Catalytic activity recovery of spent alumina:

A case study of Awash Melkassa Chemical Factory

By Amare Degu Alemie

A Thesis Submitted to the department of chemical engineering

School of mechanical, chemical and materials engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master in chemical engineering

Office of Graduate Studies

Adama Science and Technology University

June, 2023

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DECLARATION

I hereby declare that this Master thesis entitled "Catalytic activity recovery of spent alumina: A case study of Awash Melkassa Chemical Factory" 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.

Amare Degu Alemie		
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Name of student	Signature	Date

RECOMMENDATION

I, the advisor of this thesis, hereby certify that I have read the revised version of the thesis entitled “Catalytic activity recovery of spent alumina: A case study of Awash Melkassa Chemical Factory” prepared under my guidance by Amare Degu Alemie submitted in partial fulfillment of the requirements for the degree of Master of Science in chemical engineering. Therefore, I recommend the submission of revised version of the thesis to the department following the applicable procedures.

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Advisor	Signature	Date

APPROVAL

I, the advisor of the thesis entitled “Catalytic activity recovery of spent alumina: A case study of Awash Melkassa Chemical Factory” and developed by Amare Degu Alemie, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

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We, the undersigned, members of the Board of Examiners of the thesis by Amare Degu Alemie have read and evaluated the thesis entitled “Catalytic activity recovery of spent alumina: A case study of Awash Melkassa Chemical Factory” 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 chemical engineering.

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LIST OF ACRONYMS AND ABBREVIATIONS

WS	Working solution
AO	Auto-oxidation
AQ	Anthraquinone
EAQ	2-Ethyl anthraquinone
TBU	Tetra Butyl Urea
TOP	Trioctyl Phosphate
OHAHQ	2-ethyl octahydroanthrahydroquinone
OAT	2-ethyloxanthrone
AT	2-ethylanthrone
DAT	2-ethyldianthrone
AHQ	Anthrahydroquinone
THAHQ	Tetrahydroethylanthrahydroquinone
THAQ	Tetrahydroethylanthraquinone
THAQE	Tetrahydroethylanthraquinone epoxide
PLC	Private limited company
AAS	Atomic absorption spectrophotometry
XRD	X-Ray Diffraction
TGA	Thermogravimetric analysis
GC	Gas chromatography
BET	Brunauer-Emmett-Teller
OVAT	One variable at a time
w	Weight
ml	Milliliter
l	Liter
gpl	Gram per liter
gm	Gram
kg	Kilogram
mmol	Milimole
OT	Orto-terphenyl
BPT	Boiling point temperature
SPT	Set point temperature

ABSTRACT

Hydrogen peroxide was one of the major bleaching chemical 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. In this process route, activated alumina was used for converting inactive byproduct of THAQE into active form of THAQ and EAQ through regeneration mechanism. However, continuous usage of alumina resulted in losing of catalytic activity and unable to regenerate inactive THAQE. Thus, catalytic activity recovery of spent deactivated alumina by regeneration method was a subject of study. The deactivated alumina regeneration was carried out by Soxhlet solvent extraction followed by caustic treatment. In Soxhlet solvent extraction, methanol, ethyl acetate and the mixture of methanol and ethyl acetate 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. Further treatment of alumina was carried out using caustic treatment to remove the remaining adsorbed organic components and to modify the alkaline composition. The effect of caustic treatment conditions (temperature, concentration and contact time) was investigated to observe the basic sites of alumina. The highest basicity (2.19 mmol HCl/gm of catalyst) was observed at NaOH concentration of 3% w/w, temperature 70 ^{o}C and contact time of 2.5 hours. The AAS analysis also showed that the content of Na_2O in the regenerated alumina was increased to 0.42% as compared to fresh alumina (<0.01%) that implied the improvement of catalytic activity. Based on XRD analysis, the XRD pattern indicated that there was no structural change observed in the regenerated alumina caused by NaOH loading since it had similar diffraction peaks and intensities as spent and fresh alumina. The BET analysis showed that the specific surface area of regenerated alumina was 507.009 m^2/gm indicated the higher catalytic activity as compared to the spent alumina (337.762 m^2/gm). The performance test indicated that 18.9% and 13.75% of THAQE conversion was obtained by regenerated alumina and reused alumina respectively. As compared to fresh alumina of 100% performance, 72.81% and 52.99% of THAQE was converted to active quinones using regenerated alumina and reused alumina respectively. Therefore, regenerated alumina could be used instead of fresh alumina as a catalyst and an adsorbent for working solution regeneration for more than two times.

Key words: Fresh alumina, Spent alumina, Regenerated alumina, Performance test

CHAPTER ONE

1. INTRODUCTION

1.1 Background

Currently solid waste disposal has become a serious problem in the 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 as shown in Figure 1.1. The annual solid waste quantity of kaolin filter cake, sulfur filter cake and spent alumina were 3735.952 ton, 39.508 ton and 27.750 ton respectively. The disposed solid wastes of such types have collected in the factory compound as a landfill and forming mixed wastes. The mixed wastes might create environmental pollutions if they have not handled properly. The storage and handling of these solid wastes have become the most neglected operational areas of the factory. There were very little knowledge for proper storage and handling of such solid wastes in the factory. Thus, these solid waste types have found to be mixed wastes and forming a pile against an open ground. If the storage of solid wastes continued like this, there could be uncontrollable pollution of the environment. Therefore, the solid wastes should be stored and treated through regeneration mechanism in order to protect and keep the environment free from contamination.

Figure 1.1: Collection of mixed solid wastes in the factory compound

The hydrogen peroxide plant of Awash Melkassa Chemical Factory, which had designed, installed and commissioned by Nuberg Engineering PLC had used AO process to produce hydrogen peroxide based on working solution as a working media. The working solution has composed of a solute of 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 generated different types of byproducts because of the sequential hydrogenation and oxidation of EAQ. Of these byproducts, some have reversed to active quinones and some have adsorbed by activated alumina. Activated alumina has used as a catalyst for de-hydrogenation 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 has lost its activity and failed to maintain the hydrogen peroxide productivity of the working solution. This loss of activity was called deactivated alumina. The deactivated alumina had not used for working solution regeneration in that it had released to the environment as a solid waste, which was called spent alumina. The release of spent alumina to the environment was a common solid waste in the hydrogen peroxide plant as shown in Figure 1.2. The waste of deactivated alumina in this plant could result in public health and environmental problems. If this solid waste disposal could not be controllable, flammable gasses could be released freely in ambient air that resulted in fire hazard and health effect (Mahinroosta & Allahverdi, 2018). Therefore, deactivated alumina should be regenerated and reused for working solution regeneration so that to reduce the release of this solid waste to the environment.

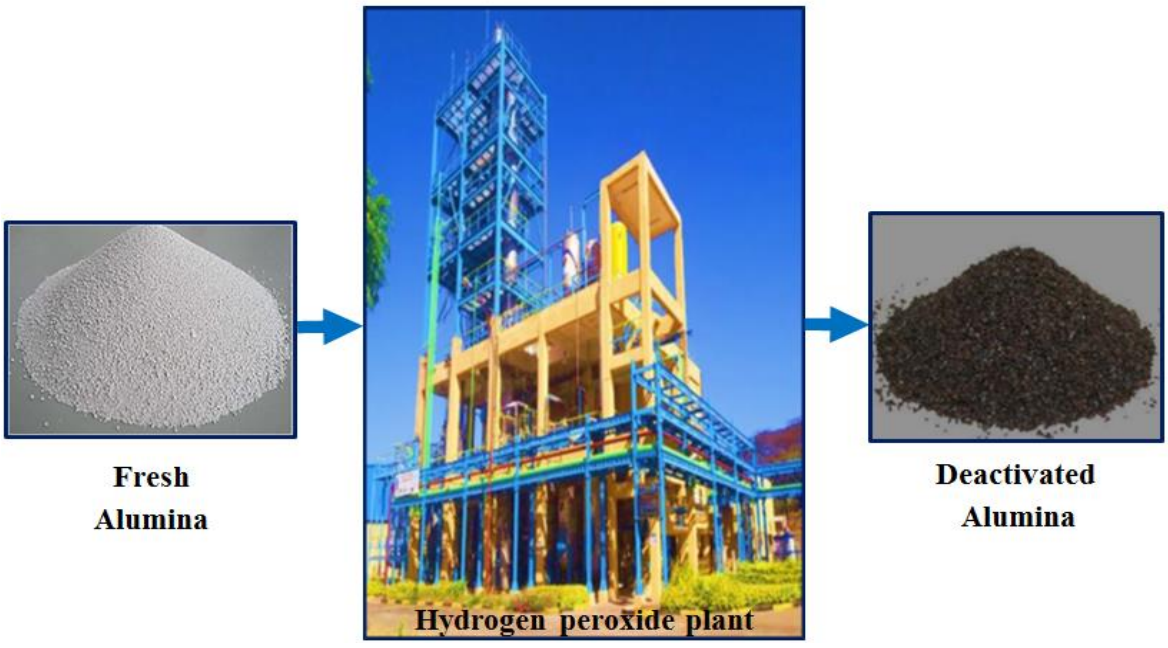


Figure 1.2: Deactivated alumina disposal from H_2O_2 plant to the environment

The active sites of deactivated alumina had been recovered by regeneration method so that the alumina had used to restore effective hydrogen peroxide synthesizing capacity of the working solution. Previous studies showed that Soxhlet solvent extraction using different organic solvents followed by caustic treatment was used to regenerate spent alumina. However, the researchers had not obtained good experimental results for regenerated alumina due to lack of proper solvent choice, lack of surface area, lack of crystal structure, lack of thermal stability and lack of caustic adsorption test. In this research, the effective regeneration of spent alumina had been carried out using Soxhlet solvent extraction followed by caustic treatment methods accompanied with instrumental analysis in order to get better result. The caustic treatment variables were studied using OVAT analysis method. The organic polar solvents such as acetone, acetonitrile, ethyl acetate and methanol had used to extract organic matters contained in deactivated alumina through Soxhlet solvent extraction thereby the porosity had opened and recovered the catalytic activity of spent alumina. The Soxhlet solvent extraction utilizing different organic solvents had carried out in the Soxhlet apparatus. The Soxhlet treated alumina had also treated with caustic solution containing low concentration of hydrogen peroxide. As hydrogen peroxide contained active oxygen, it decomposed and released free oxygen to form strong oxidizing agent of HOO^- radical while exposed to react with caustic solution. This oxidizing agent used to detach the remaining organic components contained in Soxhlet solvent treated alumina. The caustic treatment had also used to increase the sodium oxide content of the alkaline composition of deactivated alumina.

After caustic treatment of Soxhlet solvent treated alumina was completed, the treated alumina was called regenerated alumina. The surface area, crystal structure, composition and thermal stability of this regenerated alumina had been determined and compared with fresh and spent alumina. The performance of regenerated alumina had been tested by de-hydrogenation and de-epoxidation reactions by contacting this alumina with the working solution. The regenerated alumina epoxide conversion was measured and its conversion was compared with the fresh alumina epoxide conversion.

1.2 Statement of the problem

The solid activated alumina that was used as an adsorbent and a catalyst during working solution regeneration could be deactivated due to adsorption of organic degradation products typically OHAHQ, OAT, AT, DAT and water. These degradation products resulted in the loss of active quinones that could not capable to produce hydrogen

peroxide, which were responsible for blocking the active sites of the alumina catalyst. Thus, the deactivated alumina that could not be used for working solution regeneration in the next production process has discarded to the environment as landfills in the open ground thereby occupied future project expansion areas. This solid waste disposal caused not only landfills but also caused environmental pollution and health hazard. The environment might be polluted by gas emission caused by the fire of organic matters contained in deactivated alumina and this gas emission might lead to health hazard. Therefore, the spent alumina should be treated to reactivate and reuse for working solution regeneration so that the environments become free from gas emission and waste disposal.

During the production of hydrogen peroxide in the working solution circulation, a one-batch of 1850 kg activated alumina contained in reversion bed was used for continuous working solution regeneration. The surface area of this activated alumina had reduced and deactivated while working continuously for 22 working days. Since the working solution regeneration has conducted continuously, the activated alumina contained in the reversion bed has become deactivated and replaced by fresh activated alumina. This deactivated alumina has removed from the reversion bed thereby discarded to the environment as a solid waste. More foreign currency has required for replacing this solid waste deactivated alumina. The purchasing cost of 1 kg fresh activated alumina was 90.27 birr so that 1850 kg activated alumina contained in one reversion bed could be about 167,000 birr per 22 working days. The annual consumption of fresh activated alumina in the hydrogen peroxide plant was about 27,750 kg whereas the annual purchasing cost of this alumina was about 2,505,000 birr. This indicated that Awash Melkassa Chemical Factory used high quantity of fresh activated alumina with more foreign currency for replacing deactivated alumina. This research could reduce more than 5,010,000 birr per annum for the purchasing cost of fresh alumina and enabling the factory to be profitable. Therefore, the spent deactivated alumina should be regenerated using Soxhlet solvent extraction followed by caustic treatment methods so that it could reuse for working solution regeneration.

1.3 Research questions

1. Could it be possible to recycle solid waste generated from Awash Melkassa Chemical Factory?
2. Could it be possible to recover the catalytic activity of spent alumina by removing adsorbed organic matters using Soxhlet solvent extraction? What was the best solvent/solvent combination for effective regeneration of spent alumina?

3 Could it be possible to enhance the catalytic activity of Soxhlet solvent treated alumina by caustic/thermal treatment?
4 Could the alkaline composition of the surface of alumina be modified by sodium hydroxide?
5 How the caustic treatment conditions affect the catalytic activity of alumina?

5.2 Objectives of the study

5.2.1 General objective

The main objective of this study was to recover the catalytic activity of spent alumina by using Soxhlet solvent extraction followed by caustic treatment methods.

5.2.2 Specific objectives

- To collect and characterize the fresh and spent deactivated alumina
- To remove organic compounds contained in spent alumina by using Soxhlet solvent extraction method
- To remove organic compounds contained in Soxhlet solvent treated alumina and modify the alkaline composition of the surface of alumina by using caustic treatment method
- To investigate the effect of caustic treatment conditions during the regeneration of Soxhlet solvent treated alumina
- To evaluate the performance of regenerated alumina in comparison with spent alumina and fresh alumina based on epoxide conversion

5.3 Significance of the study

This study was conducted to investigate recovering catalytic activity of spent deactivated alumina that was used in working solution regeneration during hydrogen peroxide production. Regeneration of spent deactivated alumina through Soxhlet solvent extraction and caustic treatment was used to remove organic matters attached on the surface of alumina and restore the free adsorption active sites of the catalyst pore. This method of treatment helped to avoid subsequent reuse of fresh alumina for replacement. The regeneration of spent deactivated alumina could be repeated as often as desired thereby reduced the solid waste disposal to the environment. Thus, the solid waste of alumina that could cover more landfills in the near future has reduced so that fire and health hazards have minimized as well as project expansion areas have saved. On the other hand, as the catalyst was not available in domestic market, the Awash Melkassa Chemical Factory

forced to pay more foreign currency to purchase from abroad. This research was addressed to minimize the purchasing and transportation cost of fresh activated alumina as well as the environmental pollution by treating spent deactivated alumina as often as desired. Therefore, recovering catalytic activity of spent alumina was used for working solution regeneration during hydrogen peroxide production so that it could maximize profit.

5.4 Scope of the study

This research was limited to the area of hydrogen peroxide plant of Awash Melkassa Chemical Factory solid waste and bounded to the disposal of deactivated alumina. The experiment was conducted under laboratory to remove organic compounds adsorbed on the surface of alumina and recover the catalytic activity of spent alumina. The organic compounds contained in spent alumina were desorbed from the surface of alumina by using Soxhlet solvent extraction and caustic treatment methods. Solvent extraction through Soxhlet apparatus was carried out by acetone, acetonitrile, ethyl acetate, methanol and a combination of methanol and ethyl acetate whereas caustic treatment was carried out by a combination of caustic soda and hydrogen peroxide. Of those Soxhlet extraction experiments, the best extraction solvent that could avoid more organics was selected by TGA analysis. The OVAT analysis was used to investigate the effect of caustic treatment variables during the regeneration of Soxhlet solvent treated alumina. The amount of caustic soda reacted or adsorbed by the alumina during caustic treatment was determined by titration method. The qualitative and quantitative analysis of fresh, spent and regenerated alumina was determined by BET, AAS, XRD and TGA methods. The performance of regenerated alumina was tested by THAQE conversion using plant-working solution containing epoxide heated by a heating mantle under open atmosphere. The concentration of THAQE in the working solution was measured by GC analysis.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Anthraquinone autoxidation process

Hydrogen peroxide could be produced worldwide by different routes. One of which rout was AO process based on WS (Majeed et al., 2014). Hydrogen peroxide was the so called a green chemical (Shang et al., 2011) and environmentally friendly chemical (Chen, 2015) product. It was widely used in the military industry and rocket fuel as a propellant, environmental protection as disinfectant, pulp and paper bleaching, textile bleaching, chemical synthesis, food processing, medical sterilization, and others. Commercially, hydrogen peroxide was produced using anthraquinone auto-oxidation process based on working solution in the presence of palladium catalyst (Chen, 2015). Fresh working solution was prepared by dissolving active anthraquinones in an organic solvent. Industrially, the synthesis of hydrogen peroxide via auto-oxidation process was carried out through the hydrogenation of ethyl anthraquinone into ethyl anthrahydroquinone and oxidation of anthrahydroquinone with atmospheric air (Li et al., 2014).

The industrial production of hydrogen peroxide by anthraquinone route was a cyclic process that involves four major steps. These cyclic processes as shown in Figure 2.1 were hydrogenation, oxidation, extraction and regeneration of the working solution (Chen, 2015). During hydrogenation stage, AQ had dissolved first in the organic solvents and hydrogenated into AHQ in the presence of palladium catalyst. Having reached working solution maturation, part of AQ had converted to THAQ. In this cyclic process, AQ and THAQ (α and β form) have been used as a reaction carrier (Glenneberg et al., 2000). Most of the time β form of THAQ was formed along with a small amount of α form of THAQ (Yang et al., 2012). Then AHQ and THAHQ were oxidized into AQ and THAQ producing hydrogen peroxide using air or oxygen atmosphere (Shang et al., 2011). The hydrogen peroxide solution from the regenerated starting material, AQ (organic phase) has been separated by extraction with demineralized water. Then hydrogen peroxide was purified and concentrated, and the working solution was circulated back to the hydrogenation section (Sandelin et al., 2006).

During working solution circulation in the catalytic hydrogenation step, the active anthraquinone was gradually converted to degradation products. The degradation was

caused by deep hydrogenation of aromatic ring and the hydrolysis of carbonyl group. This was not capable to produce hydrogen peroxide (Chen, 2015; Lee et al., 1969; Shang et al., 2011). If the temperature of hydrogenated and oxidized working solution was increased, the rates of formation of degradation products were increased. Moreover, the amount of degradation products increased sharply as the proportion of the working solution hydrogenated per pass through the system increased. This was called depth of hydrogenation. Therefore, working solution regeneration through activated alumina was the key step in the anthraquinone process to avoid such degradation byproducts formed from the working solution.

