|------------|--------|---------|--------------|
| S.No. | Component | Peak Area | Injected sample | | % without O.T | O.T.factor | AxB | Result | |
| | | | Conc.ug/ml | % | A | B | | gpl | Sol. Ratio,% |
| 1 | Solvesso150 | 3313.5907 | 10719.9 | 74.832 | 75.89 | 0.487001 | 36.96 | | 69.2 |
| 2 | TBU | 856.3941 | 2770.5 | 19.34 | 19.61 | 0.700001 | 13.73 | | 25.7 |
| 3 | TOP | 59.15056 | 191.4 | 1.34 | 1.35 | 2.000 | 2.71 | | 5.1 |
| 4 | OT | 61.82153 | 200 | 1.40 | 0 | 0 | 0.00 | 0.0 | |
| 5 | THAQE | 0 | 0.0 | 0.00 | 0.00 | 0.961 | 0.00 | 0.0 | |
| 6 | THAQ | 0 | 0.0 | 0.00 | 0.00 | 0.961 | 0.00 | 0.00 | |
| 7 | EAQ | 137.13235 | 443.6 | 3.10 | 3.14 | 0.74009 | 2.3200 | 41.7 | |
| 8 | Total | | 14325.4 | 100 | 100 | | 0.56 | 41.7 | 100 |

Table 3 (C) working solution GC result calibration sheet for Methanol extraction

| A | StandardWS(Sol,75%,,TBU21%,TOP4%,EAQ60gpl,H4EAQ100gpl) | | | | Date | 27/03/2023 | Time | 12:30pm | |
|-------|--|-----------|-----------------|---------|--------------|------------|-------|---------|--------------|
| S.No. | Component | Peak Area | Injected sample | | %without O.T | O.T.factor | AxB | Result | |
| | | | Conc.ug/ml | % | A | B | | gpl | Sol. Ratio,% |
| 1 | Solvesso150 | 3411.0886 | 11304.7 | 75.731 | 76.76 | 0.487001 | 37.38 | | 73.8 |
| 2 | TBU | 842.62201 | 2792.8 | 18.7089 | 18.96 | 0.700001 | 13.27 | | 26.2 |
| 3 | TOP | 0 | 0.0 | 0.0 | 0 | 1.900 | 0.00 | | 0.0 |
| 4 | OT | 60.34323 | 200 | 1.34 | 0.00 | 0 | 0.00 | | |
| 5 | THAQE | 0 | 0.0 | 0.00 | 0.00 | 1.270 | 0.00 | 0.0 | |
| 6 | THAQ | 0 | 0.0 | 0.00 | 0.00 | 1.151 | 0.0 | 0.0 | |
| 7 | EAQ | 190.07286 | 630.0 | 4.22 | 4.28 | 0.74009 | 3.17 | 58.8 | |
| 8 | Total | | 14927.5 | 100 | 100 | | 0.54 | 58.8 | 100 |

Table 4 (D) working solution GC result calibration sheet for acetonitrile extraction