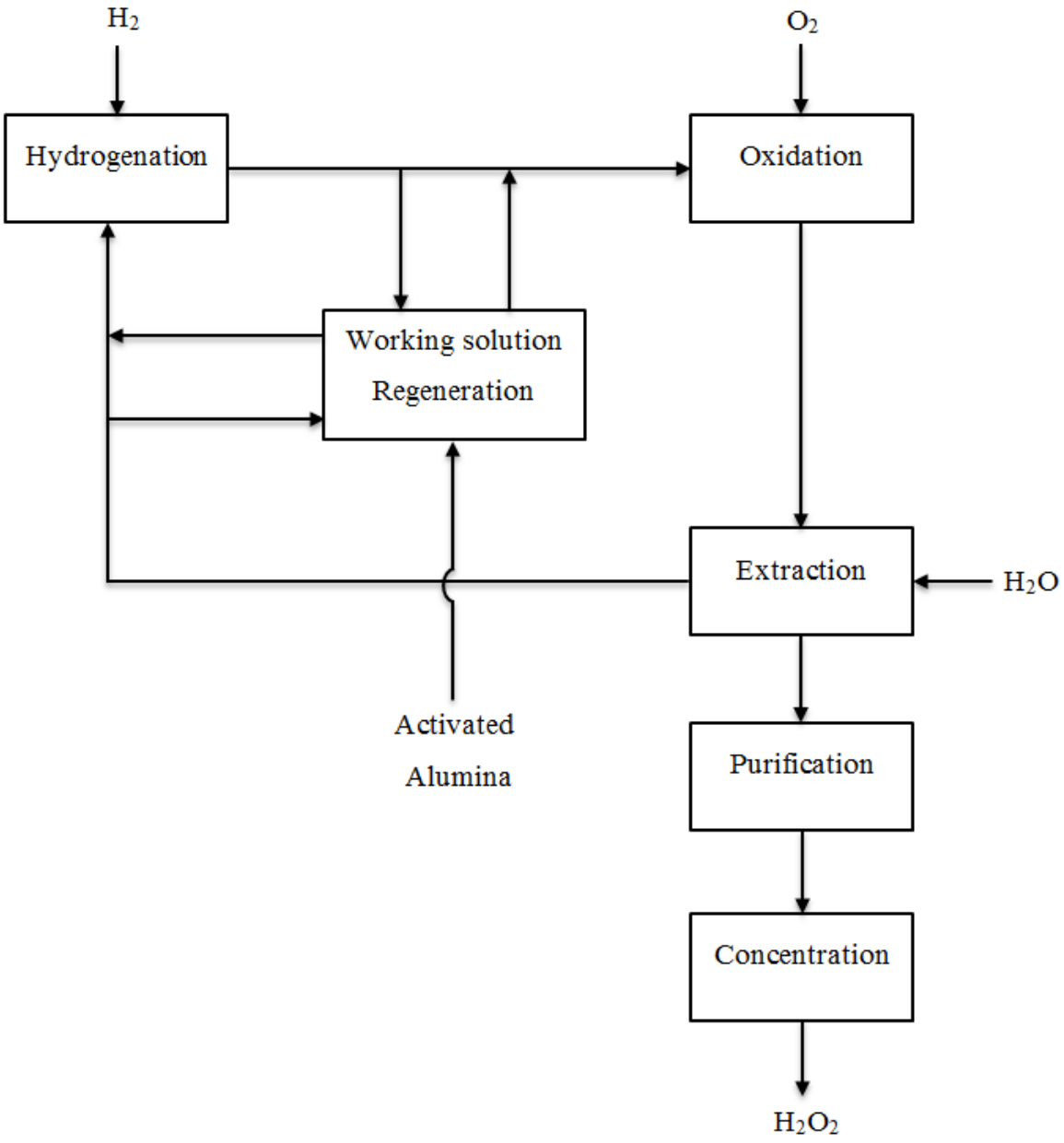


Figure 2.1: Schematic representation of H_2O_2 production process (Sandelin et al., 2006)

2.2 Working solution composition and anthraquinone solubility

Working solution was composed of a solute of AQ dissolved in carrier solvents of tetrabutyl urea, trioctyl phosphate and trimethyl benzene (Majeed et al., 2014). The solvents present in the working solution had the capability to dissolve all quinones and hydroquinones formed during hydrogenation and oxidation processes. Quinones and hydroquinones had different solubility tendency. In the working solution, quinones readily dissolved in a non-polar organic aromatic solvent while hydroquinones well dissolved in polar organic solvents. The solubility degree indicated that THAQ had high solubility in reduced form and lower solubility in oxidized form or slower oxidation rate. On the other hand, AQ had low solubility in reduced form and high solubility in oxidized form (Yang et al., 2012). The high solubility of THAQ in reduced form showed that the rate of reduction reaction was faster than AQ and less susceptible to side reaction causing loss of active quinones. The high oxidation rate and side reaction of AQ result in higher quinone loss in the repeated cycle of working solution operation. Keeping the optimum molar ratio of AQ and THAQ provided the highest solubility of reduced AHQ and THAHQ, low byproduct formation and faster reaction rate. Therefore, the preferred optimum molar ratio of AQ and THAQ for solubility, rate of reduction reaction, and rate of oxidation reaction must be from 3:7 to 2:8 for efficient and economical production of hydrogen peroxide. In the working solution, the optimum molar ratio of THAQ was maintained and reduced by the reaction of 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 from 20 to 25% w/w as well.

The generation of byproducts in the side reaction was minimized through not only the quinone composition but also maintaining the degree of hydrogenation based on the total THAQ. The allowable limit of hydrogenation degree should be from 70 to 100% mol/mol, preferably from 80 to 90% mol/mol of the total available THAQ (Yang et al., 2012). If hydrogenation degree greater than 100% mol/mol of the total available THAQ, AQ might participate in the side reactions and result in degradation of active quinones. If hydrogenation degree became below 70% mol/mol, the hydrogen peroxide productivity became getting low.

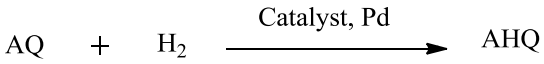
2.3 Formatiom of degradation products

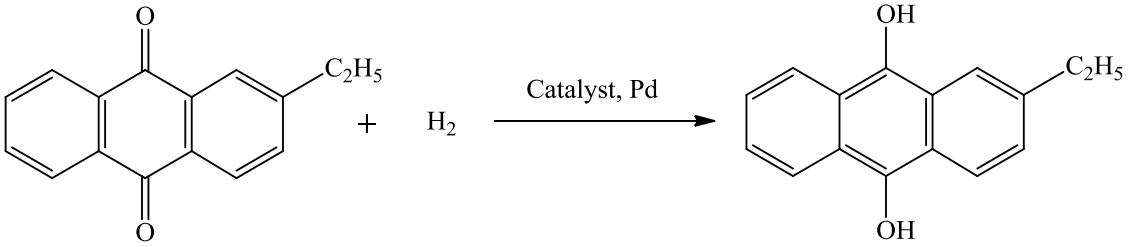
In the cyclic production of hydrogen peroxide, unwanted or inert AQ degradation products (Eiler & Snyder, 1959) were generated in every cycle of operation. The degradation of AQ

was mainly caused by the deep hydrogenation of its aromatic rings, hydrolysis of the C=O bonds and over-oxidation of THAQ (Chen, 2015; Shang et al., 2011). The side reactions were generated and the degradation products were formed in continuous hydrogenation and oxidation stages. These include OHAHQ, OAT, H_2O, AT, DAT and THAQE (Aksela et al., 2005; Chen, 2015). The main reactions and side reactions in the hydrogenation and oxidation process had shown in the reaction mechanism. The OHAHQ could be generated as a side reaction byproduct during hydrogenation of THAHQ. Theoretically, hydrogen peroxide could be generated from oxidized OHAHQ. However, the rate of oxidation was very slow and it was not form hydrogen peroxide at all. Therefore, OHAHQ could be viewed as degradation byproduct. During hydrogenation of anthraquinone, OAT was formed as a byproduct and further hydrogenation of OAT accelerated the formation of H_2O, AT and DAT. THAQE was a dominating byproduct (Sandelin et al., 2006) appearing in the working solution. This was formed with hydrogen peroxide in the oxidation step. However, the concentration of the effective anthraquinones the so-called AQ, AHQ, and THAQ were reduced due to the accumulation of such degradation products from many repeated cycles of operation in the working solution. All of these degradation products represent a loss of active AQ, which were not oxidized to form hydrogen peroxide.

The degradation products which were unable to produce hydrogen peroxide were collectively known as inerts (Majeed et al., 2014; Sethi, 1987). When inerts had accumulated over a critical level, they might cause increased total organic content in the quality of hydrogen peroxide, and the changed in specific gravity and viscosity of the working solution. Indirectly, such types of inerts could 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 ^{o}C should have from 0.89 to 0.97, preferably from 0.91 to 0.94. The allowable limits of the inert ingredients in the working solution was from 3 to 20% w/w, preferably 5 to 13% w/w (Yang et al., 2012). However, the maximum concentration of THAQE in the working solution was limited to 25 gpl (Kabisch & Kunkel, 1973). 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 H_2O. The main reactions and side reactions in the hydrogenation and oxidation processes were shown in the following reaction mechanisms.

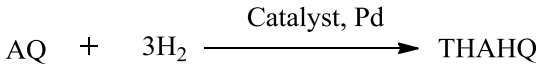
Reaction mechanism-1:

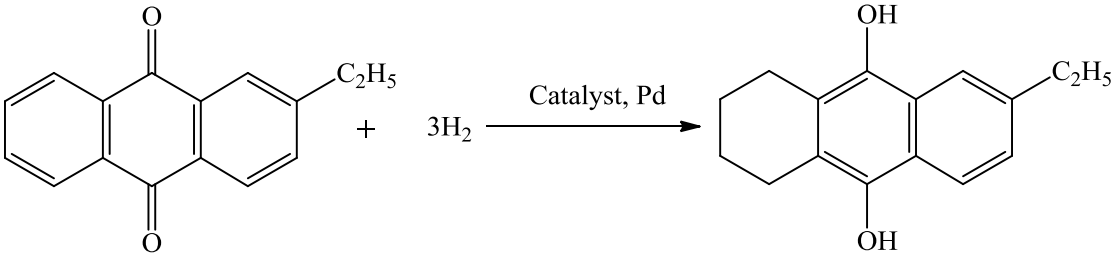




2-Ethylanthraquinone 2-Ethylanthrahydroquinone

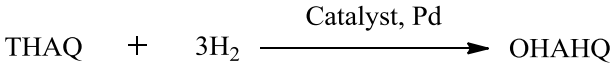
Reaction mechanism-2:

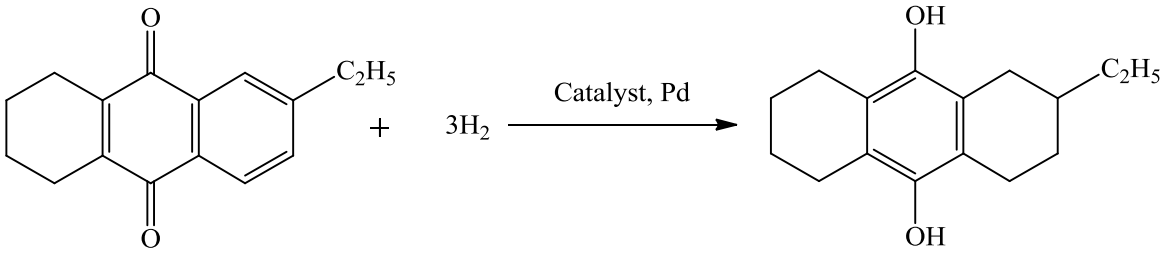




2-Ethylanthraquinone 2-Ethyltetrahydroanthrahydroquinone

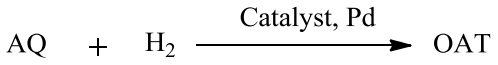
Reaction mechanism-3:

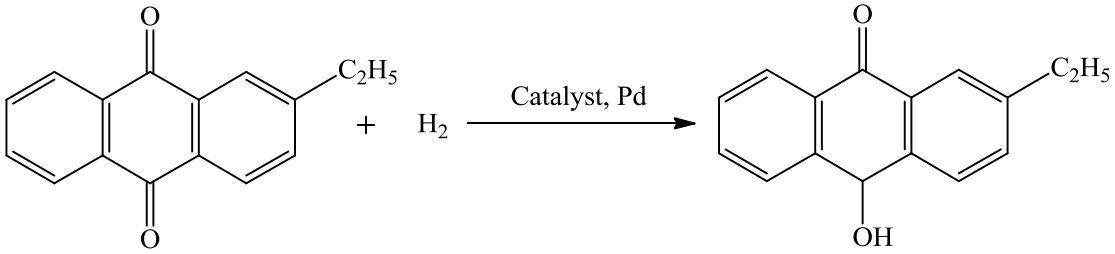




2-Ethyltetrahydroanthraquinone 2-Ethyloctahydroanthrahydroquinone

Reaction mechanism-4:

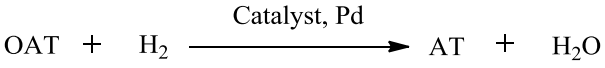


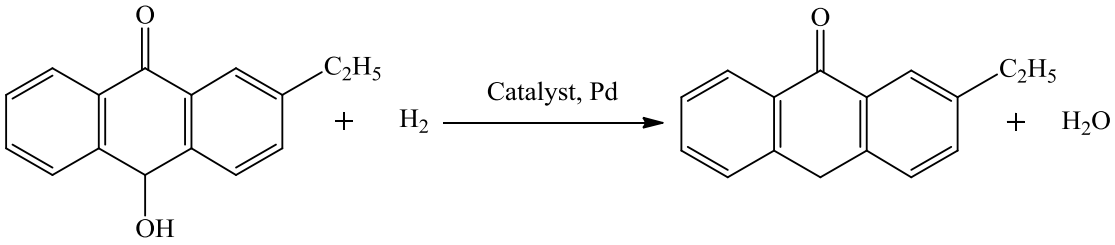


2-Ethylanthraquinone

2-Ethyloxanthrone

Reaction mechanism-5:

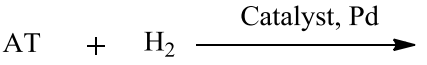


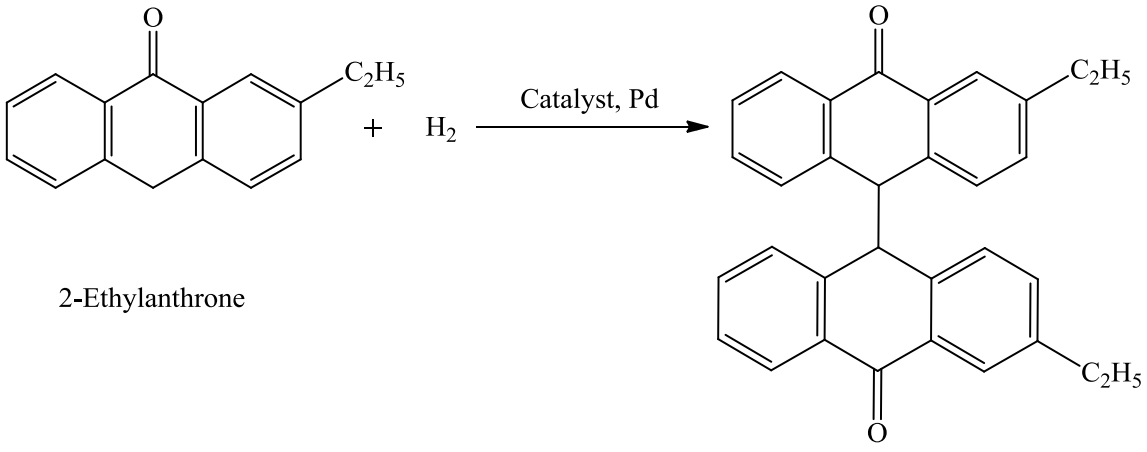


2-Ethyloxanthrone

2-Ethylanthrone

Reaction mechanism-6:

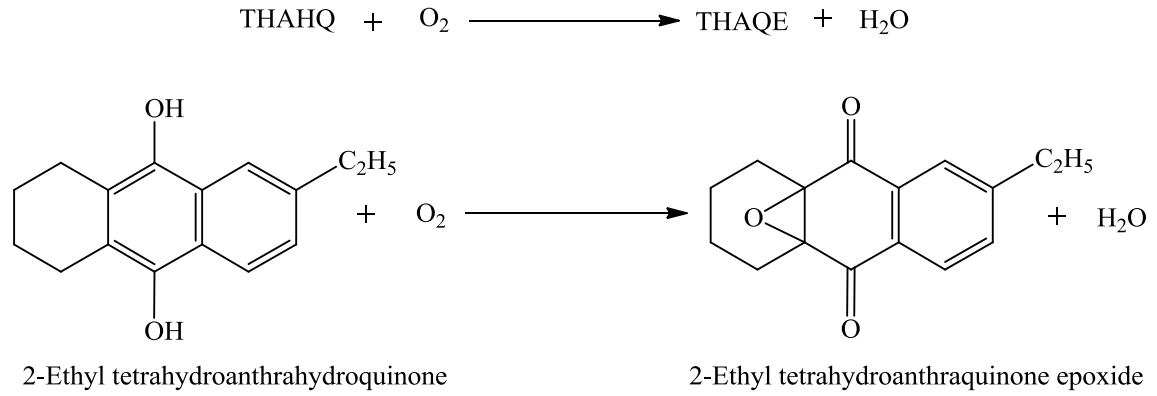




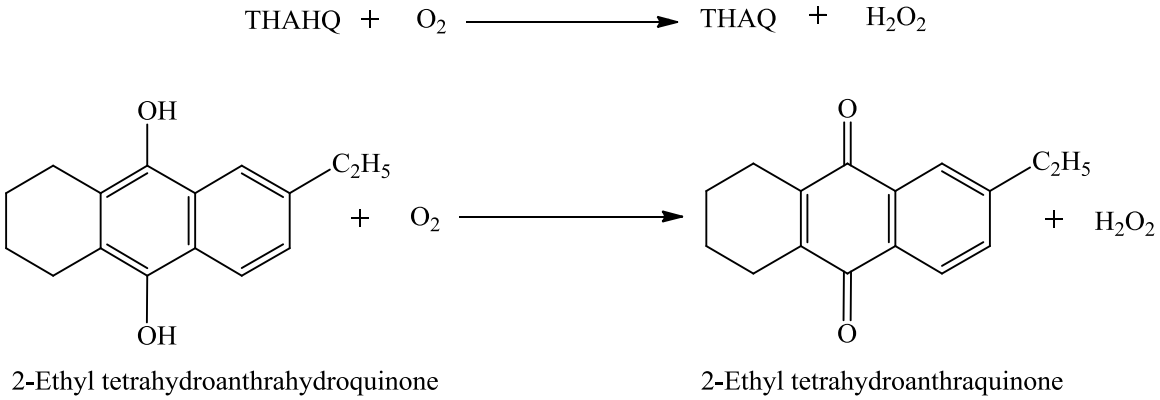
2-Ethylanthrone

2-Ethyldianthrone

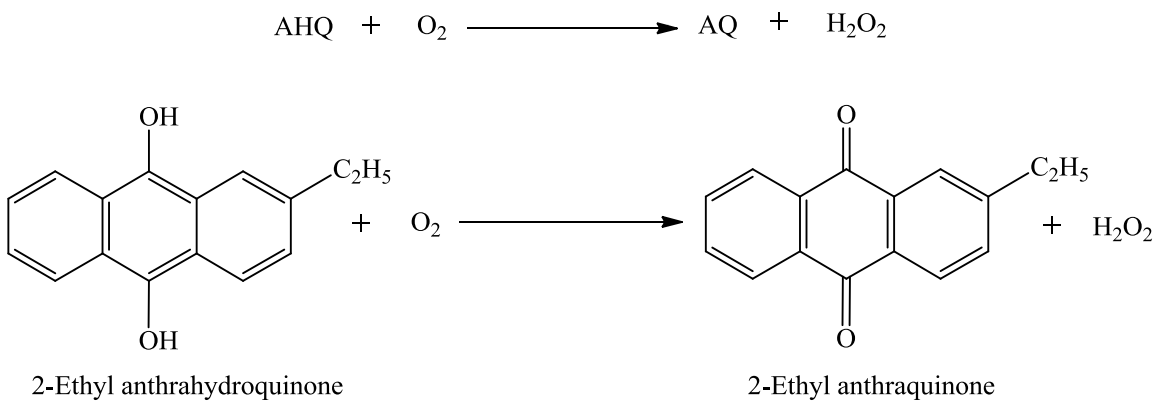
Reaction mechanism-7:



Reaction mechanism-8:



Reaction mechanism-9:



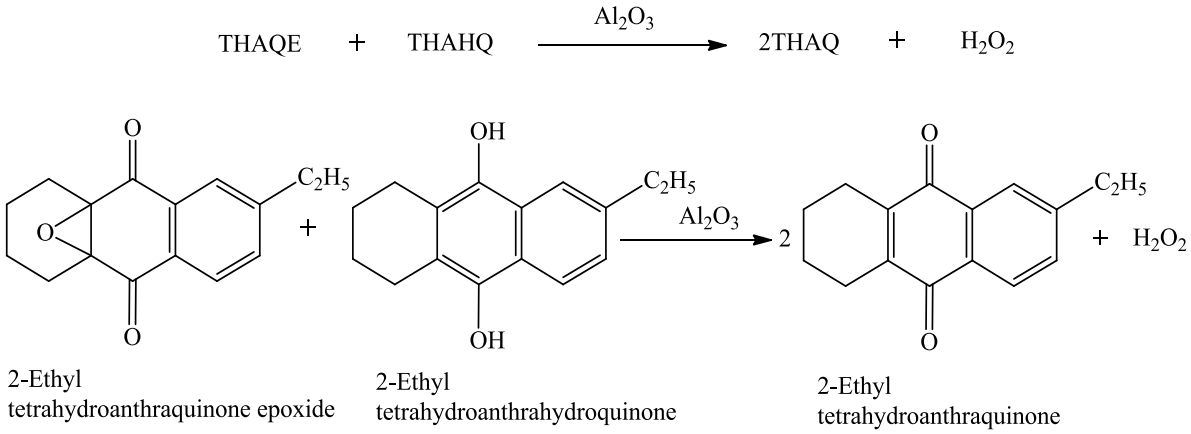
2.4 Regeneration of the working solution

The process of cyclic hydrogenation and oxidation of anthraquinone generated not only peroxide-producing anthrahydroquinones but also some by-products. These byproducts of anthraquinone species could be converted back to useful quinones by the use of regeneration method. Degraded working solution could be regenerated by caustic soda and

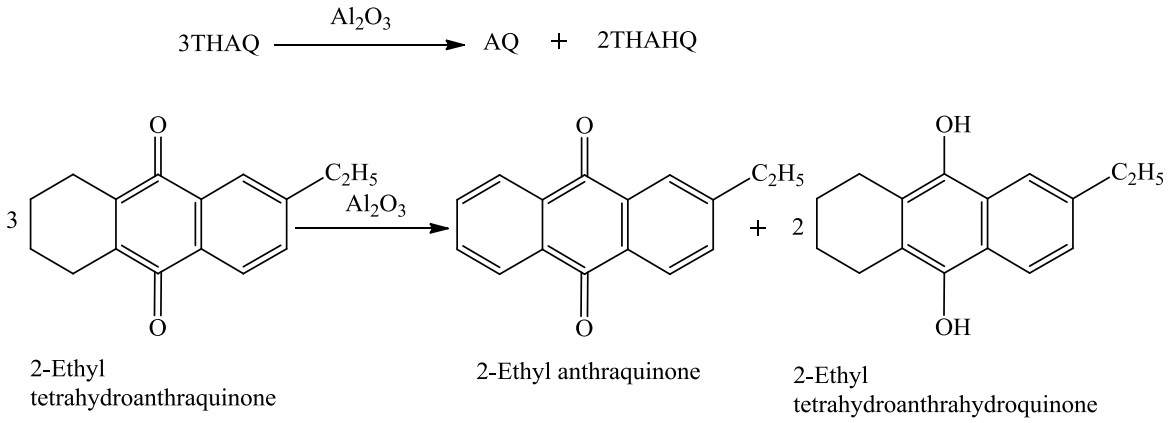
activated alumina. Regeneration of working solution with aqueous caustic soda was accomplished by extracting the anthrahydroquinone from hydrogenated degraded working solution and recovering the solvent component of the resulting working solution (Eiler & Snyder, 1959). The aqueous extract containing the salt of anthrahydroquinones was oxidized at room temperature with oxygen to convert anthrahydroquinones to precipitated anthraquinones. In the industry, the working solution was regenerated by contacting the working solution with activated alumina at the temperature of 50 to 100 ^{o}C (Aksela et al., 2005) thereby converting the degradation products into effective anthraquinones. Working solution regeneration was accomplished by feeding a side-stream of the working solution into a bed of activated alumina. The degradation product of THAQE has transformed into THAQ by reduction of THAHQ in the presence of basic activated alumina as shown in the reaction mechanism. In the process of transforming THAQ into AQ and THAHQ, 3 mole of THAQ has converted into 1 mole of AQ and 2 mole of THAHQ (Wu et al., 2014). The immediate regeneration after reduction reaction indicated that there was low conversion efficiency of THAQ and there was high amount of by-products generated.

Activated alumina was the basic regeneration catalyst that could convert epoxidised anthraquinones and THAQs to their corresponding active anthraquinones as shown in the following reaction mechanisms.

Reaction mechanism-1:



Reaction mechanism-2:



2.5 Activated alumina

2.5.1 Phases of alumina

Aluminum oxide or gamma alumina (γ-Al_2O_3) was the forms of alumina between the aluminum hydroxide ($Al(OH)_3$) and corundum or alpha alumina (α-Al_2O_3) (Rajamani Balasubramanian, 2020). Activated alumina could be produced by the thermal decomposition of aluminum hydrates contained in bayerite, gibbsite and boehmite minerals (Rajamani Balasubramanian, 2020). During thermal dehydration process of the aluminum hydrates, different types of transitional aluminas could be formed. The thermal decomposition of boehmite in air at the temperature range of 300 to 500 ^oC had given the phase of γ-Al_2O_3 (gamma alumina). Further increased in temperatures, from 700 to 800 ^oC had given the phase of δ-Al_2O_3 and from 900 to 1000 ^oC had given the phase of θ-Al_2O_3 (Vasile et al., 2021). The final anhydrous form of alumina obtained at 1100 ^oC was α-Al_2O_3 (corrundum alumina) (Rajamani Balasubramanian, 2020). The transitional gamma alumina had observed at the intermediate temperatures from 250 to 800 ^oC. Of which phases of alumina, gamma alumina (γ-Al_2O_3) 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 2.2.

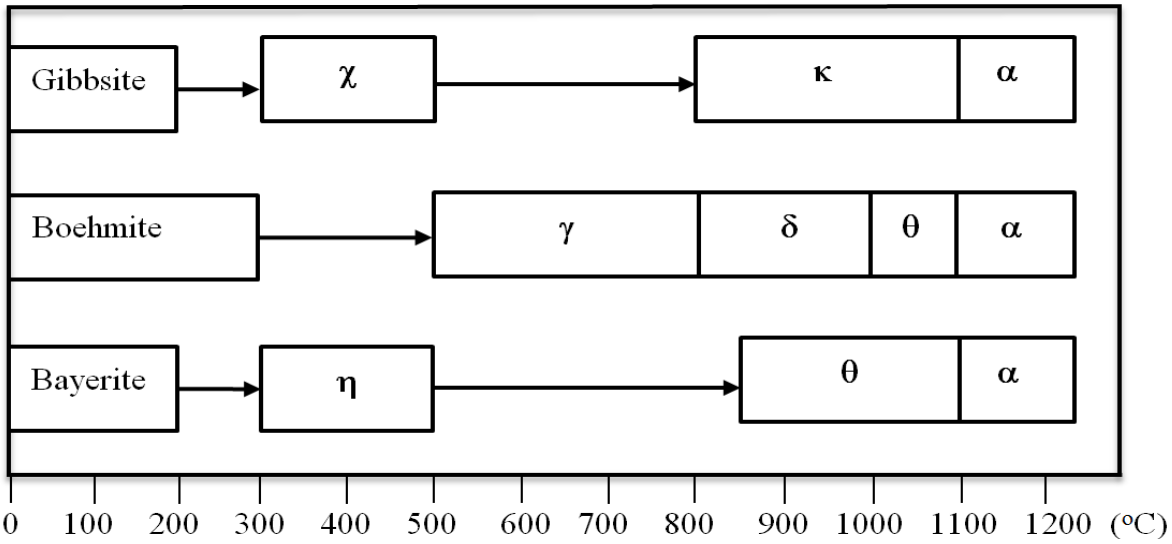


Figure 2.2: Phase diagrams of bayerite, boehmite and gibbsite minerals (Rajamani Balasubramanian, 2020)

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 Balasubramanian, 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 acid sites, which could accept electron pair by coordination bond and were represented by small number of low coordinated surface of Al^{3+} 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 hydroquinones present in the working solution were non-ionic proton donors and proton acceptors (Rajamani Balasubramanian, 2020). The presence of hydrogen bonding with oxygen atoms in the quinones and hydroquinones 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 base of O^{2-} atoms and Lewis 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 base (O^{2-}) sites remain on the surface of alumina. After calcination at temperatures above 470 ^{o}C, strong acidity was formed on the surface of alumina. Further increased in temperatures up to 700 ^{o}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 2.3.

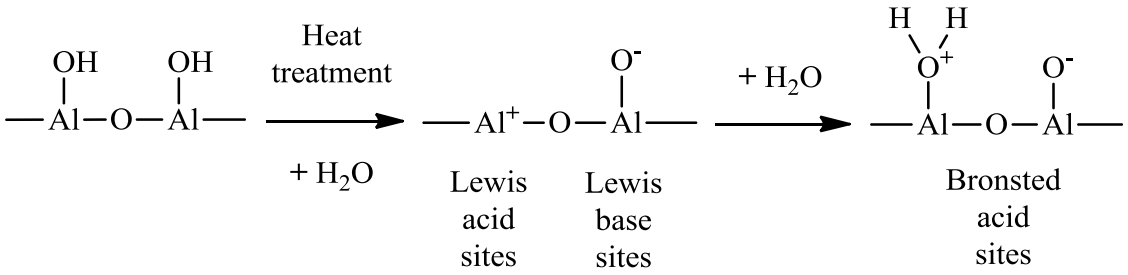


Figure 2.3: Different acid sites of activated alumina (Rajamani Balasubramanian, 2020)

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 Balasubramanian, 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 Balasubramanian, 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 Van der Waals forces, dipole interactions, and hydrogen bonding. In chemical adsorption mechanism, there was a 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 was 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 chemisorption 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 multilayers 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 has 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 m^2/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 rout 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 proven to adsorb the hydrogenation degradation products, reduce the consumption of ethyl anthraquinone 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 ^{o}C.

2.6 Regeneration of spent deactivated alumina

The crystallization and precipitation of degradation products and polymers of the solvent ingredients on the activated alumina resulted in the decline of active surface area and the loss of alkaline composition (Wu et al., 2014). Upon time, this alumina was deactivated and unable to regenerate THAQE due to the blockage of active sites occupied by surface adsorption of highly polar inerts. The inert impurities such as OHAHQ, OAT, AT, DAT and H_2O (Li et al., 2014) were responsible for adhering on the surface of alumina via the acid sites and the hydroxyl-groups (Rajamani Balasubramanian, 2020). These inert impurities made the alumina to be deactivated. Catalyst deactivation was caused by the loss of catalytic activity, which was a problem of great industrial concern in the catalytic processes (Argyle & Bartholomew, 2015). If catalyst activity declined to a critical level, four alternative ways were placed to made decision. The first alternative was regeneration and reuse the catalyst. The second alternative was using the catalyst for another application. The third alternative was reclaim and recycle important and expensive component of catalyst, the four alternative was discarding the catalyst. Among those alternatives, the first alternative of regeneration and reuse the catalyst had always preferred. There were three well-known methods proposed to remove the adsorbed organics and regenerate the spent alumina catalyst. These methods were calcination with

caustic treatment, Soxhlet solvent extraction with caustic treatment, and Soxhlet solvent extraction with alkaline solution containing active oxygen.

2.6.1 Calcination with caustic treatment

In this method, regeneration was carried out by roasting the alumina at about 300-400 ^{o}C until the adsorbed organic and carbonaceous matter has been removed (Browning, 1974). Then contacting the roasted alumina with Na_2O contained in an aqueous sodium hydroxide solution. Again roasting the caustic-treated alumina at about 300-400 ^{o}C until the reaction of the remaining Na_2O and the alumina were completed. This processing method required a 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.

2.6.2 Soxhlet solvent extraction with caustic treatment

Solvent extraction through Soxhlet apparatus was used to remove the adsorbed organics and carbonaceous matters. Since alumina was highly polar in nature due to the presence of both positive and negative species, the preferred compatible extraction solvents had been highly polar in nature (Rajamani Balasubramanian, 2020). The nature of the solvent was the most important factor during extraction which determined by the solubility of the target compound (Dulo et al., 2021). The extracting polar solvents had contained low boiling point temperature, flash point, auto-ignition temperature, liquid and vapor density, and latent heat of vaporization (Dulo et al., 2021; Rajamani Balasubramanian, 2020). Separation of solvents at low temperature had reduced the energy demand and side reactions with coloring agents.

The compatible organic polar solvents used to extract organic matters contained in spent alumina were acetone, methanol, ethyl acetate and acetonitrile. They have had better tendency on extracting polar compounds from the solid matrix of deactivated alumina. The solvents acetone and methanol were suitable for removing all polar compounds while ethyl acetate was suitable for removing phenolic compounds. The presence of red-brown color in the solvent during extraction was an indication of extracted organic compounds. Color was an indication of solvents extraction power such that a darker color indicated the presence of large concentration of organics. The extraction power of ethyl acetate, methanol, acetonitrile and acetone increased from high to low order respectively.

The Soxhlet solvent treated alumina was also treated with caustic solution (Rajamani Balasubramanian, 2020). Caustic had known to dissolve organic materials and might

dissolve alumina at high concentration. The concentration of the aqueous caustic solution for treating the alumina was 0.5 to 5% w/w (Browning, 1974) so that the alumina became stable in the caustic environment. Usually 1.5% w/w caustic solution (Rajamani Balasubramanian, 2020) was used to treat alumina at room temperature (25 ^{o}C). During the contact time, the residual Na_2O were fixed on the external and internal surfaces of the alumina (Browning, 1974). After complete reaction, the sodium hydroxide solution drained from alumina had lower concentration than the fresh sodium hydroxide solution. In this treatment, the solid crystalline structure of gamma alumina had not changed and structural disintegration had not occurred. Even though the caustic concentration was maintained within the recommended range, it was impossible to find high recovery of the active sites.

2.6.3 Solvent extraction with alkaline solution containing active oxygen

Solvent extraction methods could be Soxhlet, supercritical fluid, maceration, microwave assisted, ultrasonic assisted, ultrasonic-microwave assisted, reflux, enzyme assisted, sublimation assisted and pressurized liquid extractions (Dulo et al., 2021). Of these extraction methods, Soxhlet solvent extraction was the most efficient technique that gave the highest removal of organics from spent alumina. The highest removal of organics during this extraction was the result of continuous renewal of the solvent diffusion.

Soxhlet solvent treated alumina was treated with alkaline solution containing active oxygen (Kabisch & Kunkel, 1973). Alkaline solutions could be sodium hydroxide, potassium hydroxide, calcium hydroxide, barium hydroxide or ammonium hydroxide. Since sodium hydroxide provided a pH above 10, it was preferred to use for alumina regeneration in the concentration range of 0.1 to 3% w/w. Active oxygen-containing compounds could be sodium perborate, sodium percarbonate, potassium perborate, potassium percarbonate, sodium persulfate, potassium persulfate, percarbamide or hydrogen peroxide. Hydrogen peroxide as a strong oxidizing agent was preferred to use for alkaline solution additive. Hydrogen peroxide at 10% w/w could not generate explosive mixture while contacted with caustic solution (Hart et al., 2013). Thus, hydrogen peroxide at concentration below 10% w/w together with caustic solution could be used for oxidizing organic matters. Caustic treatment containing hydrogen peroxide as active oxygen followed by solvent extraction was used to regenerate deactivated alumina. In this process, it was possible to find 100% recovery of the active sites in a surprising manner. The regeneration had carried out at a temperature between 25 and 90 ^{o}C.

In this case, the regeneration process could be repeated successfully as often as desired (Kabisch & Kunkel, 1973).

2.7 Regenerated alumina performance test

The most regeneratable byproduct of ethyl anthraquinone was THAQE that formed from oxidation process. Activated alumina was used to convert inactive THAQE to active form of THAQ and EAQ that capable to produce hydrogen peroxide. Therefore, epoxide conversion was the most exact measure for the activity of regenerated alumina (Kabisch & Kunkel, 1973). The performance of regenerated alumina was an indication of its activity and was measured by THAQE conversion. The regenerated alumina quality was tested by putting the working solution containing epoxide into regenerated alumina for 2 to 4 days at a temperature of 50 to 100 ^{o}C. Thus, the performance of alumina was tested by contacting 0.7 gm solid sample with 25 ml of epoxide solution in a 50 ml glass flask (Rajamani Balasubramanian, 2020). After cooling the samples to room temperature, the working solution from alumina was separated by using 0.5 µm filter paper. The conversion of THAQE to active quinones was then determined by using GC analysis (Chen, 2015).

CHAPTER THREE

3. MATERIALS AND METHODS

3.1 Materials

The materials used for regenerating spent alumina were Soxhlet apparatus, rotary evaporator, oven dryer, filter funnel, 0.5μm filter paper, analytical balance, 25 ml pipette, 50 ml burette, 250 ml conical flask, 500 ml volumetric cylinder, 250 ml beaker, 500 ml round bottom flask, 300 ml measuring cylinder, electric heating mantle and mechanical shaker.

Analytical grade Soxhlet extraction solvents were purchased from local market with purity as methanol 99.5%, ethyl acetate 99.95%, acetone 99.5% and acetonitrile 99.5%. The chemicals and reagents used for caustic treatment were obtained from Awash Melkassa Chemical Factory with purity as hydrochloric acid 37%, sodium hydroxide 99%, hydrogen peroxide 3% and phenolphthalein indicator 1%. The solid waste of spent alumina was also obtained from Awash Melkassa Chemical Factory.

3.2 Methods

The recovering of catalytic activity of spent alumina was carried out using Soxhlet solvent extraction followed by caustic treatment methods.

3.2.1 Soxhlet solvent extraction

Soxhlet solvent extraction was carried out using Soxhlet apparatus that consisted of a thimble, distillation flask, 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 Balasubramanian, 2020). The polar nature of these organic solvents used to dissolve and extract polar organic compounds. Since all solvents were colorless in nature as shown in Figure 3.1, the presence of colored organics removed from spent alumina were 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 Balasubramanian, 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 200 gm of 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)	BPT[1] (^oC)	SPT[2] (^oC)
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

Figure 3.1: Pure organic solvents used for Soxhlet solvent extraction

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

[1] BPT stand for boiling point temperature of the solvents.

[2] SPT stand for set point temperature of the solvents.

extracted organics obtained from rotary evaporator were oven dried at 110 ^{o}C for 2 hours. The experimental set up of Soxhlet solvent extraction was shown in Figure 3.2.

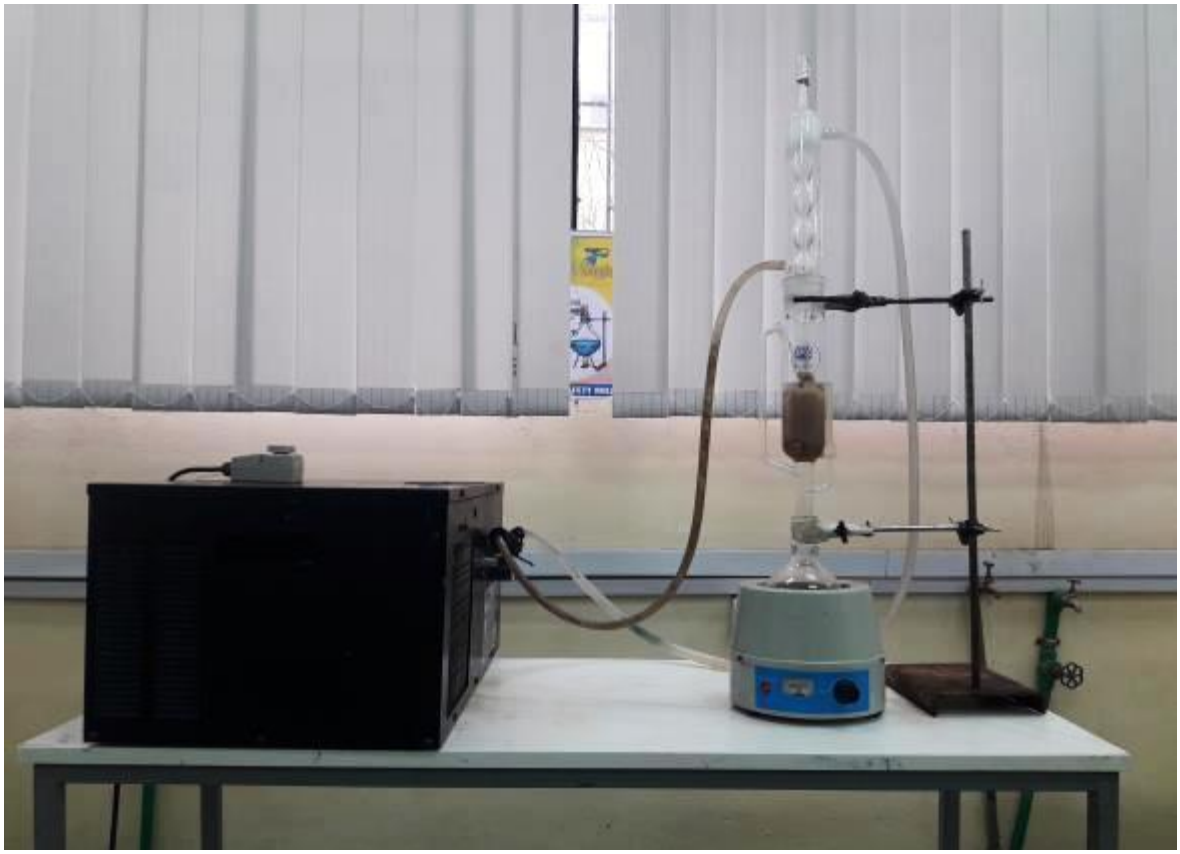


Figure 3.2: Experimental set up of Soxhlet solvent extraction

3.2.2 Caustic treatment

The Soxhlet solvent treated alumina was oven dried at 110 ^{o}C for 2 hours (Rajamani Balasubramanian, 2020) and treated with alkaline solution containing active oxygen to remove the remaining organics and to modify the alkaline composition of the surface of alumina (Kabisch & Kunkel, 1973). The alkaline solution used for regenerating Soxhlet treated alumina was sodium hydroxide. Since sodium hydroxide could provide relatively higher pH value (above 10), it is preferable to use the concentration range of 0.1 to 3% w/w for alumina regeneration. Hydrogen peroxide as a strong oxidizing agent was preferred relative to other alkaline additives due to the ability of releasing active oxygen at low concentration while contact with caustic solution. Thus, caustic treatment experiments were conducted at different temperature, concentration and contact time in the 500 ml round bottom flask that contained caustic solution with hydrogen peroxide and Soxhlet solvent treated alumina. The experimental set up of caustic treatment experiment was shown in Figure 3.3.