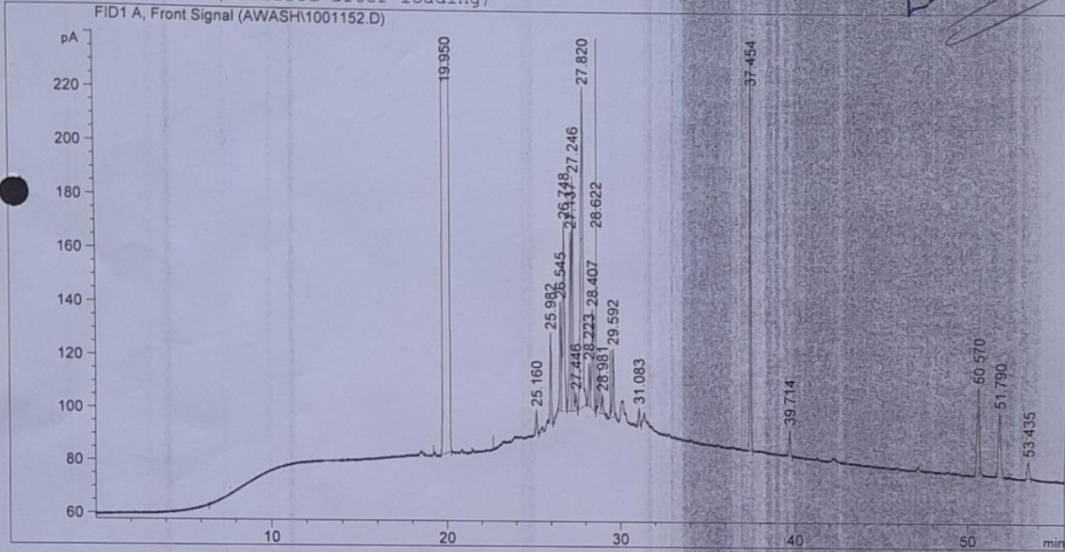
| A | StandardWS(Sol,75%,,TBU21%,TOP4%,EAQ60gpl,H4EAQ100gpl) | | | | Date | 27/03/2023 | Time | 12:30pm | |
|-------|--|------------|-----------------|--------|--------------|------------|-------|---------|--------------|
| S.No. | Component | Peak Area | Injected sample | | %without O.T | O.T.factor | AxB | Result | |
| | | | Conc.ug/ml | % | A | B | | gpl | Sol. Ratio,% |
| 1 | Solvesso150 | 3966.36531 | 11593.3 | 75.978 | 76.98 | 0.487001 | 37.49 | | 77.7 |
| 2 | TBU | 964.96228 | | | | | | | 20.5 |
| 3 | TOP | 41.87198 | 122.4 | 1.31 | 0 | 0 | 0.00 | | 1.8 |
| 4 | OT | 68.42532 | 200 | 0.00 | 0.00 | 1.270 | 0.00 | | |
| 5 | THAQE | 0 | 0 | 0.00 | 0.00 | 1.151 | 0.00 | 0.0 | |
| 6 | THAQ | 0 | 0 | 3.43 | 3.47 | 0.886879 | 3.08 | 0.0 | |
| 7 | EAQ | 179.00453 | 523.2 | 0.80 | 0.81 | 1.900 | 1.54 | 34.2 | |
| 8 | Total | | 15259.3 | 100 | 100 | | 0.90 | 34.2 | 100 |

Table 5 (E) Working solution GC result calibration sheet for Acetone extraction

| A | Standard WS (Sol, 75%, TBU 21%, TOP 4%, EAQ 60gpl, H4EAQ 100gpl) | | | | Date | 27/03/2023 | Time | 12:30pm | |
|-------|--|------------|-----------------|-------------|---------------|------------|-------|---------|--------------|
| S.No. | Component | Peak Area | Injected sample | | % without O.T | O.T.factor | AxB | Result | |
| | | | Conc.ug/ml | % | A | B | | gpl | Sol. Ratio,% |
| 1 | Solvento150 | 4009.85965 | 11624.2 | 76.734 | 77.76 | 0.878899 | 68.34 | | 78.4 |
| 2 | TBU | 937.33740 | 2717.2 | 17.937 2 | 18.18 | 0.955007 | 17.36 | | 19.9 |
| 3 | TOP | 39.54863 | 200 | 1.32 | 0 | 0 | 0.00 | | 1.7 |
| 4 | OT | 68.99181 | 0.0 | 0.00 | 0.00 | 1.270 | 0.00 | | |
| 5 | THAQE | 0 | 0.0 | 0.00 | 0.00 | 1.151 | 0.00 | 0.0 | |
| 6 | THAQ | 0 | 492.6 | 3.25 | 3.30 | 0.886879 | 2.92 | 0.0 | |
| 7 | EAQ | 169.92032 | 114.6 | 0.76 | 0.77 | 1.900 | 1.46 | 32.4 | 0.0 |
| 8 | Total | | 15148.6 | 100 | 100 | | 0.90 | 32.4 | 100 |

Acq. Operator :
 Acq. Instrument : Instrument 1 Location : Vial 1
 Injection Date : 3/24/2023 7:44:38 PM Inj Volume : 5 µl
 Acq. Method : C:\CHEM32\1\METHODS\AWASHPERO.M
 Last changed : 3/24/2023 7:35:01 PM
 (modified after loading)
 Analysis Method : C:\CHEM32\1\METHODS\AWASHPERO.M
 Last changed : 3/24/2023 8:40:09 PM
 (modified after loading)