Figure 3.3: Experimental set up of caustic treatment

OVAT method was used to determine the individual effects of each caustic treatment conditions at five levels. The presence of optimized temperature and caustic concentration in previous studies made OVAT to be selected over other method. In OVAT method, only one variable was varied at a time while keeping the other variables constant. The caustic solution with constant addition of hydrogen peroxide was used for each caustic treatment experiments such that 60 ml of 0.1 to 3% w/w caustic solution with 14 ml of 3% w/w hydrogen peroxide was prepared for 30 gm of dried Soxhlet treated alumina sample (Kabisch & Kunkel, 1973). The dried Soxhlet treated alumina was immersed into caustic solution containing hydrogen peroxide and the experiments were tested at a concentration of 0.1 to 3% w/w, at a temperature of 25 to 90 ^{o}C and at a contact time of 1 to 4 hours. The electrical heating mantles connected in series were used to heat the solution and alumina contained in each round bottom flask. The regenerated alumina was separated from the solution containing desorbed quinones with low caustic solution concentration by using 0.5 µm filter paper. This alumina was washed with deionized water until neutral PH obtained. Caustic treatment conditions with their experimental runs were shown in Table 3.2.

Table 3.2: Caustic treatment regeneration experiment

Variables	Unit	Experimental runs				
Caustic concentration	% w/w	0.1	0.8	1.5	2.2	3
Temperature	^{o}C	25	40	55	70	90
Time	hour	1	1.5	2.5	3.5	4

3.2.2.1 Titration method

The basicity of regenerated alumina was measured by titration method using the procedure reported by (Intarapong et al., 2013; Leyva-Ramos et al., 2008). The activity of this alumina was represented by the amount of basic sites. The basic sites available in the regenerated alumina were determined by adding 1 gm of regenerated alumina to a beaker that contained 25 ml of 0.1 N HCl solution. The solid and acid mixture was allowed to shake for 1 hour at room temperature using mechanical shaker. The remaining unreacted excess acid was then titrated in the presence of three drop of phenolphthalein indicator using 0.1 N aqueous NaOH as the titrant. Phenolphthalein indicator was used to know the color change of the equivalence point since it was used for strong acid-strong base titration. The titration had eventually stopped while the color of the solution changed from colorless to pink. This was the end of titration called stoichiometric equivalence point. The titration of equivalence point ensured that the calculated mole of HCl solution was as close to the exact value of neutralization reaction. The reaction conducted by the acidic agent with the basic sites of the solid catalyst suggested that the basicity determined from the titration experiment represent the total basic sites of the bulk catalyst. The amount of caustic soda reacted or adsorbed by alumina was directly related to the basicity that capable to regenerate epoxidized working solution. The basicity, which is the number of basic sites per unit weight of a solid catalyst expressed in mmol HCl/gm of alumina, was calculated by the following equation.

$$\text{Basicity} = \frac{V_{HCl} * N_{HCl} - V_{NaOH} * N_{NaOH}}{M_{catalyst}}$$

Where V_{HCl} was volume of HCl (ml), N_{HCl} was normality of HCl, V_{NaOH} was the volume of NaOH (ml), N_{NaOH} was normality of NaOH and $M_{catalyst}$ was mass of the catalyst

3.2.3 Performance test of alumina

The performance test of regenerated alumina was measured by epoxide conversion, which was used to indicate the catalytic activity of this alumina (Kabisch & Kunkel, 1973). The oxidized state of the plant working solution containing epoxide that already treated with spent alumina was used to measure the performance test of alumina. The regenerated alumina and reused alumina performance experiments were conducted by immersing 6 gm of the alumina samples into 200 ml of plant working solution-containing epoxide in a 500 ml glass flask (Rajamani Balasubramanian, 2020). However, the sample of 6 gm of fresh alumina had also used to immerse into 200 ml of working solution-containing epoxide for

comparison. The immersed samples were then placed in the heating mantle at a set point temperature of 70 ^{o}C. The samples were shaken daily over the next 4 days to ensure maximum conversion. Thereupon the epoxide content of the working solution was reduced significantly within these days of treatment. After 4 days, the samples were removed from the heating mantle and were allowed to cool to room temperature. The working solution was then separated from the alumina using 0.5 µm filter paper and treated working solution was collected in the 500 ml of round bottom flask.

3.2.4 Characterization of solvent treated alumina, regenerated alumina, fresh alumina, spent alumina and working solution components

3.2.4.1 Thermogravimetric analysis

TGA analysis was a thermo-analytical technique used to determine the thermal analysis of Soxhlet solvent treated alumina samples as well as fresh, spent and regenerated alumina samples. The TGA analysis of spent and fresh alumina was used to compare their weight loss with Soxhlet solvent treated alumina and regenerated alumina samples. 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 ^{o}C with a heating rate of 20 ^{o}C/min and the decomposition of the sample weight (%) against temperature (^{o}C) was recorded.

3.2.4.2 Atomic absorption spectrophotometer

AAS analysis was an analytical technique used to determine the chemical composition of fresh, spent and regenerated alumina samples through the application of characteristic wavelengths of electromagnetic radiation from a light source. VARIAN instrument model SPECTRAA 20 PLUS was used in this study. The AAS instrumental analysis method coupled with $LiBO_2$ fusion, Hydrogen fluoride attack, Gravimetric and Colorimetric methods was used to determine the chemical composition of the samples. In this analysis, the sample was measured by qualitative analysis followed by quantitative analysis. Qualitative analysis was determined which elements were present from the measured radiant energy emitted by the sample while quantitative analysis was determined how much of the concentration or composition of the elements were present in the sample from the measured intensity of the emitted energies. During excitation, electrons move up one

energy level in their respective atoms when those atoms absorb a specific energy. This energy corresponds to a specific wavelength that represents the characteristic element.

3.2.4.3 X-Ray Diffraction

XRD analysis was an analytical technique used to determine the crystalline structure of fresh, spent and regenerated alumina. PANalytical Xpert Pro Powder X-ray diffractometer was used in this study with the source of Cu radiation, with the scanning range of 2θ from 10^o to 80^o, with step size (2θ) of 0.017 and scan speed of 3^o/minute. This instrument was used to identify the crystalline phases and degrees of crystallinity of fresh, spent and regenerated alumina thereby provided the information of chemical composition. The purity of regenerated alumina was then compared with fresh and spent alumina.

3.2.4.4 BET surface area analysis

The specific surface area, pore size and pore volume distribution of fresh, spent and regenerated alumina were studied by BET surface area analysis in nitrogen adsorption and desorption environment. Quantachrome instruments version 11.0 was used in this study in a relative pressure (P/Po) between 0.01 and 0.35. The physical adsorption of nitrogen gas revealed important information about the catalyst structure. The physical property of the sample surface area, pore size and pore volume distribution were obtained by recording nitrogen adsorption-desorption isotherms at -196 ^{o}C. The samples were degassed at 120 ^{o}C overnight before the measurements were taken and the overall surface area, pore size and pore volume distribution were determined by using the BET theory.

3.2.4.5 Gas chromatography

GC analysis was an analytical technique used to determine the chemical composition of various organic components of the working solution treated with spent, regenerated, reused regenerated and fresh alumina samples. 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 of length 30 meters and internal diameter 0.25 mm coiled to fit inside the instrument. The sample of each alumina treated working solution of volume 5µl was introduced into the GC column via the automated injection port using a microliter 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 ^{o}C to 280 ^{o}C at a rate of 3 ^{o}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 a 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 performance of regenerated alumina was tested by the epoxide conversion, the concentration of THAQE, THAQ and EAQ were determined from the total peak area of chromatogram.

CHAPTER FOUR

4. RESULT AND DISCUSSION

In this chapter, the results obtained from the regeneration process using Soxhlet solvent extraction followed by caustic treatment were discussed in detail. The characterization results of fresh, spent and regenerated alumina were also discussed comparatively and the performance test results 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 distilled 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: Observation of Soxhlet extraction solvent cycles

Trial number	Types of solvent	SPT[1] (^{o}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 Balasubramanian, 2020). The color observation of desorbed quinones and carbon deposits obtained from Soxhlet solvent extraction were shown in Figure 4.1.

Solvent treated alumina samples were oven dried at a temperature of 110 ^{o}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 4.2. From this observation, a definite conclusion was not made in order to compare the solvents extraction efficiency (Rajamani Balasubramanian, 2020).

[1] SPT stand for set point temperature of the solvents.

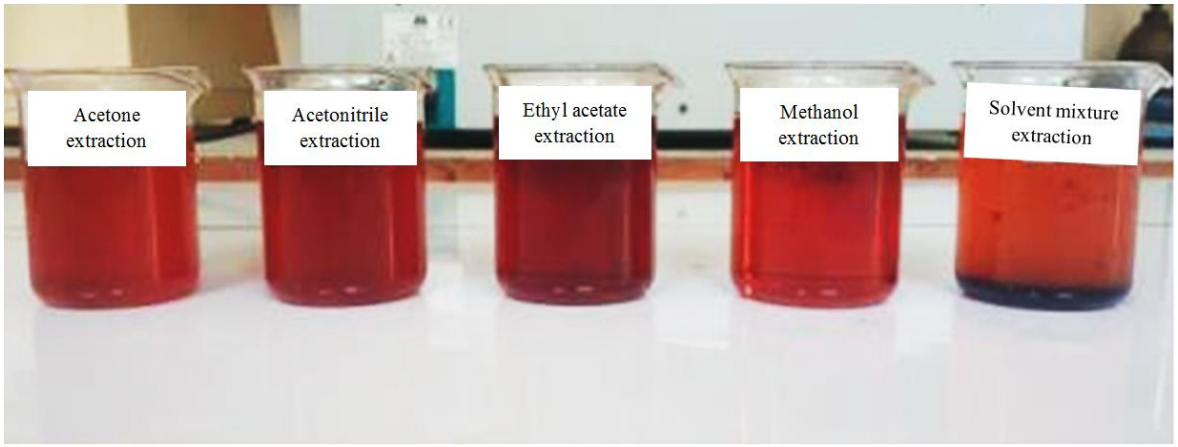


Figure 4.1: Soxhlet solvent extraction color observation

Figure 4.2: Soxhlet extraction solvent treated alumina

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 ^{o}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), 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 efficincy 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 these solvent mixture was caused by the dissolving potential of different polar components at the same time. 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 analysed using TGA (Figure 4.4) inorder 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 setforth 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 Thermogravimetric 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 (^{o}C) as shown in Figure 4.4. 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, fresh alumina and spent alumina were observed at 527.4 ^{o}C, 523.9 ^{o}C, 535.9 ^{o}C, 531.5 ^{o}C, 524.5 ^{o}C, 534.8 ^{o}C and 408.3 ^{o}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 4.4 (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.

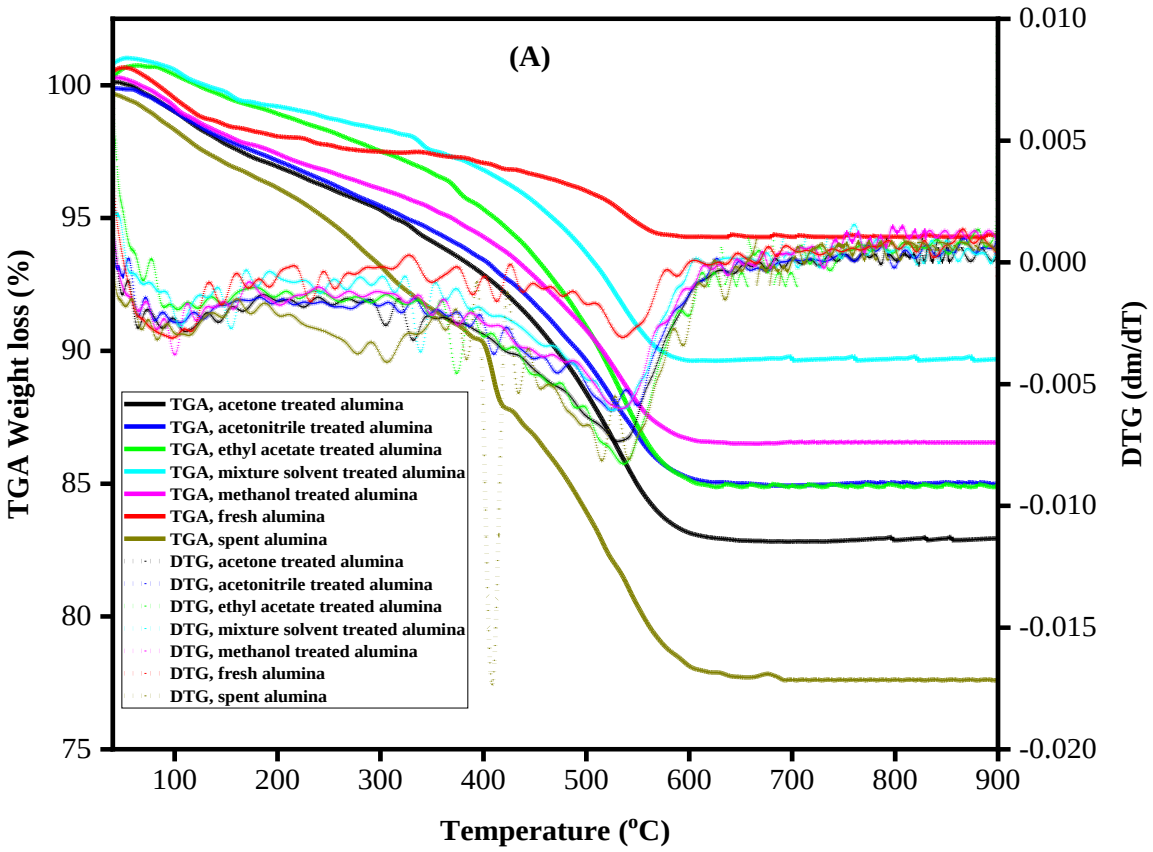


Figure 4.4 (A): TGA and DTG profiles for solvent treated, fresh and spent alumina

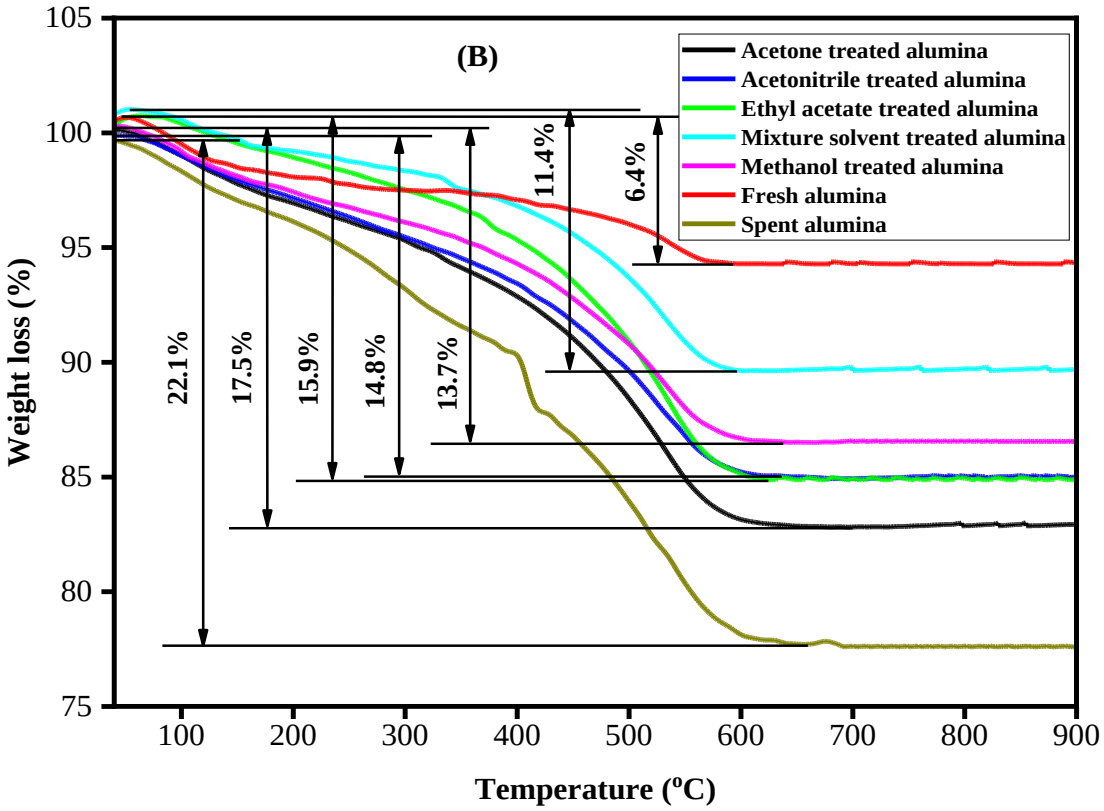


Figure 4.4 (B): Weight loss in TGA curves for solvent treated, fresh and spent alumina

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 Caustic treatment

The caustic treatment of mixture solvent (ethyl acetate and methanol) treated alumina was conducted and the amount of caustic soda reacted or adsorbed by the alumina was determined by titration method. In this case, two titration experiments trial-1 and trial-2 were made until the point of neutralization reaction had reached. The success of titration was obtained by adding NaOH approximately 1 drop per second until the equivalence point had reached. The titration result showed different amount of basic sites that determined the activity of the treated alumina catalyst. The caustic treatment conditions affecting the regeneration of mixture solvent treated alumina were studied by OVAT method in the following manner.

4.2.1 Effect of NaOH concentration

The effect of NaOH concentration on the basicity of mixture solvent treated alumina and the removal potential of the remaining adsorbed organics was studied. The experiments were carried out at five different concentrations of 0.1% w/w, 0.8% w/w, 1.5% w/w, 2.2% w/w and 3.0% w/w while the contact time and temperature were kept constant at 3.5 hour and 70 ^{o}C respectively. The volume of caustic soda solution taken for each experiment was 60 ml with constant addition of 14 ml of 3.0% w/w hydrogen peroxide. In this experiment, the basicity of regenerated alumina at different caustic concentration was determined by using titration method.

The effect of NaOH concentration on the basicity of alumina was illustrated graphically as shown in Figure 4.5. The basicity of titration result showed that the basic sites slightly

increased while NaOH concentration increased from 0.1% w/w to 3% w/w. When NaOH adsorption increased with concentration, the mass transfer from the aqueous phase to the solid phase increased. The mass transfer of NaOH was caused by the driving force of the metal ions towards the active sites of the solid adsorbent. Even though a slight increase in basicity was observed by NaOH adsorption, the catalytic activity of alumina increased. However, the maximum declined basicity of alumina was not observed during NaOH adsorption due to the presence of recommended concentration range (Kabisch & Kunkel, 1973). Therefore, the highest catalytic activity of regenerated alumina was obtained at the basicity of 2.19 mmol HCl/gm of alumina with NaOH concentration of 3% w/w.

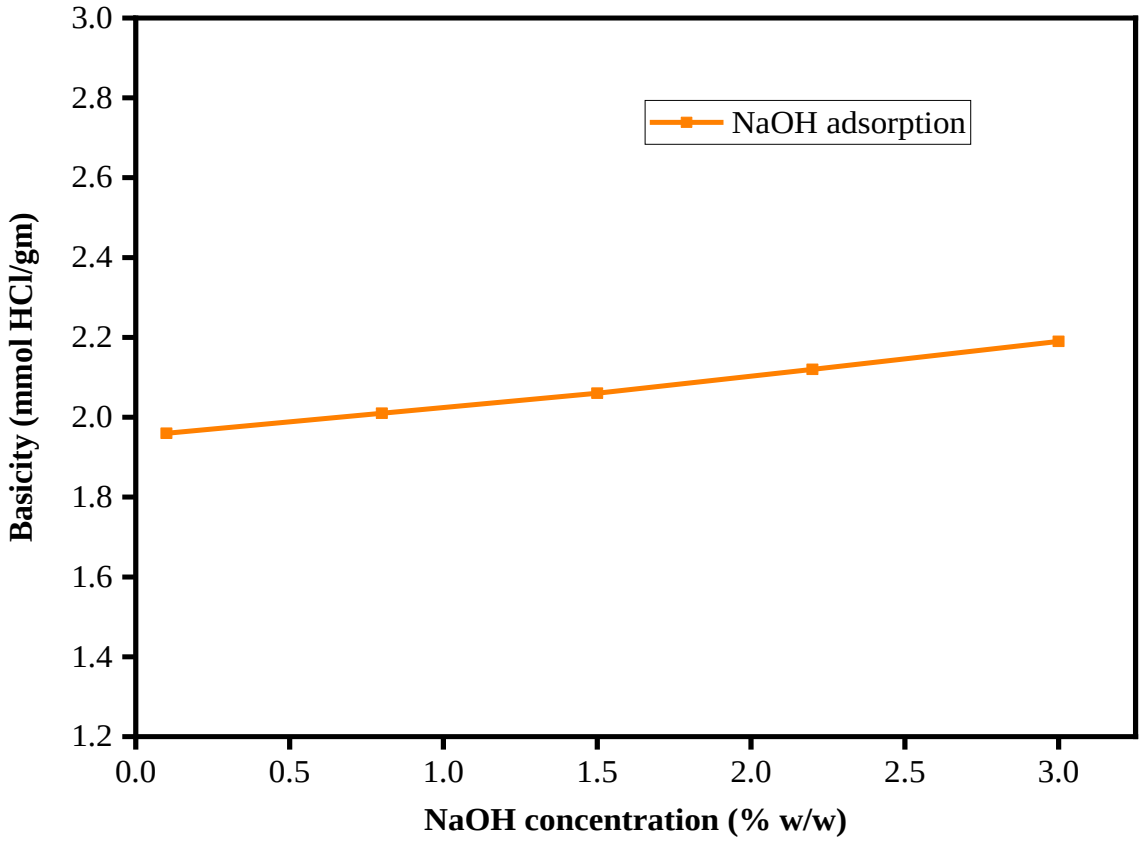


Figure 4.5: Effect of NaOH concentration on NaOH adsorption

4.2.2 Effect of temperature

The effect of caustic solution temperature on the basicity of mixture solvent treated alumina and the removal potential of the remaining adsorbed organics was studied. The experiments were carried out at five different temperatures of 25 ^{o}C, 40 ^{o}C, 55 ^{o}C, 70 ^{o}C and 90 ^{o}C while the contact time and caustic concentration were kept constant at 3.5 hour and 3% w/w respectively. The volume of caustic soda solution taken for each experiment

was 60 ml with constant addition of 14 ml of 3.0% w/w hydrogen peroxide. The basicity of regenerated alumina at different temperature was determined by titration method.

The effect of caustic solution temperature on the basicity of alumina was illustrated graphically as shown in Figure 4.6. The basicity of titration result showed that the basic sites slightly increased while the temperature of the caustic solution increased from 25 ^{o}C to 70 ^{o}C. However, the basicity declined when the temperature raised up to 90 ^{o}C. When the caustic solution temperature increased from 25 ^{o}C to 70 ^{o}C, the NaOH adsorption caused by the mass transfer from the aqueous phase to the solid phase increased. Even though a slight increase in basicity was observed from 25 ^{o}C to 70 ^{o}C, the catalytic activity of alumina increased. When the solution temperature increased from 70 ^{o}C to 90 ^{o}C, the basicity caused by NaOH adsorption decreased. Therefore, the highest catalytic activity of regenerated alumina was obtained at the basicity of 2.19 mmol HCl/gm of alumina with caustic solution temperature of 70 ^{o}C.

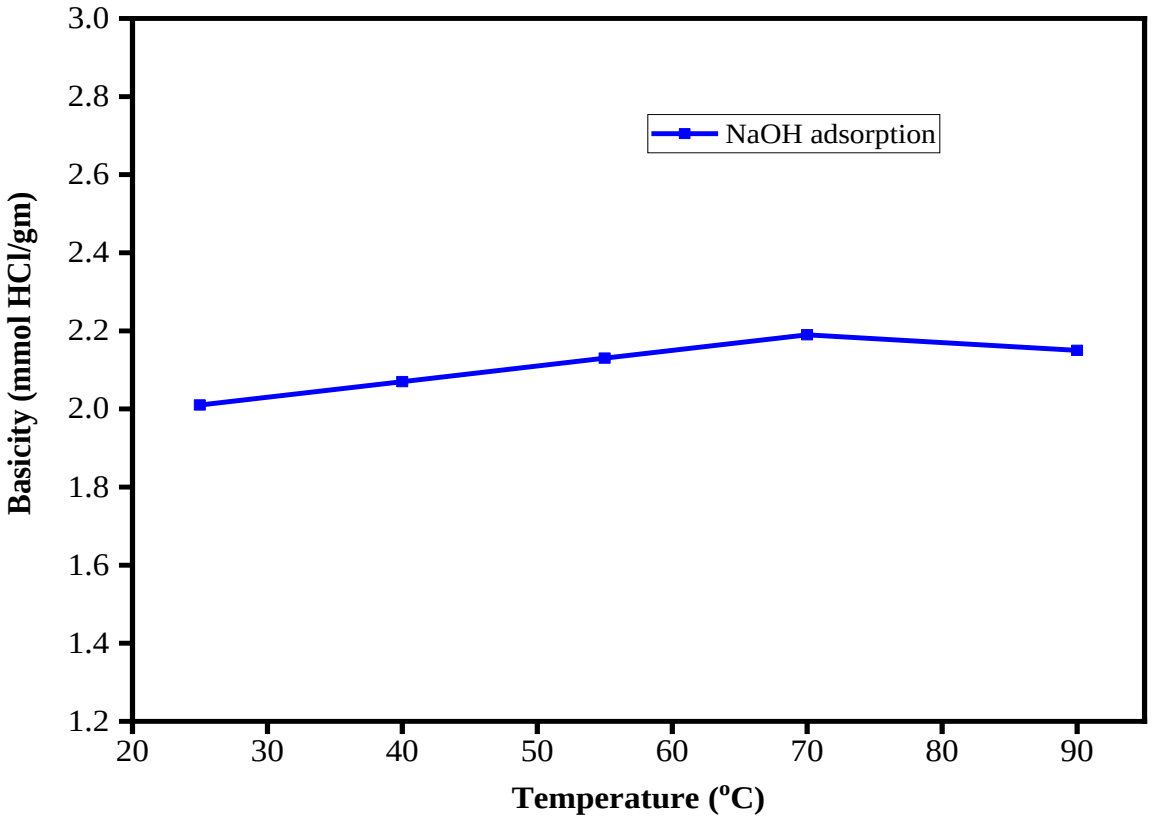


Figure 4.6: Effect of temperature on NaOH adsorption

4.2.3 Effect of contact time

The effect of contact time on the basicity of mixture solvent treated alumina and the removal potential of the remaining adsorbed organics was studied. The experiments were

carried out at five different contact times of 1 hour, 1.5 hour, 2.5 hour, 3.5 hour and 4 hour while the temperature and caustic concentration were kept constant at 3% w/w and 70 ^{o}C respectively. The volume of caustic soda solution taken for each experiment was 60 ml along with constant addition of 14 ml of 3.0% w/w hydrogen peroxide. The basicity of regenerated alumina at different contact time was determined by titration method.

The effect of contact time on the basicity of alumina was illustrated graphically as shown in Figure 4.7. The basicity of titration result showed that the basic sites slightly increased while the contact time of the caustic solution increased from 1 hour to 3.5 hour. However, the basicity declined when the contact time raised up to 4 hour. When the contact time of the caustic solution increased from 1 hour to 3.5 hour, the NaOH adsorption caused by the mass transfer from the aqueous phase to the solid phase increased. Even though a slight increase in basicity was observed from 1 hour to 3.5 hour, the catalytic activity of alumina increased. When the contact time increased from 3.5 hour to 4 hour, the basicity caused by NaOH adsorption decreased. However, no more basicity caused by NaOH adsorption had occurred in the contact time of 2.5 hour to 4 hour in that the optimum contact time was chosen at 2.5 hour. Therefore, the highest catalytic activity of regenerated alumina was obtained at the basicity of 2.19 mmol HCl/gm of alumina with contact time of 2.5 hour.

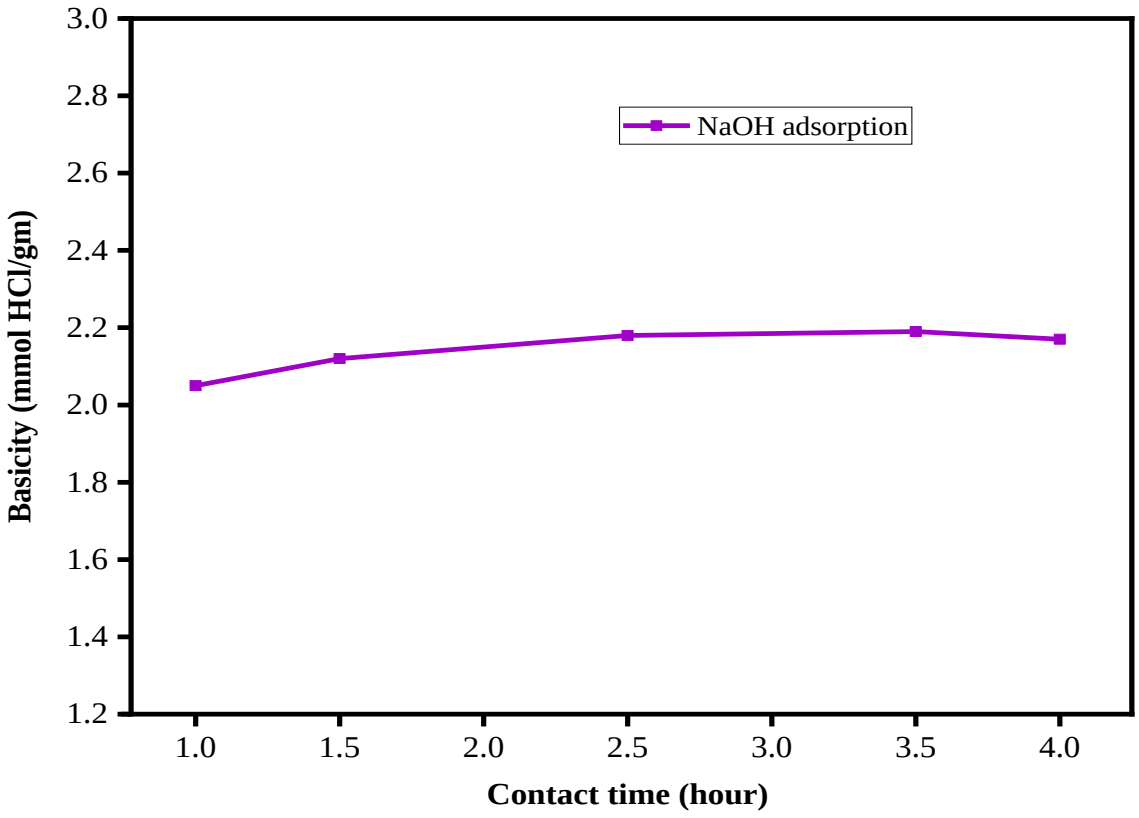


Figure 4.7: Effect of contact time on NaOH adsorption

4.3 Characterization of fresh alumina, spent alumina and regenerated alumina

4.3.1 Atomic absorption spectrophotometry

The chemical composition of fresh, spent and regenerated alumina samples were determined by using AAS instrumental analysis method coupled with $LiBO_2$ fusion, Hydrogen fluoride attack, Gravimetric and Colorimetric methods. In this analysis, the major and minor oxides of the samples were measured and the results were shown in Table 4.3. The results of chemical analysis revealed that the alumina samples were mainly composed of Al_2O_3. The percentage purity of Al_2O_3 in the regenerated alumina was in between the spent and fresh alumina. The AAS result showed that the moisture content of fresh alumina was 3.83%, which was higher than the moisture content of regenerated and spent alumina. The presence of large surface area and free adsorption active sites on the surface of fresh alumina led to the attraction of more water molecules strongly that resulted in higher moisture content. On the other hand, the AAS result showed that the moisture content of regenerated alumina was 2.75% whereas the moisture content of spent alumina was 1.74%. It was observed that the regenerated alumina moisture content was higher than spent alumina. Since the surface catalytic activity of regenerated alumina was recovered by treatment, its surface area and free adsorption active sites was higher than spent alumina. This indicated that the water molecules were easily attracted by the active surface of regenerated alumina that led to higher moisture content. The AAS analysis result had also shown the loss on ignition (LOI) for fresh, regenerated and spent alumina. The higher LOI content of 19.67% was obtained from spent alumina whereas the lower LOI content of 9.49% was obtained from fresh alumina. However, the LOI content of regenerated alumina of 12.22% was in between fresh and spent alumina. Since spent alumina contained high amount of adsorbed organics during working solution regeneration, heating of this alumina at high temperature led to higher LOI content caused by the release of more volatile components. Moreover, the LOI content of regenerated alumina was more than fresh alumina due to the presence of some adsorbed organics that remained during the treatment. As the name indicated, the fresh alumina had not contaminated in that it contained low LOI content. The AAS analysis result had also shown the Na_2O content for fresh, regenerated and spent alumina. As indicated from the table, the Na_2O content of regenerated alumina was higher than the Na_2O content of fresh and spent alumina. The highest Na_2O content of 0.42% was obtained in the regenerated alumina due to the presence of caustic treatment. Therefore, the highest percentage of Na_2O in the regenerated alumina indicated the highest

adsorption efficiency whereas the highest percentage of Al_2O_3 in fresh alumina indicated the highest catalytic activity.

Table 4.3: AAS analysis of fresh, spent and regenerated alumina samples

Types of alumina	Chemical composition (%w/w)								
	Al_2O_3	SiO_2	Fe_2O_3	Na_2O	K_2O	MgO	CaO	H_2O	LOI
Fresh	77.56	6.60	<0.01	<0.01	0.64	0.18	0.86	3.83	9.49
Regenerated	77.36	6.26	<0.01	0.42	0.36	0.10	0.54	2.75	12.22
Spent	72.16	6.12	<0.01	<0.01	0.64	0.08	0.50	1.74	19.67

4.3.2 TGA analysis

The thermal analysis of the spent, regenerated and fresh alumina samples were carried out to analyse thermal stability and compare the weight loss with the increase in temperature. The thermal analysis of regenerated alumina, fresh alumina and spent alumina were indicated by the decomposition of the sample weight (%) against temperature (^oC) as shown in Figure 4.8. The degradation temperature of all alumina samples had easily seen in the DTG profile of Figure 4.8 (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 regenerated alumina, fresh alumina and spent alumina were observed at 538.1 ^oC, 534.8 ^oC and 408.3 ^oC respectively.

The simple presentation for the percentage weight loss of the spent, fresh and regenerated alumina samples had shown in the TGA curve of Figure 4.8 (B). In this curve, the percentage weight loss of spent, fresh and regenerated alumina samples were 22.1%, 6.4% and 12.2% respectively. The TGA curve showed that the weight loss of regenerated alumina was in between the weight loss of fresh and spent alumina. Relative to the weight loss of spent alumina, the percentage weight loss of regenerated alumina was reduced by 9.9%. However, the percentage weight loss of regenerated alumina was increased by 0.8% when compared to mixture solvent treated alumina. This percentage increment indicated that the adsorbed organics removal efficiency of caustic treatment was reduced but the catalytic activity of alumina caused by the adsorption of NaOH was increased slightly.

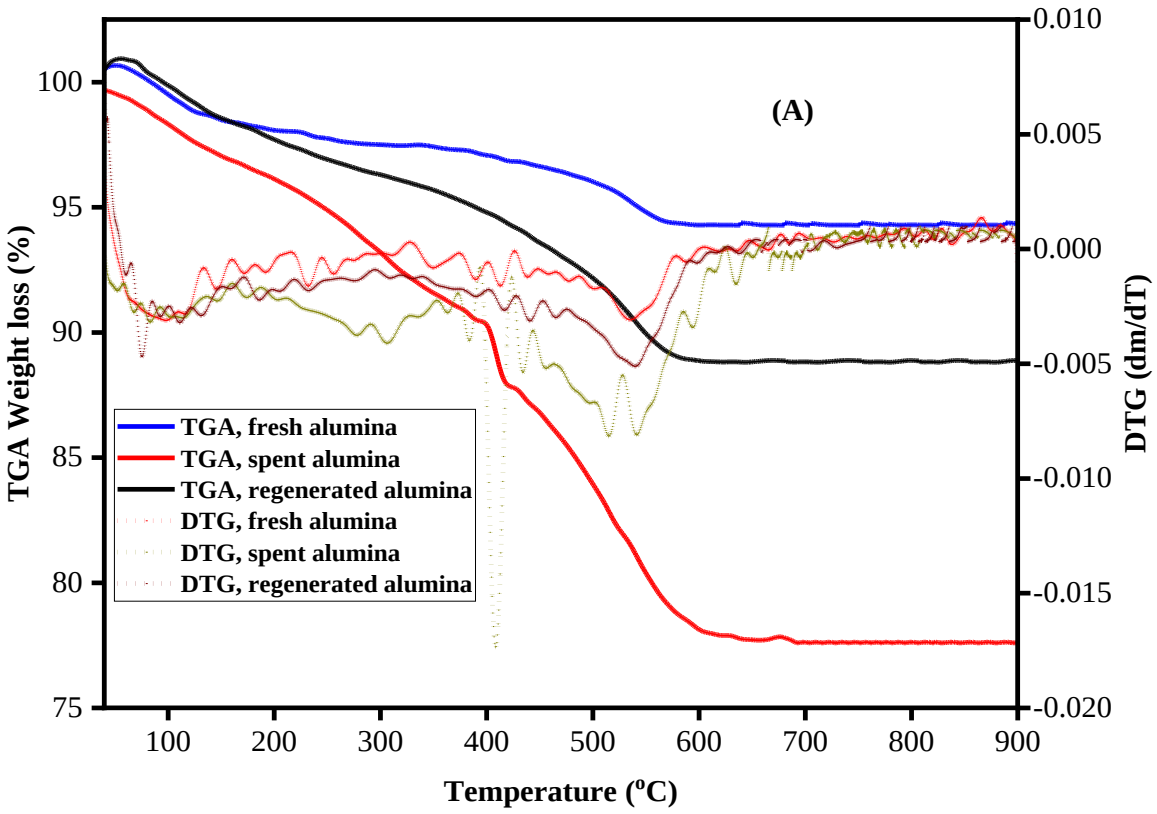


Figure 4.8 (A): TGA and DTG profiles for spent, regenerated and fresh alumina

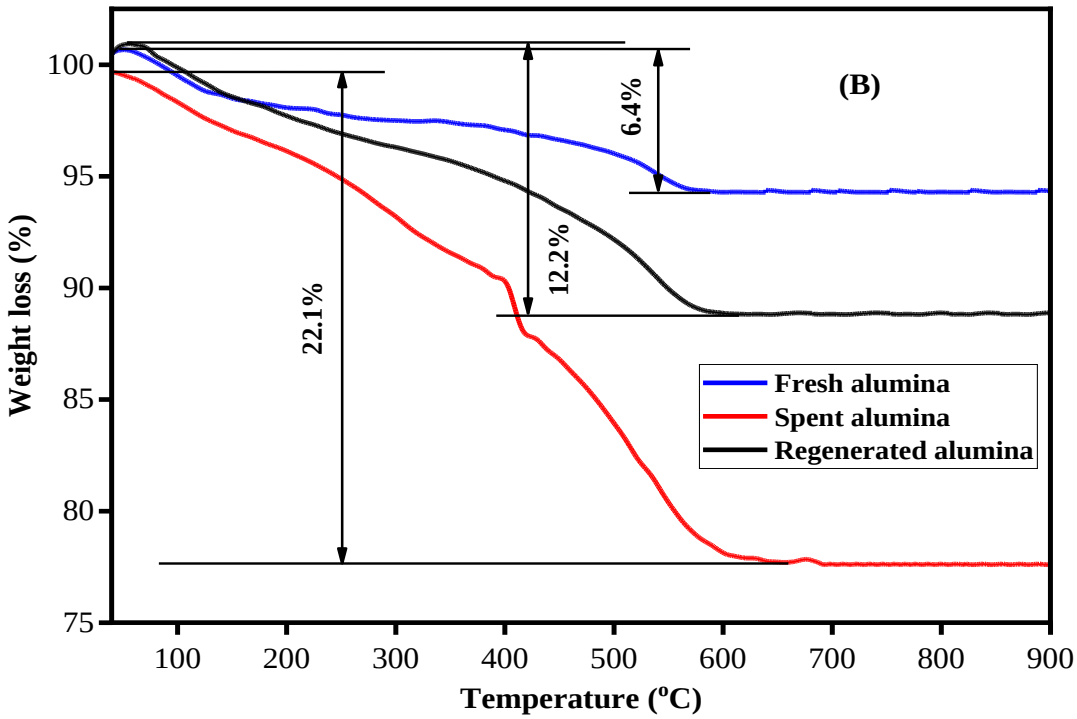


Figure 4.8 (B): Weight loss in TGA curves for spent, regenerated and fresh alumina

4.3.3 BET surface area analysis

The BET surface area of fresh, spent and regenerated alumina was shown in the bar graph of Figure 4.9. The higher specific surface area was obtained from fresh alumina followed by regenerated alumina and spent alumina. Relative to fresh alumina, the specific surface area of regenerated alumina was reduced by 48.096 m^2/gm whereas the specific surface area of spent alumina was reduced by 217.343 m^2/gm. Relative to regenerated alumina, the specific surface area of spent alumina was reduced by 169.247 m^2/gm. The higher specific surface area of alumina helped to improve the more passage of working solution into the porosity. This indicated that the conversion of THAQE was highly increased to active quinones when increased in the surface area of alumina. Thus, fresh alumina with specific surface area of 555.105 m^2/gm had shown higher THAQE conversion followed by regenerated alumina and spent alumina with specific surface area of 507.009 m^2/gm and 337.762 m^2/gm respectively. The lower specific surface area of spent alumina was caused by the adsorption of organic compounds during hydrogen peroxide production. Hence, the specific surface area of regenerated alumina indicated that 91.33% of the spent alumina catalytic activity was recovered by using solvent extraction and caustic treatment method.