*Stop
 Sensitivity
 24/05/23
 Lab us*



Internal Standard Report

Sorted By : Signal
 Multiplier: : 1.9000
 Dilution: : 1.0000
 Sample Amount: : 1.00000 [%] (not used in calc.)
 Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A, Front Signal

Area Percent Report

Sorted By : Signal
 Multiplier: : 1.9000
 Dilution: : 1.0000
 Sample Amount: : 1.00000 [%] (not used in calc.)
 Do not use Multiplier & Dilution Factor with ISTDs

Data File C:\CHEM32\1\DATA\AWASH\1001152.D
 Sample Name: 24032023 Lab.WS

Signal 1: FID1 A, Front Signal

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|--------|---------------|------|-------------|-------------|-------------|----------|
| 1 | 19.950 | BB S | 0.1411 | 2.07268e5 | 1.78523e4 | 97.55656 |
| 2 | 25.160 | BB | 0.0710 | 49.79891 | 8.99002 | 0.02344 |
| 3 | 25.982 | BB | 0.0754 | 172.69322 | 33.91524 | 0.08128 |
| 4 | 26.545 | BV | 0.0803 | 223.96040 | 41.16682 | 0.10541 |
| 5 | 26.748 | VB | 0.1102 | 563.74963 | 71.03115 | 0.26534 |
| 6 | 27.137 | BV | 0.0957 | 436.47379 | 67.23995 | 0.20544 |
| 7 | 27.246 | VB | 0.0671 | 447.22318 | 88.24524 | 0.21050 |
| 8 | 27.446 | BV | 0.0670 | 35.18088 | 6.77789 | 0.01656 |
| 9 | 27.820 | VB | 0.1255 | 1135.79907 | 120.16949 | 0.53460 |
| 10 | 28.223 | BV | 0.0721 | 92.37238 | 16.00404 | 0.04348 |
| 11 | 28.407 | VB | 0.1028 | 273.35837 | 37.45170 | 0.12866 |
| 12 | 28.622 | BB | 0.0240 | 130.97409 | 68.09816 | 0.06165 |
| 13 | 28.981 | BB | 0.0815 | 43.27196 | 7.09562 | 0.02037 |
| 14 | 29.592 | BB | 0.0891 | 160.50502 | 25.88440 | 0.07555 |
| 15 | 31.083 | BB | 0.0716 | 31.99924 | 6.52605 | 0.01506 |
| 16 | 37.454 | BB | 0.0768 | 741.00305 | 150.14655 | 0.34877 |
| 17 | 39.714 | BB | 0.0719 | 60.35629 | 10.12715 | 0.02841 |
| 18 | 50.570 | BB | 0.1201 | 305.62738 | 33.21677 | 0.14385 |
| 19 | 51.790 | BB | 0.1170 | 238.03522 | 24.23742 | 0.11204 |
| 20 | 53.435 | BB | 0.0924 | 48.93127 | 6.51696 | 0.02303 |

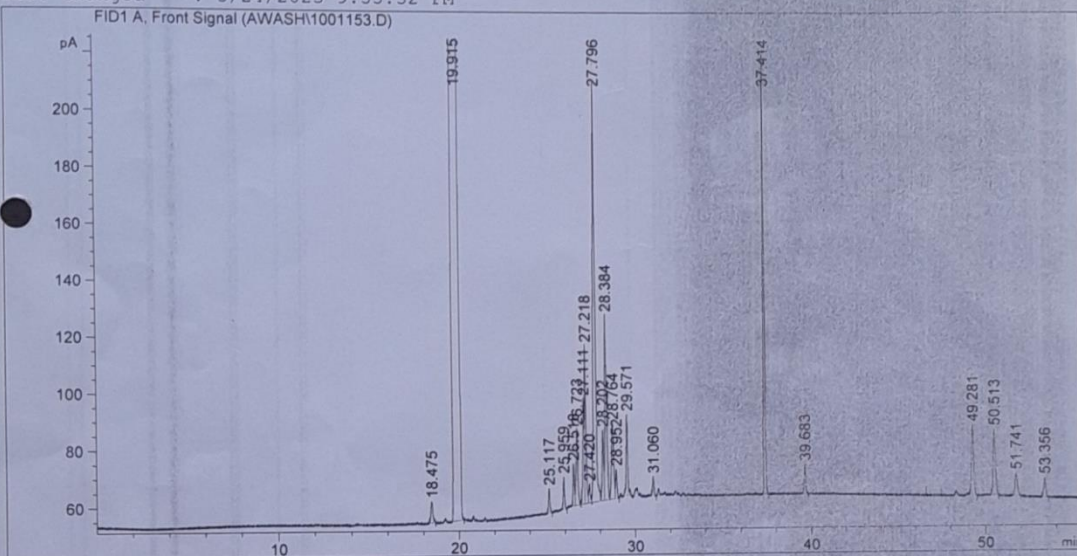
Totals : 2.12459e5 1.86751e4

GC profiles (chromatogram) of standard working solution

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Acq. Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 3/24/2023 8:40:10 PM
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 3/24/2023 9:55:32 PM
=====

2403123
Plant
WS



=====
Internal Standard Report
=====

Sorted By : Signal
Multiplier: : 1.9000
Dilution: : 1.0000
Sample Amount: : 1.00000 [%] (not used in calc.)
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A, Front Signal

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.9000
Dilution: : 1.0000
Sample Amount: : 1.00000 [%] (not used in calc.)
Do not use Multiplier & Dilution Factor with ISTDs

Data File C:\CHEM32\1\DATA\AWASH\1001153.D
 Sample Name: 24032023 PLANT.WS

Signal 1: FID1 A, Front Signal

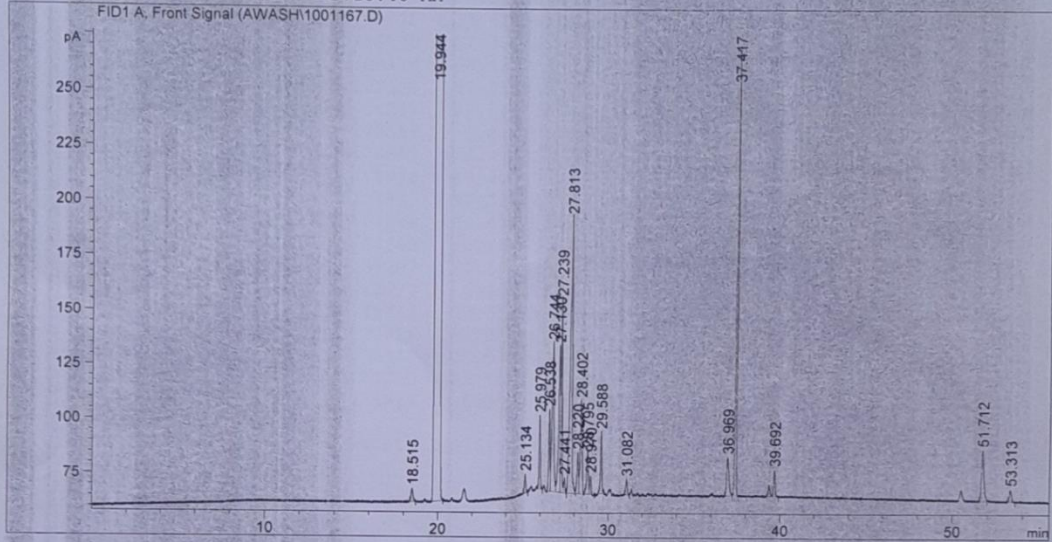
| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|--------|---------------|------|-------------|-------------|-------------|----------|
| 1 | 18.475 | BB | 0.1211 | 59.71419 | 7.41577 | 0.02779 |
| 2 | 19.915 | BB | 0.1884 | 2.10073e5 | 1.80762e4 | 97.76959 |
| 3 | 25.117 | BB | 0.0872 | 46.45264 | 8.36061 | 0.02162 |
| 4 | 25.959 | BB | 0.0838 | 59.20378 | 11.24884 | 0.02755 |
| 5 | 26.518 | BV | 0.0841 | 77.63004 | 14.68724 | 0.03613 |
| 6 | 26.723 | VB | 0.1030 | 193.28951 | 26.90699 | 0.08996 |
| 7 | 27.111 | BV | 0.0889 | 221.40691 | 37.06352 | 0.10304 |
| 8 | 27.218 | VB | 0.0789 | 301.88153 | 55.95653 | 0.14050 |
| 9 | 27.420 | BV | 0.0902 | 38.81050 | 6.37797 | 0.01806 |
| 10 | 27.796 | VB | 0.1194 | 1272.88220 | 148.23466 | 0.59241 |
| 11 | 28.202 | BV | 0.0920 | 154.41176 | 24.76173 | 0.07186 |
| 12 | 28.384 | VB | 0.1053 | 465.27155 | 65.50389 | 0.21654 |
| 13 | 28.764 | BV | 0.1461 | 238.61618 | 26.64446 | 0.11105 |
| 14 | 28.952 | VB | 0.0846 | 56.51054 | 10.08274 | 0.02630 |
| 15 | 29.571 | BB | 0.0899 | 163.68713 | 28.28699 | 0.07618 |
| 16 | 31.060 | BB | 0.0893 | 37.26845 | 6.50371 | 0.01734 |
| 17 | 37.414 | BB | 0.0768 | 773.25537 | 156.72966 | 0.35988 |
| 18 | 39.683 | BB | 0.0963 | 61.73345 | 10.18765 | 0.02873 |
| 19 | 49.281 | BB | 0.1386 | 219.28810 | 24.74786 | 0.10206 |
| 20 | 50.513 | BB | 0.1472 | 217.10875 | 23.27723 | 0.10104 |
| 21 | 51.741 | BB | 0.1574 | 80.19385 | 7.85921 | 0.03732 |
| 22 | 53.356 | BB | 0.1227 | 53.77847 | 6.67896 | 0.02503 |