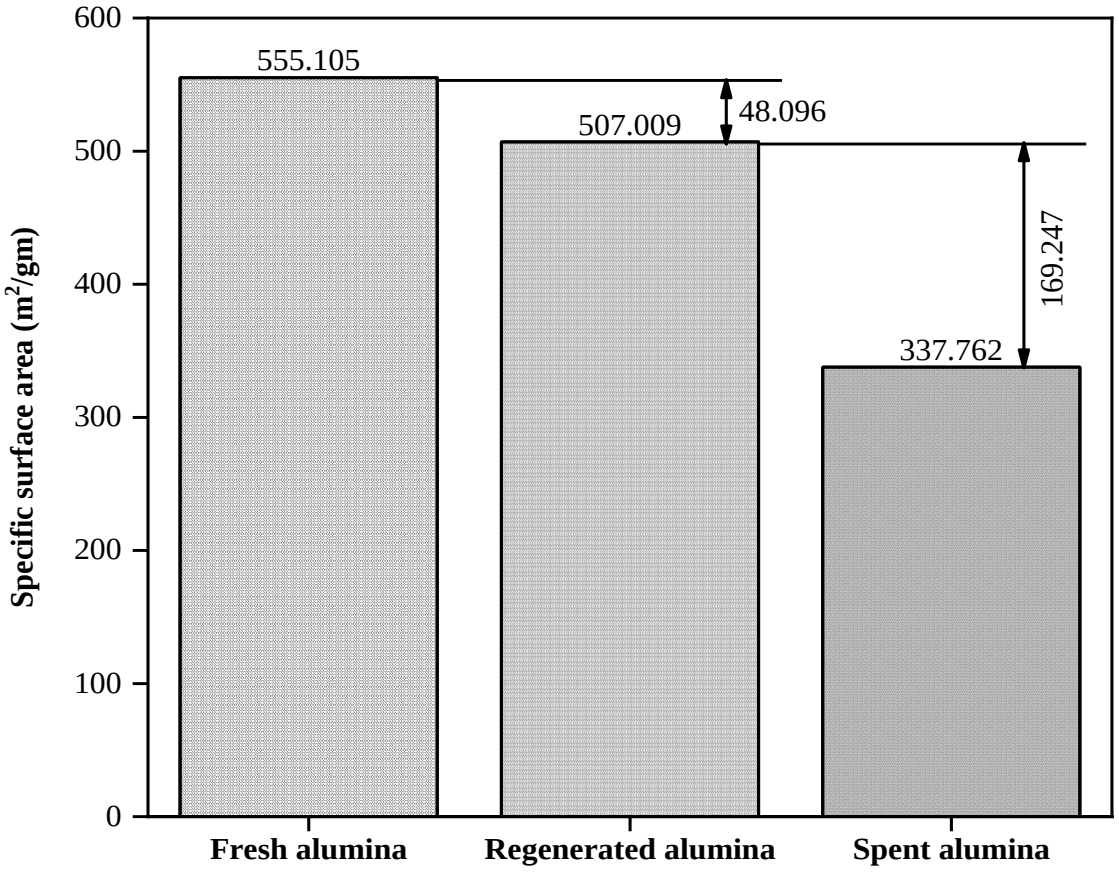


Figure 4.9: Specific surface area of fresh, regenerated and spent alumina

4.3.4 XRD analysis

XRD analysis was used to identify the crystal structure of the crystalline species presented in spent, regenerated and fresh alumina samples. The XRD patterns of these samples of alumina were shown in Figure 4.10 and revealed that all alumina samples presented the same degree of chrystalization. On the other hand, the XRD patterns of spent, regenerated and fresh alumina indicated that all the diffraction peaks matched well with eachother. The maximum diffraction peaks observed in the whole X-ray pattern of alumina types were the properties of gamma (γ) alumina, which indicated well-crystalline material as all the peaks are quite sharp and narrow. The loading effect of NaOH on the regenerated alumina was not observed when compared to the XRD pattern of fresh alumina. Since there was similar diffraction peaks observed, the gamma phase of regenerated alumina was not changed in the XRD pattern. Therefore, the XRD patterns of regenerated alumina had the same crystal arrangement to that of fresh alumina.

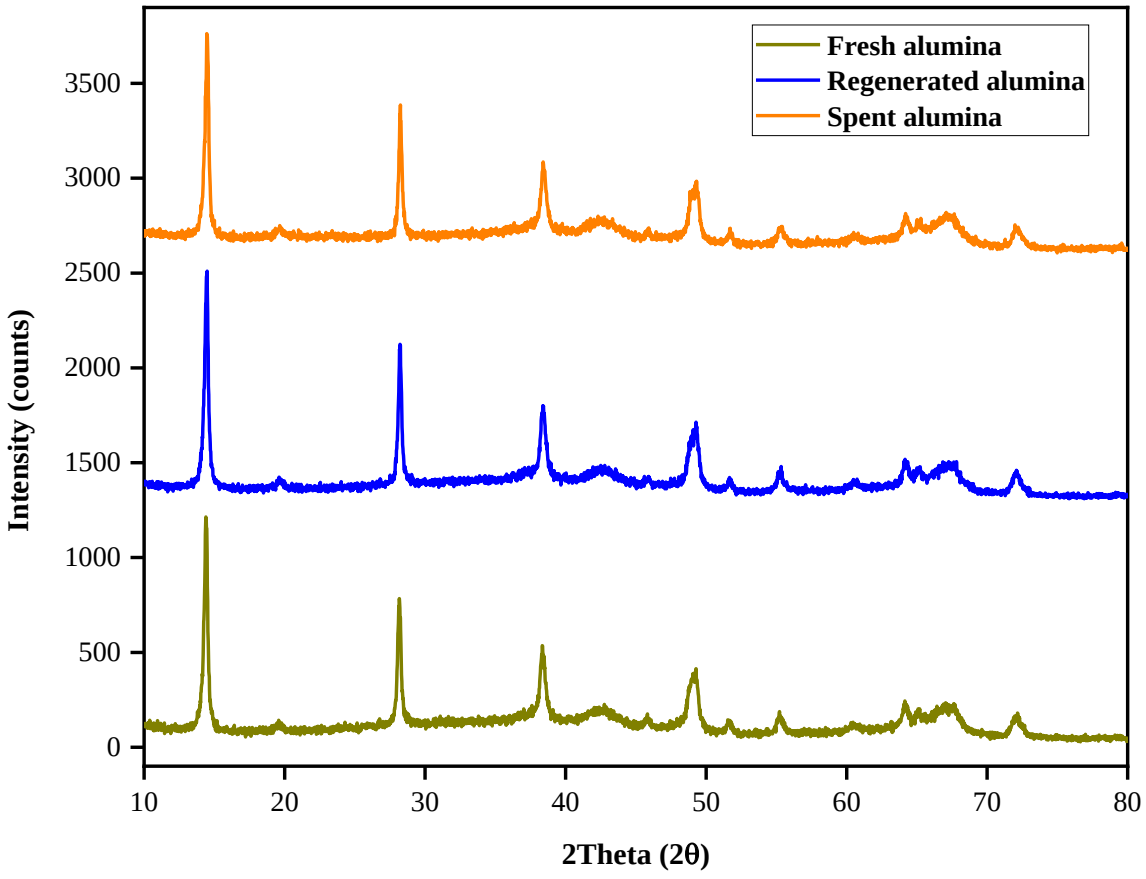


Figure 4.10: XRD patterns of spent, regenerated and fresh alumina

4.3.5 Performance test of alumina

The performance test was carried out by contacting fresh, regenerated and reused alumina with plant working solution containing THAQE concentration of 83.6 gm/l or 16.72 gm. The plant working solution treated with these solid samples was measured using GC instrument. The order of working solution components observed on the peak area of GC chromatogram from lowest to highest retention time was cyclohexane, solvesso-150, TBU, orto-terphenyl, THAQE, THAQ, EAQ and TOP respectively. From these working solution components, the only concentration of THAQE, THAQ and EAQ were responsible to determine the performance of regenerated alumina. Since the performance of regenerated alumina was tested by the epoxide conversion, the concentration of THAQE, THAQ and EAQ were determined from the total peak area of the chromatogram. The concentration of these components provided by the peak area of the computer output chromatogram was shown in Table 4.4.

Table 4.4: Component peak area and concentration of computer output chromatogram

WS treated with	Types of component	Component retention time (minute)	Component peak area (cm^2)	Component concentration (gm/l)	Standard concentration (gm/l)
Spent alumina	THAQE	49.265	307.41656	83.6	0-25
	THAQ	50.488	156.78648	40.4	100
	EAQ	51.708	84.948730	16.7	60
Fresh alumina	THAQE	49.265	263.03232	61.9	0-25
	THAQ	50.497	227.57420	58.3	100
	EAQ	51.712	104.61083	20.5	60
Regenerated alumina	THAQE	49.266	289.86542	67.8	0-25
	THAQ	50.496	198.33112	54.2	100
	EAQ	51.714	89.237720	18.7	60
Reused alumina	THAQE	49.262	287.58401	72.1	0-25
	THAQ	50.487	201.44223	51.9	100
	EAQ	51.708	84.874430	16.7	60

The percentage conversion of THAQE for the working solution treated with fresh alumina, regenerated alumina and reused alumina were shown in the bar graph of Figure 4.11. Since the specific surface area was related with the catalytic activity, the higher conversion of

THAQE was obtained at the fresh alumina surface area of 555.105 m^2/gm followed by the regenerated alumina surface area of 507.009 m^2/gm. The adsorbed organics had not completely avoided on the surface of regenerated alumina in that the epoxide conversion was found to be lower than fresh alumina. On the other hand, the epoxide conversion of reused alumina was found to be lower than regenerated and fresh alumina. Relative to fresh alumina, the percentage conversion of THAQE with regenerated alumina was reduced by 7.05% whereas the percentage conversion of THAQE with reused alumina was reduced by 12.21%. Relative to regenerated alumina, the percentage conversion of THAQE with reused alumina was reduced by 5.15%. The performance test indicated that 72.81% and 52.99% of THAQE was converted to active quinones using regenerated alumina and reused alumina respectively when compared to 100% performance of fresh alumina. As the plant working solution was dominated by the inert epoxide, the mass of THAQE could not be converted further to active quinones of THAQ and EAQ. As a result, the catalytic activity of fresh alumina, regenerated alumina and reused alumina were indicated by the minimum percentage conversion of THAQE.

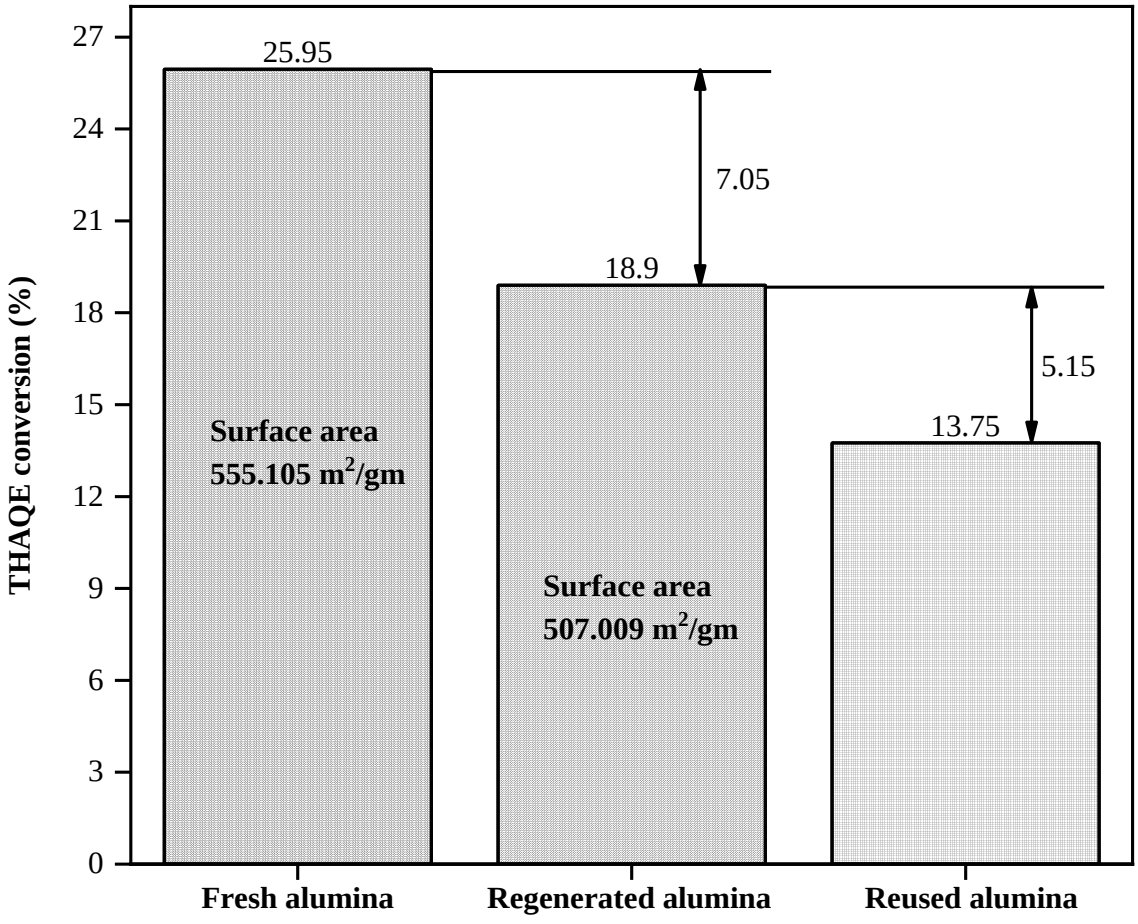


Figure 4.11: The percentage conversion of THAQE to active quinones

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 not only brought about environmental pollution but also requested high foreign currency for replacement. Therefore, spent alumina should be regenerated to minimize the waste and foreign currency so that it can reuse for working solution regeneration.

In this research, spent alumina was regenerated to recover its catalytic activity using Soxhlet solvent extraction followed by caustic treatment methods. 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. Caustic treatment conditions (concentration, temperature and contact time) that affect the regeneration of mixture solvent treated alumina were studied with OVAT method. The highest basicity of 2.19 mmol HCl/gm of regenerated alumina was obtained which indicated that the regenerated alumina had higher adsorption efficiency and catalytic activity relative to spent alumina. The AAS analysis showed that the regenerated alumina contained 0.42% Na_2O that enabled to improve adsorption efficiency and catalytic activity. The BET analysis showed that the regenerated alumina with specific surface area of 507 m^2/gm confirmed the more surface adsorption and epoxide conversion capacity.

The performance of regenerated alumina was tested using working solution of the plant containing 83.6 gm/l of THAQE at constant temperature of 70 ^oC. The GC analysis result showed the percentage conversion of 83.6 gm/l of THAQE. Conversion of THAQE using fresh, regenerated and reused alumina were 25.95%, 18.90% and 13.75% respectively. This indicated that the highest percentage conversion of THAQE was obtained from fresh alumina followed by regenerated alumina and reused alumina. Hence, fresh alumina of

100% performance implied that 72.81% and 52.99% of THAQE could be converted to active quinones using regenerated alumina and reused alumina respectively. Therefore, regenerated alumina could be used as fresh alumina for working solution regeneration or THAQE conversion for more than two times.

5.2 Recommendation

- This research was conducted to recover the catalytic activity of spent alumina using Soxhlet solvent extraction followed by caustic treatment methods. However, the organic compounds adsorbed on spent alumina were not completely removed during regeneration process. Hence, there was some difference relative to fresh alumina in terms of surface area and THAQE conversion efficiency. Therefore, other treatment methods can be used such as thermal treatment/calcination method.
- The GC-MS instrument can be used to characterize the organic compounds removed from spent alumina during Soxhlet solvent extraction and caustic treatment experiments. The useful quinones can be separated from the removed mixture so that it could be reused for working solution make up during hydrogen peroxide production.
- Best performance of regenerated alumina can be obtained by repeating the treatment of Soxhlet solvent treated alumina with fresh caustic solution of 3% w/w for more than one times.
- The effect of solvent to solid ratio on the extraction efficiency during Soxhlet solvent extraction and the effect of working solution to solid catalyst ratio on the percentage conversion of THAQE can be studied to optimize the liquid volume and the solid sample weight.
- Calcination of spent alumina at 600 ^{o}C can remove all adsorbed organics and it can be used for a variety of applications such as production of aluminum sulphate by contacting it with concentrated sulphuric acid and production of impregnated metal catalysts.
- As the experiment was conducted under laboratory, feasibility study was required before implementing this research on the existing plant.

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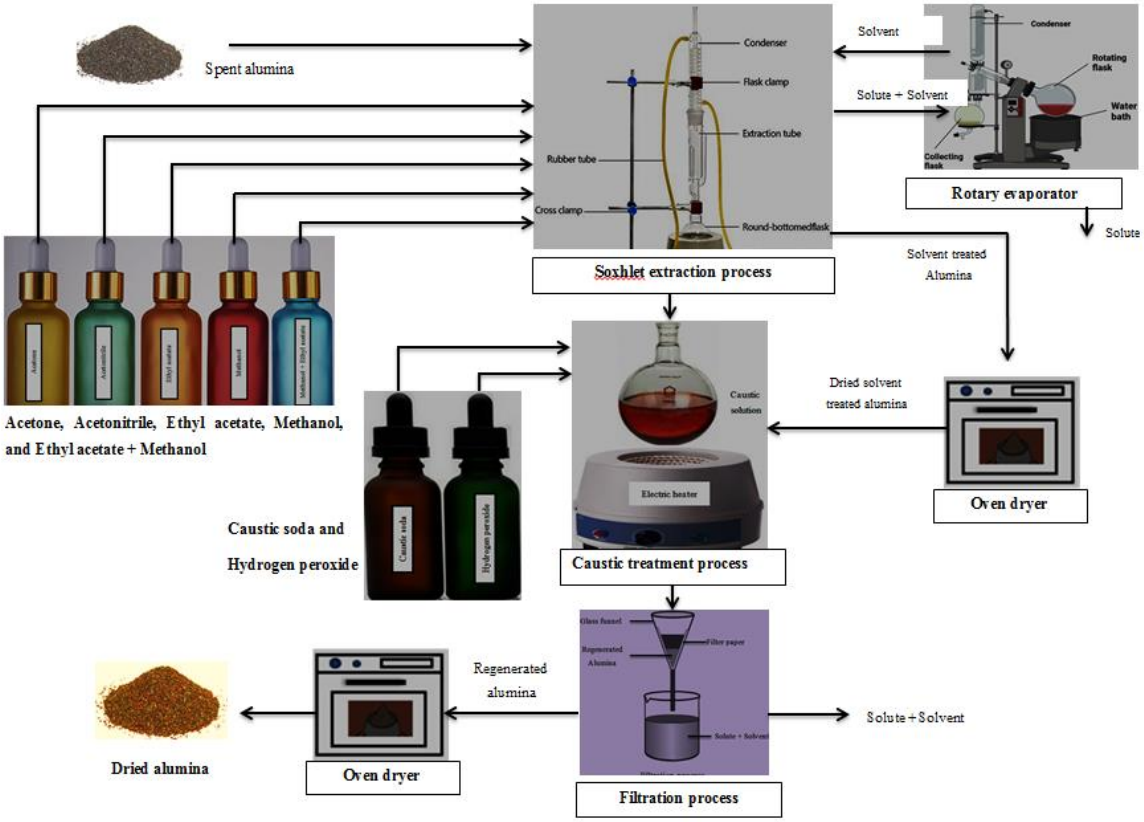
APPENDICES

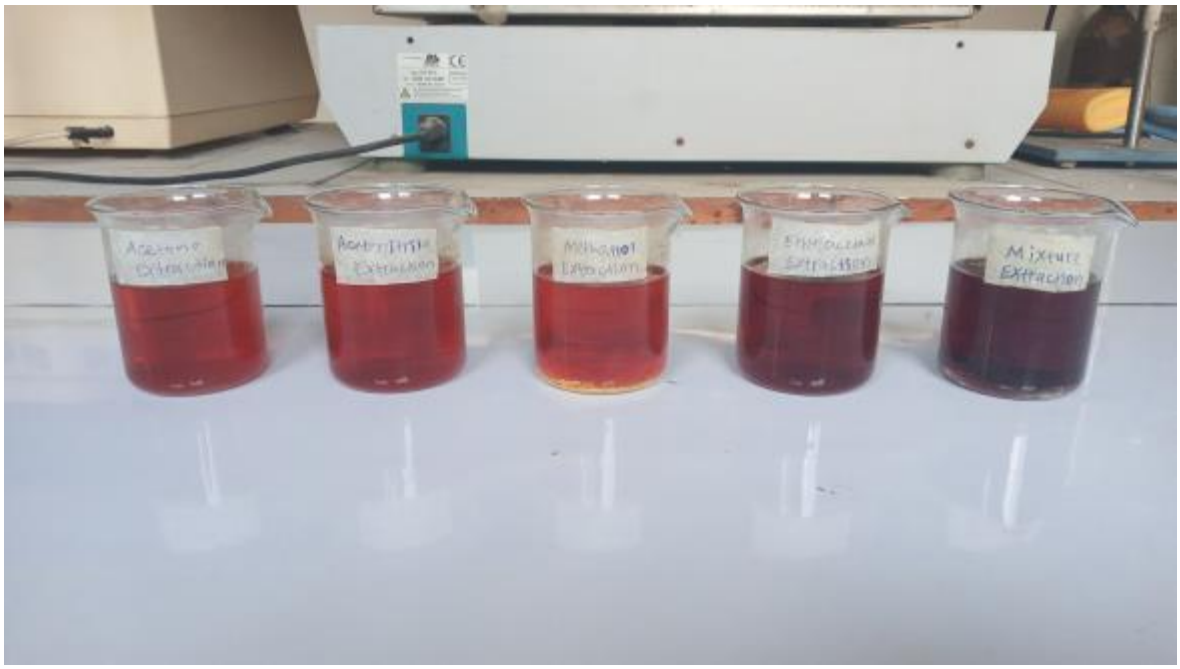
Experimental set up of regenerating spent alumina



Soxhlet solvent extraction experiment

Extracted organics color observation for Soxhlet solvent extraction

The color of organics extracted by acetone, acetonitrile, methanol, ethyl acetate and mixture of ethyl acetate and methanol from left to right respectively were shown below.