Totals : 2.14866e5 1.87837e4

GC profiles (chromatogram) of commercial plant working solution

Data File C:\CHEM32\1\DATA\AWASH\1001167.D
Sample Name: 27032023 M + E.A

=====
Acq. Operator :
Acq. Instrument : Instrument 1 Location : Vial 1
Injection Date : 3/28/2023 6:45:17 PM Inj Volume : 5 µl
Acq. Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 3/24/2023 10:01:36 PM
Analysis Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 6/15/2023 2:18:40 AM
=====



=====
Internal Standard Report
=====

Sorted By : Signal
Multiplier: : 1.9000
Dilution: : 1.0000
Sample Amount: : 1.00000 [%] (not used in calc.)
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A, Front Signal

=====
Area Percent Report
=====

Sorted By : Signal
Multiplier: : 1.9000
Dilution: : 1.0000
Sample Amount: : 1.00000 [%] (not used in calc.)
Do not use Multiplier & Dilution Factor with ISTDs

Data File C:\CHEM32\1\DATA\AWASH\1001167.D
Sample Name: 27032023 M + E.A

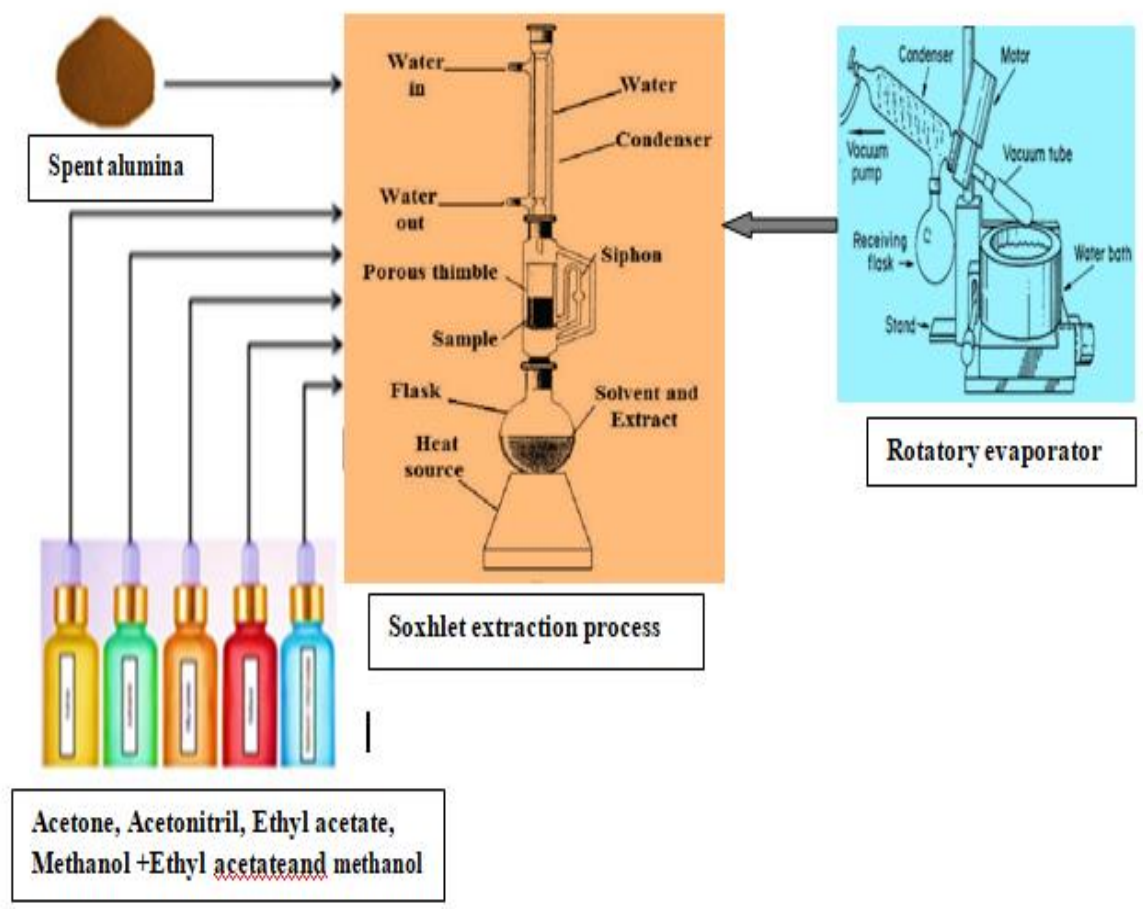
Signal 1: FID1 A, Front Signal

| Peak # | RetTime [min] | Type | Width [min] | Area [pA*s] | Height [pA] | Area % |
|--------|---------------|------|-------------|-------------|-------------|----------|
| 1 | 18.515 | BB | 0.1223 | 46.55761 | 5.80980 | 0.02322 |
| 2 | 19.944 | BB | 0.1777 | 1.95119e5 | 1.73341e4 | 97.29689 |
| 3 | 25.134 | BB | 0.0879 | 46.11435 | 8.21602 | 0.02300 |