Caustic treatment experiment

Basisity determination of caustic treated alumina using titration method

1. Effect of NaOH concentration

Basicity at 0.1% w/w caustic concentration:

$$\text{Basicity} = \frac{25 * 0.1 - (5.4 \pm 0.2) * 0.1}{1} = 1.96 \pm 0.2$$

Basicity at 0.8% w/w caustic concentration:

$$\text{Basicity} = \frac{25 * 0.1 - (4.9 \pm 0.1) * 0.1}{1} = 2.01 \pm 0.1$$

Basicity at 1.5% w/w caustic concentration:

$$\text{Basicity} = \frac{25 * 0.1 - (4.4 \pm 0.1) * 0.1}{1} = 2.06 \pm 0.1$$

Basicity at 2.2% w/w caustic concentration:

$$\text{Basicity} = \frac{25 * 0.1 - (3.8 \pm 0.2) * 0.1}{1} = 2.12 \pm 0.2$$

Basicity at 3% w/w caustic concentration:

$$\text{Basicity} = \frac{25 * 0.1 - (3.1 \pm 0.1) * 0.1}{1} = 2.19 \pm 0.1$$

2. Effect of temperature

Basicity at the temperature of 25 ^{o}C:

$$\text{Basicity} = \frac{25 * 0.1 - (4.9 \pm 0.1) * 0.1}{1} = 2.01 \pm 0.1$$

Basicity at the temperature of 40 ^{o}C:

$$\text{Basicity} = \frac{25 * 0.1 - (4.3 \pm 0.2) * 0.1}{1} = 2.07 \pm 0.2$$

Basicity at the temperature of 55 ^{o}C:

$$\text{Basicity} = \frac{25 * 0.1 - (3.7 \pm 0.1) * 0.1}{1} = 2.13 \pm 0.1$$

Basicity at the temperature of 70 ^{o}C:

$$\text{Basicity} = \frac{25 * 0.1 - (3.1 \pm 0.1) * 0.1}{1} = 2.19 \pm 0.1$$

Basicity at the temperature of 90 ^{o}C:

$$\text{Basicity} = \frac{25 * 0.1 - (3.5 \pm 0.1) * 0.1}{1} = 2.15 \pm 0.1$$

3. Effect of contact time

Basicity at the time of 1 hour:

$$\text{Basicity} = \frac{25 * 0.1 - (4.5 \pm 0.1) * 0.1}{1} = 2.05 \pm 0.1$$

Basicity at the time of 1.5 hour:

$$\text{Basicity} = \frac{25 * 0.1 - (3.8 \pm 0.2) * 0.1}{1} = 2.12 \pm 0.2$$

Basicity at the time of 2.5 hour:

$$\text{Basicity} = \frac{25 * 0.1 - (3.2 \pm 0.1) * 0.1}{1} = 2.18 \pm 0.1$$

Basicity at the time of 3.5 hour:

$$\text{Basicity} = \frac{25 * 0.1 - (3.1 \pm 0.1) * 0.1}{1} = 2.19 \pm 0.1$$

Basicity at the time of 4 hour:

$$\text{Basicity} = \frac{25 * 0.1 - (3.3 \pm 0.2) * 0.1}{1} = 2.17 \pm 0.2$$

The basicity expressed in mmol HCl/gm of alumina that determined from the titration results was summarized in the following table.

NaOH concentration (%w/w)	Types of trial	HCl solution volume (ml)	Burette initial reading (ml)	Burette final reading (ml)	Delivered volume of NaOH (ml)	Basicity mmol HCl/gm of alumina
0.1	Trial-1	25	50.0	44.4	5.4 ± 0.2	1.96 ± 0.2
	Trial-2	25	44.4	39.2		
0.8	Trial-1	25	50.0	45.0	4.9 ± 0.1	2.01 ± 0.1
	Trial-2	25	45.0	40.2		
1.5	Trial-1	25	50.0	45.5	4.4 ± 0.1	2.06 ± 0.1
	Trial-2	25	45.5	41.2		
2.2	Trial-1	25	50.0	46.0	3.8 ± 0.2	2.12 ± 0.2
	Trial-2	25	46.0	42.4		
3.0	Trial-1	25	50.0	47.0	3.1 ± 0.1	2.19 ± 0.1
	Trial-2	25	47.0	43.8		

Temperature (^{o}C)	Types of trial	HCl solution volume (ml)	Burette initial reading (ml)	Burette final reading (ml)	Delivered volume of NaOH (ml)	Basicity mmol HCl/gm of alumina
25	Trial-1	25	50.0	45.0	4.9 ± 0.1	2.01 ± 0.1
	Trial-2	25	45.0	40.2		
40	Trial-1	25	50.0	45.5	4.3 ± 0.2	2.07 ± 0.2
	Trial-2	25	45.5	41.4		
55	Trial-1	25	50.0	46.2	3.7 ± 0.1	2.13 ± 0.1
	Trial-2	25	46.2	42.6		
70	Trial-1	25	50.0	46.8	3.1 ± 0.1	2.19 ± 0.1
	Trial-2	25	46.8	43.8		
90	Trial-1	25	50.0	46.4	3.5 ± 0.1	2.15 ± 0.1
	Trial-2	25	46.4	43.0		

Contact time (hour)	Types of trial	HCl solution volume (ml)	Burette initial reading (ml)	Burette final reading (ml)	Delivered volume of NaOH (ml)	Basicity mmol HCl/gm of alumina
1	Trial-1	25	50.0	45.4	4.5 ± 0.1	2.05 ± 0.1
	Trial-2	25	45.4	41.0		
1.5	Trial-1	25	50.0	46.0	3.8 ± 0.2	2.12 ± 0.2
	Trial-2	25	46.0	42.4		
2.5	Trial-1	25	50.0	46.7	3.2 ± 0.1	2.18 ± 0.1
	Trial-2	25	46.7	43.6		
3.5	Trial-1	25	50.0	46.8	3.1 ± 0.1	2.19 ± 0.1
	Trial-2	25	46.8	43.8		
4	Trial-1	25	50.0	46.5	3.3 ± 0.2	2.17 ± 0.2
	Trial-2	25	46.5	43.4		

BET analysis result, equation and plot

$$\frac{1}{\left[W\left(\frac{Po}{P}\right)\text{-}1\right]} = \frac{1}{W_m C} - \frac{C-1}{W_m C}\left(\frac{P}{Po}\right)$$

$$\text{Intercept} = \frac{1}{W_m C}, \qquad \text{Slope} = \frac{C-1}{W_m C}, \qquad W_m = \frac{1}{\text{Intercept} + \text{Slope}}$$

$$S_T = \frac{W_m N_A A}{M} \qquad\qquad S_{BET} = \frac{S_T}{m}$$

Where:

P_O is the saturation presure of an adsorbate

P is the equilibrium pressure

W is the amount of adsorbed gas

W_m is the amount of gas for the monolayer coverage

C is the BET constant

S_T is total surface area

N_A is avogadro's number (6.023×10^{23})

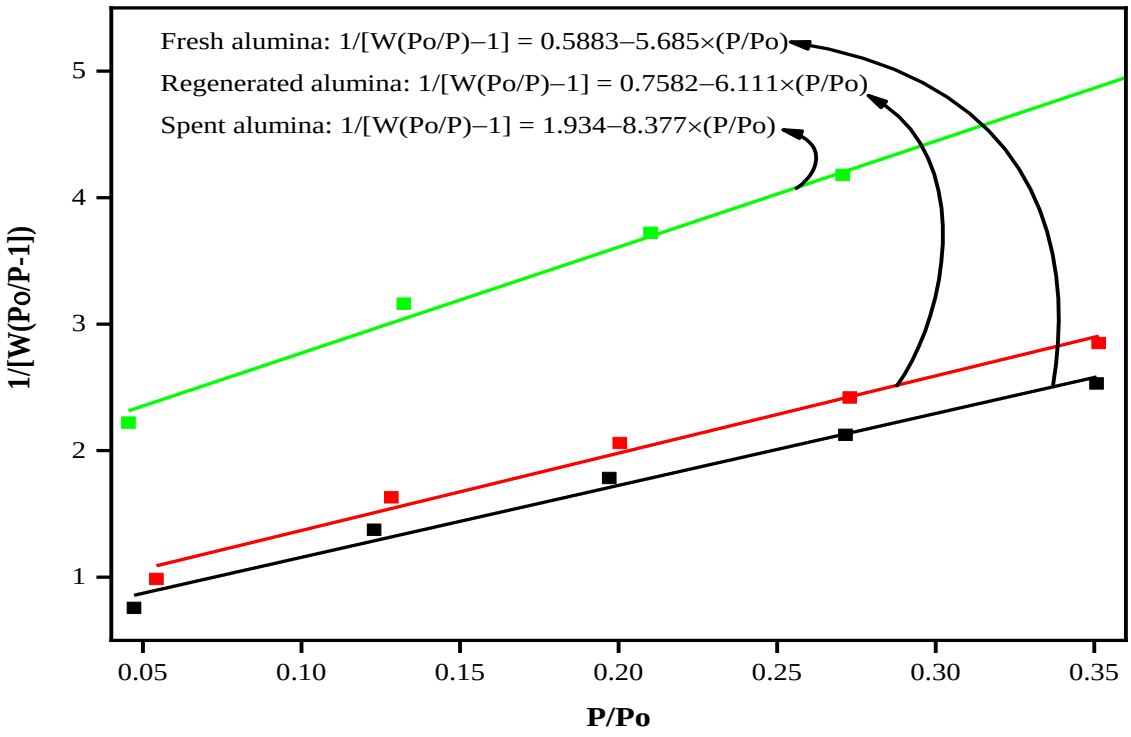
M is molecular weight of adsorbate (28.013 gm)

A is cross sectional area of nitrogen gas (16.2 $Å^2$)

S_{BET} is BET specific surface area

m is mass of a sample (0.07 gm)

Item	Fresh alumina	Regenerated alumina	Spent alumina
Slope	5.685	6.111	8.377
Intercept	0.5883	0.7582	1.934
Correlation coefficient, r	0.992995	0.993322	0.997008
BET constant, C	10.663	9.059	5.331
S_{BET}, m^2/g	555.105	507.009	337.762



Sample name	Relative pressure (P/Po)	Volume at STP (cm^3/gm)	$\frac{1}{\left[W\left(\frac{Po}{P}\right)-1\right]}$
Fresh alumina	0.047209	52.4618	0.75567
	0.122933	81.577	1.3747
	0.197058	110.1631	1.7825
	0.271567	140.3945	2.1246
	0.350785	170.8752	2.5300
Regenerated alumina	0.054242	46.5449	0.98590
	0.128341	72.2258	1.6311
	0.200386	97.3884	2.0589
	0.272921	124.1037	2.4200
	0.351458	152.1106	2.8505
Spent alumina	0.045432	17.1452	2.2211
	0.132253	38.5788	3.1609
	0.210109	57.1855	3.7217
	0.270682	71.0421	4.1800
	0.361772	91.9468	4.9326

The specific surface area, pore size and pore volume distribution of fresh, spent and regenerated alumina samples were shown in the following table.

Sample name	Specific surface area (m^2/gm)	Pore size (Å)	Pore volume (cm^3/gm)
Fresh alumina	555.105	1.838	0.1438
Spent alumina	337.762	1.838	0.0671
Regenerated alumina	507.009	1.838	0.1247

AAS analysis result for spent alumina (SP-A), regenerated alumina (REG-A) and fresh alumina (Fr-A)

	GEOLOGICAL INSTITUTE OF ETHIOPIA	Doc. Number: GLD/F5.10.2	Version No: 1
	Geochemical Laboratory Desk		Page 1of 1
Document Title:-	Complete Silicate Analysis Report	Effective date:	Nov. 2022

Customer Name:- Anmare Degu
Sample type :-Powder
Sample Preparation: -200 Mesh
Date Submitted:- 08/05/2023
Analytical Result: In percent (%) Element to be determined Major Oxides & Minor Oxides.
Analytical Method: $LiBO_2$ FUSION, HF attack, GRAVIMETERIC, COLORIMETRIC and AAS

Issue Date:-30/05/2023
Request No:- GLD/RQ/1242/23
Report No:- GLD/RN/1863/23
Number of Sample:-Three (03)

Collector's code	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_5	TiO_2	H_2O	LOI	Weight of Sample
REG-A	6.26	77.36	<0.01	0.54	0.10	0.42	0.36	<0.01	0.10	<0.01	2.75	12.22	120.00 gm
SP-A	6.12	72.16	<0.01	0.50	0.08	<0.01	0.64	<0.01	0.13	<0.01	1.74	19.67	150.00 gm
Fr-A	6.60	77.56	<0.01	0.86	0.18	<0.01	0.64	<0.01	0.06	0.13	3.83	9.49	150.00 gm

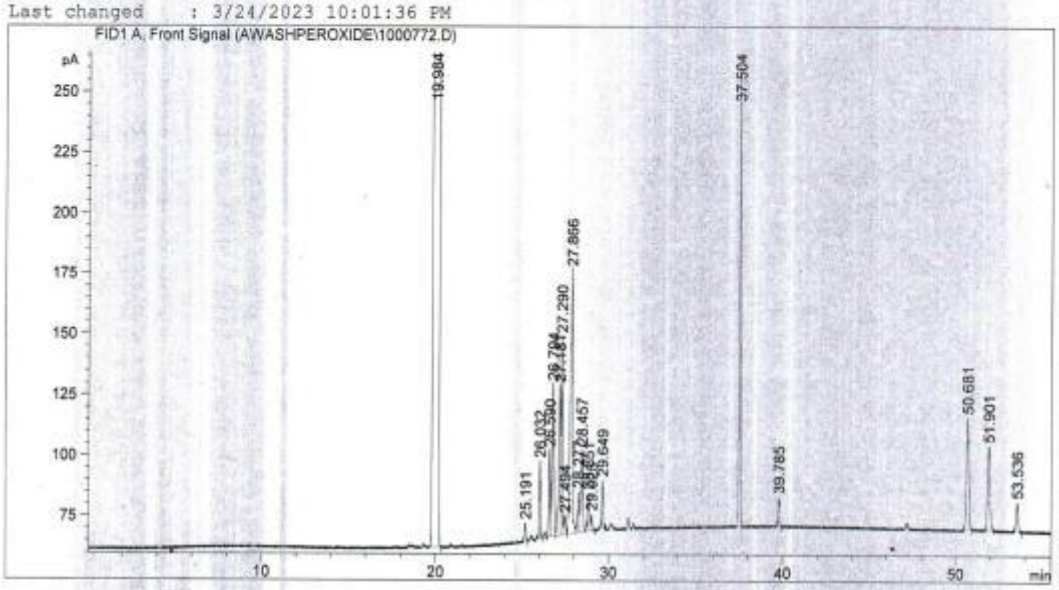
Note:- This result represent only for the sample submitted to the laboratory.

Analysts: Haimanot Bayeh, Gadisa Wakuma, Nigist Fikadu
Checked By: Lidet Endeshaw
Approved By: Yohannes Getachew
Quality Control: Negash Worku

Standard/reference working solution GC chromatogram

Data File C:\CHEM32\1\DATA\AWASHPEROXIDE\1000772.D
Sample Name: 01/02/2023 BLANTWS2

Acq. Operator :
Acq. Instrument : Instrument 1 Location : Vial 1
Injection Date : 2/2/2023 3:03:36 AM
Inj Volume : 5 µl
Acq. Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 2/2/2023 1:40:08 AM
Analysis Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 3/24/2023 10:01:36 PM



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

ata File C:\CHEM32\1\DATA\AWASHPEROXIDE\1000772.D
ample Name: 01/02/2023 BLANTWS2

Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.984	BB	0.1677	1.89590e5	1.71041e4	97.31541
2	25.191	BB	0.0882	41.87708	7.42973	0.02150
3	26.032	BB	0.0810	157.57243	31.38933	0.08088
4	26.590	BV	0.0807	182.50589	35.54096	0.09368
5	26.794	VV	0.1108	482.00150	62.50378	0.24741
6	27.181	VV	0.0957	393.92712	61.32759	0.20220
7	27.290	VV	0.0791	428.70459	81.38422	0.22005
8	27.494	VV	0.0911	43.38463	7.19966	0.02227
9	27.866	VB	0.1266	998.01935	108.45737	0.51228
10	28.277	BV	0.0944	105.90633	16.42526	0.05436
11	28.457	VB	0.1110	262.96497	34.00670	0.13498
12	28.851	BV	0.1060	103.14570	15.26824	0.05294
13	29.025	VB	0.0795	31.64659	6.28772	0.01624
14	29.649	BB	0.0884	110.56402	19.54764	0.05675
15	37.504	BB	0.0787	935.91217	188.62321	0.48040
16	39.785	BB	0.0968	71.59923	11.72571	0.03675
17	50.681	BB	0.1507	438.73141	46.22796	0.22520
18	51.901	BB	0.1561	344.19928	34.58823	0.17668
19	53.536	BB	0.1348	97.46619	11.79898	0.05003
Totals :				1.94820e5	1.78839e4	

*** End of Report ***

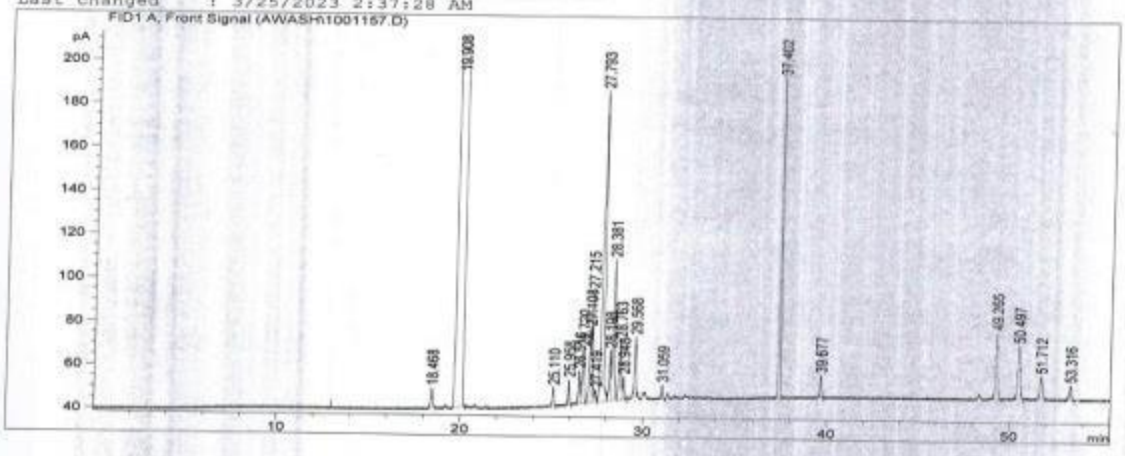
nstrument 1 3/25/2023 5:02:02 AM Page 2 of 2