| 4 | 25.979 | BB | 0.0819 | 171.47670 | 33.62896 | 0.08551 |
| 5 | 26.538 | BV | 0.0784 | 189.55199 | 37.35948 | 0.09452 |
| 6 | 26.744 | VV | 0.1064 | 529.89478 | 68.41675 | 0.26423 |
| 7 | 27.130 | VV | 0.0962 | 444.27130 | 67.35094 | 0.22154 |
| 8 | 27.239 | VV | 0.0804 | 465.88287 | 88.81676 | 0.23231 |
| 9 | 27.441 | VV | 0.0822 | 36.88594 | 6.83130 | 0.01839 |
| 10 | 27.813 | VB | 0.1230 | 1125.76563 | 126.47381 | 0.56137 |
| 11 | 28.220 | BV | 0.0932 | 114.15536 | 18.80340 | 0.05692 |
| 12 | 28.402 | VB | 0.1083 | 315.24893 | 42.79314 | 0.15720 |
| 13 | 28.795 | BV | 0.1039 | 132.24649 | 19.69820 | 0.06595 |
| 14 | 28.970 | VB | 0.0783 | 41.77665 | 8.24865 | 0.02083 |
| 15 | 29.588 | BB | 0.0886 | 159.59207 | 28.14131 | 0.07958 |
| 16 | 31.082 | BB | 0.0969 | 41.11977 | 6.73287 | 0.02050 |
| 17 | 36.969 | BB | 0.1522 | 171.45413 | 17.57999 | 0.08550 |
| 18 | 37.417 | BB | 0.0775 | 1012.29816 | 202.73288 | 0.50479 |
| 19 | 39.692 | BB | 0.1295 | 106.26168 | 11.93089 | 0.05299 |
| 20 | 51.712 | BB | 0.1505 | 226.62210 | 22.92773 | 0.11301 |
| 21 | 53.313 | BB | 0.1334 | 43.64249 | 5.35841 | 0.02176 |

Totals : 2.00540e5 1.81619e4

*** End of Report ***

GC profiles (chromatogram) of solvent mixture extraction



Experimental Setup of Organic Matters Extraction on the Surface of Deactivated Alumina