Working solution treated with fresh alumina GC chromatogram

Data File C:\CHEM32\1\DATA\AWASH\1001157.D
Sample Name: 24032023 WS with F.A

Acq. Operator :
Acq. Instrument : Instrument 1 Location : Vial 3
Injection Date : 3/25/2023 1:41:59 AM Inj Volume : 5 µl

Acq. Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 3/25/2023 1:24:26 AM
Analysis Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 3/25/2023 2:37:28 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

trument 1 3/25/2023 2:37:28 AM Page 1 of 2

Data File C:\CHEM32\1\DATA\AWASH\1001157.D
Sample Name: 24032023 WS with F.A

Signal 1: FID1 A, Front Signal

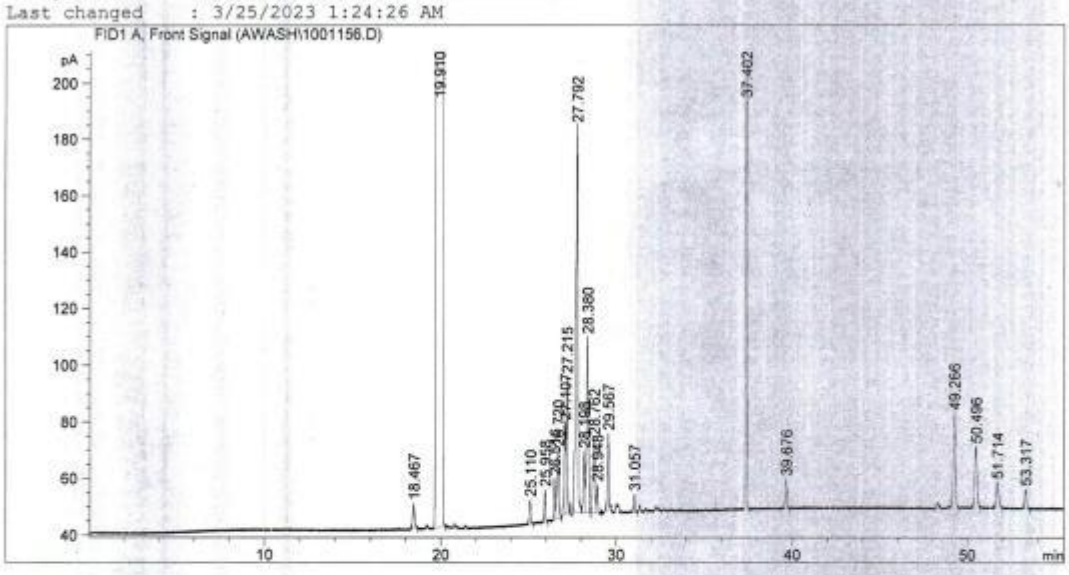
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.468	BB	0.1175	69.36585	8.96348	0.03209
2	19.908	BB	0.1836	2.11427e5	1.81856e4	97.80726
3	25.110	BB	0.0875	46.13202	8.26334	0.02134
4	25.958	BB	0.0829	58.36552	11.24804	0.02700
5	26.516	BV	0.0812	77.01875	14.86603	0.03563
6	26.720	VB	0.1030	180.27205	25.08749	0.08339
7	27.108	BV	0.0905	203.45340	34.06289	0.09412
8	27.215	VB	0.0805	275.74188	51.11884	0.12756
9	27.419	BV	0.0862	31.76353	5.53221	0.01469
10	27.793	VB	0.1189	1215.88611	142.26425	0.56247
11	28.198	BV	0.0937	146.62128	22.97204	0.06783
12	28.381	VB	0.1012	451.93912	64.32133	0.20907
13	28.763	BV	0.1413	240.33537	27.24860	0.11118
14	28.948	VB	0.0825	56.25574	10.37579	0.02602
15	29.568	BB	0.0875	153.35521	27.48304	0.07094
16	31.059	BB	0.0872	33.95256	6.11671	0.01571
17	37.402	BB	0.0785	790.56445	159.85309	0.36572
18	39.677	BB	0.0956	61.02539	9.94162	0.02823
19	49.265	BB	0.1355	263.03232	30.10218	0.12168
20	50.497	BB	0.1431	227.57420	24.23790	0.10528
21	51.712	BB	0.1604	104.61083	10.27528	0.04839
22	53.316	BB	0.1241	52.72699	6.56458	0.02439
Totals :				2.16167e5	1.88865e4	

*** End of Report ***

Working solution treated with regenerated alumina GC chromatogram

ata File C:\CHEM32\1\DATA\AWASH\1001156.D
ample Name: 24032023 WS with R.A

Acq. Operator :
Acq. Instrument : Instrument 1 Location : Vial 2
Injection Date : 3/25/2023 12:28:57 AM
Inj Volume : 5 µl
Acq. Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 3/25/2023 12:12:29 AM
Analysis Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 3/25/2023 1:24:26 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

nstrument 1 3/25/2023 1:24:26 AM Page 1 of 2

Data File C:\CHEM32\1\DATA\AWASH\1001156.D
Sample Name: 24032023 WS with R.A

Signal 1: FID1 A, Front Signal

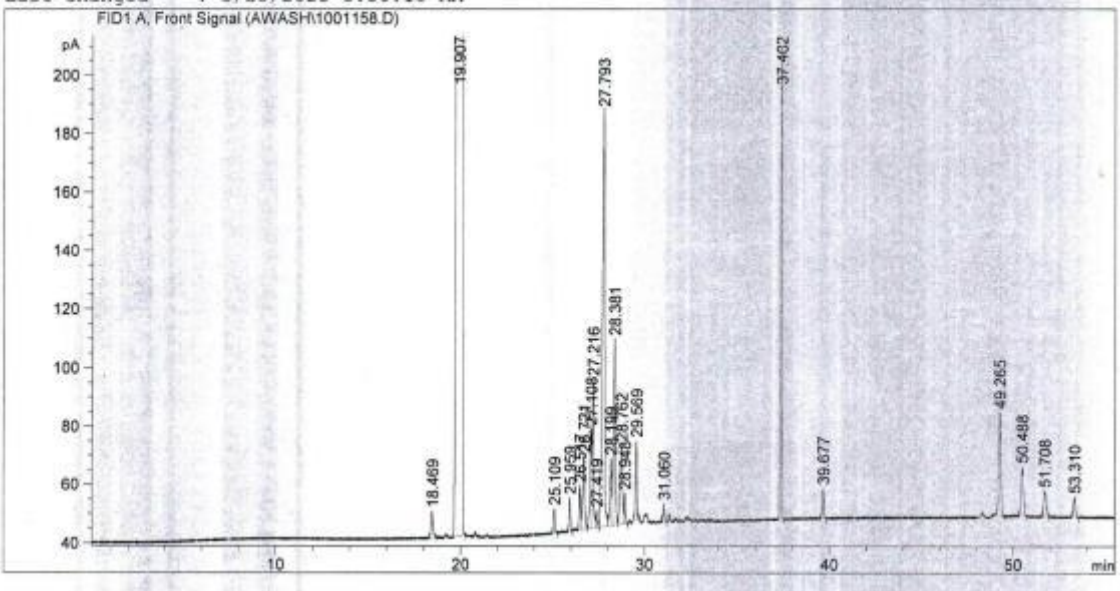
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.467	BB	0.1215	68.85586	8.82131	0.03236
2	19.910	BB	0.1915	2.08321e5	1.79337e4	97.90211
3	25.110	BB	0.0886	46.38376	8.17825	0.02180
4	25.958	BB	0.0826	56.46471	10.94698	0.02654
5	26.516	BV	0.0794	73.96563	14.32973	0.03476
6	26.720	VB	0.1003	166.41751	23.93221	0.07821
7	27.107	BV	0.0894	182.23480	31.72559	0.08564
8	27.215	VB	0.0785	242.56689	47.72482	0.11400
9	27.792	BB	0.1167	1139.87622	136.35049	0.53569
10	28.198	BV	0.0892	127.68594	21.27946	0.06001
11	28.380	VV	0.1029	424.81897	61.59064	0.19965
12	28.762	VV	0.1394	224.42067	25.92316	0.10547
13	28.948	VB	0.0786	48.79581	9.58263	0.02293
14	29.567	BB	0.0940	158.78816	27.07958	0.07462
15	31.057	BB	0.0884	33.90204	5.98834	0.01593
16	37.402	BB	0.0803	778.57733	156.75365	0.36590
17	39.676	BB	0.0942	61.06625	9.92045	0.02870
18	49.266	BB	0.1376	289.86542	33.02328	0.13622
19	50.496	BB	0.1452	198.33112	21.03150	0.09321
20	51.714	BB	0.1615	89.23772	8.68131	0.04194
21	53.317	BB	0.1283	51.74567	6.48240	0.02432
Totals :				2.12785e5	1.86031e4	

*** End of Report ***

Working solution treated with spent alumina GC chromatogram

Data File C:\CHEM32\1\DATA\AWASH\1001158.D
Sample Name: 24032023 WS with S.A

Acq. Operator :
Acq. Instrument : Instrument 1 Location : Vial 4
Injection Date : 3/25/2023 2:54:47 AM
Inj Volume : 5 µl
Acq. Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 3/25/2023 2:37:28 AM
Analysis Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 3/25/2023 3:50:18 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

Instrument 1 3/25/2023 3:50:18 AM Page 1 of 2

Data File C:\CHEM32\1\DATA\AWASH\1001158.D
Sample Name: 24032023 WS with S.A

Signal 1: FID1 A, Front Signal

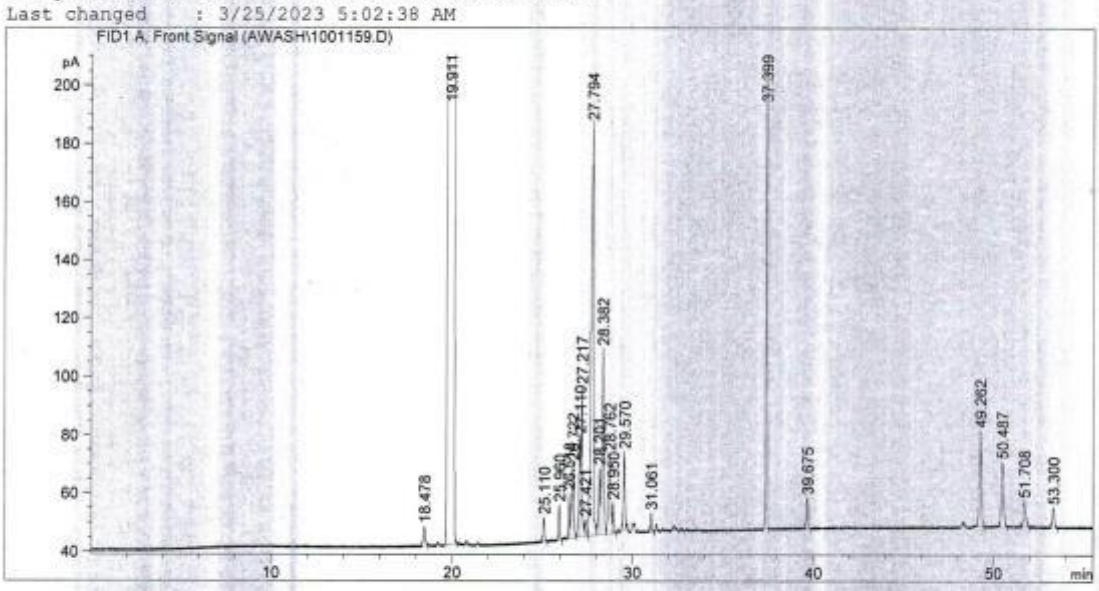
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.469	BB	0.1218	68.99346	8.80574	0.03279
2	19.907	BB	0.1773	2.05710e5	1.78956e4	97.78051
3	25.109	BB	0.0886	45.41380	8.00930	0.02159
4	25.959	BB	0.0809	57.61224	11.18347	0.02738
5	26.517	BV	0.0811	76.66772	14.82401	0.03644
6	26.721	VB	0.1031	179.29102	24.93729	0.08522
7	27.108	BV	0.0903	201.93758	33.88964	0.09599
8	27.216	VB	0.0805	273.22189	50.68674	0.12987
9	27.419	BV	0.0848	31.66320	5.49432	0.01505
10	27.793	VB	0.1166	1205.29724	142.10861	0.57292
11	28.199	BV	0.0937	145.90659	22.84286	0.06935
12	28.381	VB	0.1049	448.66922	63.46905	0.21327
13	28.762	BV	0.1416	239.01190	27.01372	0.11361
14	28.948	VB	0.0845	56.04486	10.26525	0.02664
15	29.569	BB	0.0879	151.90285	27.05726	0.07220
16	31.060	BB	0.0881	34.11826	6.06173	0.01622
17	37.402	BB	0.0784	791.11145	160.34177	0.37604
18	39.677	BB	0.0963	60.63947	10.01048	0.02882
19	49.265	BB	0.1364	307.41656	35.42648	0.14612
20	50.488	BB	0.1474	156.78648	16.77718	0.07453
21	51.708	BB	0.1476	84.94873	8.57237	0.04038
22	53.310	BB	0.1279	52.69800	6.63040	0.02505
Totals :				2.10379e5	1.85900e4	

*** End of Report ***

Working solution treated with reused alumina GC chromatogram

Data File C:\CHEM32\1\DATA\AWASH\1001159.D
Sample Name: 24032023 WS with Reu.A

Acq. Operator :
Acq. Instrument : Instrument 1 Location : Vial 5
Injection Date : 3/25/2023 4:07:07 AM
Inj Volume : 5 µl
Acq. Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 3/25/2023 3:50:18 AM
Analysis Method : C:\CHEM32\1\METHODS\AWASHPERO.M
Last changed : 3/25/2023 5:02:38 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

Instrument 1 3/25/2023 5:02:39 AM Page 1 of 2

ata File C:\CHEM32\1\DATA\AWASH\1001159.D
ample Name: 24032023 WS with Reu.A

Signal 1: FID1 A, Front Signal

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	18.478	BB	0.1236	50.93149	6.26967	0.02468
2	19.911	BB	0.1830	2.01682e5	1.78471e4	97.73577
3	25.110	BB	0.0881	44.90403	7.96896	0.02176
4	25.960	BB	0.0827	60.26450	11.65814	0.02920
5	26.518	BV	0.0826	77.94688	15.09773	0.03777
6	26.722	VB	0.1031	181.45618	25.22951	0.08793
7	27.110	BV	0.0883	202.53122	34.21718	0.09815
8	27.217	VV	0.0787	273.72217	50.96622	0.13265
9	27.421	VV	0.0901	32.54598	5.35399	0.01577
10	27.794	VB	0.1188	1204.68860	141.08034	0.58380
11	28.201	BV	0.0937	144.40152	22.60900	0.06998
12	28.382	VB	0.1046	445.36969	63.18481	0.21583
13	28.762	BV	0.1382	238.83827	27.06310	0.11574
14	28.950	VB	0.0830	55.30751	10.10920	0.02680
15	29.570	BB	0.0886	150.67862	26.57022	0.07302
16	31.061	BB	0.0889	34.04354	5.97021	0.01650
17	37.399	BB	0.0772	784.80872	157.93567	0.38032
18	39.675	BB	0.0966	62.08733	10.20653	0.03009
19	49.262	BB	0.1377	287.58401	32.73003	0.13936
20	50.487	BB	0.1460	201.44223	21.84053	0.09762
21	51.708	BB	0.1518	84.87443	8.49541	0.04113
22	53.300	BB	0.1320	53.90535	6.49734	0.02612
Totals :				2.06354e5	1.85382e4	

*** End of Report ***

Working solution GC result calibration sheet

A.	Standard W.S (Sol. 75%, TBU 21%, TOP 4%, EAQ 60 gpl, H4EAQ 100 gpl)					Date	27/03/2023	Time	12:34pm
S.No.	Component	Peak Area	Injected sample		% without O.T.	O.T. factor	A x B	Result	
			conc. ug/ml	%	A	B		gpl	Sol. Ratio, %
1	Solvesso 150	3342.2202	1400.4	63.90321409	64.79	0.971505	62.94	0.00	75.0
2	TBU	935.91217	392.1	17.89463057	18.14	0.972515	17.64	0.00	21.0
3	TOP	97.46619	40.8	1.863552499	1.89	1.779991	3.36	0.00	4.0
4	OT (Standard)	71.59923	30	1.37	0.00	0.000	0.00	0.00	0.0
5	THAQE	0.000	0.000	0.000	0.000	0.000	0.00	0.00	0.0
6	THAQ	438.73141	183.8	8.39	8.50	1.175151	9.99	100.0	0.0
7	EAQ	344.19928	144.2	6.58	6.67	0.898040	5.99	60.0	0.0
8	Total		2191.4	100	100		1.00	160.0	100

B.	Working solution treated with spent alumina					Date	27/03/2023	Time	12:34pm
S.No.	Component	Peak Area	Injected sample		% without O.T.	O.T. factor	A x B	Result	
			conc. ug/ml	%	A	B		gpl	Sol. Ratio, %
1	Solvesso 150	3146.75837	1556.8	68.40245139	69.32	0.971505	67.34	0.00	78.0
2	TBU	791.11145	391.4	17.19673268	17.43	0.972515	16.95	0.00	19.5
3	TOP	52.698	26.1	1.14551928	1.16	1.779991	2.07	0.00	2.5
3	OT (Standard)	60.63947	30.0	1.32	0.00	0.000	0.00	0.00	0.0
4	THAQE	307.416560	152.1	6.68	6.77	1.240	8.40	83.6	0.0
5	THAQ	156.78648	77.6	3.41	3.45	1.175151	4.06	40.4	0.0
6	EAQ	84.94873	42.0	1.85	1.87	0.898040	1.68	16.7	0.0
8	Total		2275.9	100	100		1.00	140.7	100

C.	Working solution treated with regenerated alumina					Date	27/03/2023	Time	12:34pm
S.No.	Component	Peak Area	Injected sample		% without O.T.	O.T. factor	A x B	Result	
			conc. ug/ml	%	A	B		gpl	Sol. Ratio, %
1	Solvesso 150	2926.32111	1437.6	66.58076953	67.52	0.971505	65.59	0.00	78.0
2	TBU	778.57733	382.5	17.71448717	17.96	0.972515	17.47	0.00	19.5
3	TOP	51.74567	25.4	1.177337141	1.19	1.779991	2.13	0.00	2.5
3	OT (Standard)	61.06625	30.0	1.39	0.00	0.000	0.00	0.00	0.0
4	THAQE	289.865420	142.4	6.60	6.69	1.005	6.72	67.8	0.0
5	THAQ	198.33112	97.4	4.51	4.58	1.175151	5.38	54.2	0.0
6	EAQ	89.23772	43.8	2.03	2.06	0.898040	1.85	18.7	0.0
8	Total		2159.2	100	100		0.99	140.7	100

D.	Working solution treated with reused alumina					Date	27/03/2023	Time	12:34pm
S.No.	Component	Peak Area	Injected sample		% without O.T.	O.T. factor	A x B	Result	
			conc. ug/ml	%	A	B		gpl	Sol. Ratio, %
1	Solvesso 150	3146.69871	1520.5	68.08971695	69.02	0.971505	67.05	0.00	78.0
2	TBU	784.80872	379.2	16.98205279	17.21	0.972515	16.74	0.00	19.5
3	TOP	53.90535	26.0	1.166428807	1.18	1.779991	2.10	0.00	2.5
3	OT (Standard)	62.08733	30.0	1.34	0.00	0.000	0.00	0.00	0.0
4	THAQE	287.584010	139.0	6.22	6.31	1.142	7.20	72.1	0.0
5	THAQ	201.44223	97.3	4.36	4.42	1.175151	5.19	51.9	0.0
6	EAQ	84.87443	41.0	1.84	1.86	0.898040	1.67	16.7	0.0
8	Total		2233.0	100	100		1.00	140.7	100

E.	Working solution treated with fresh alumina					Date	27/03/2023	Time	12:34pm
S.No.	Component	Peak Area	Injected sample		% without O.T.	O.T. factor	A x B	Result	
			conc. ug/ml	%	A	B		gpl	Sol. Ratio, %
1	Solvesso 150	3171.09254	1558.9	67.894369	68.79	0.971505	66.83	0.00	78.0
2	TBU	790.56445	388.6	16.92630341	17.15	0.972515	16.68	0.00	19.5
3	TOP	52.72699	25.9	1.128906101	1.14	1.779991	2.04	0.00	2.5
3	OT (Standard)	61.02539	30.0	1.31	0.00	0.000	0.00	0.00	0.0
4	THAQE	263.032320	129.3	5.63	5.71	1.080	6.16	61.9	0.0
5	THAQ	227.5742	111.9	4.87	4.94	1.175151	5.80	58.3	0.0
6	EAQ	104.61083	51.4	2.24	2.27	0.898040	2.04	20.5	0.0
8	Total		2296.1	100	100		1.00	140.7	100

Based on the given concentration of chromatogram, the mass of THAQE, THAQ and EAQ were determined from 200 ml of working solution that was used in the performance test. Therefore, the percentage conversion of THAQE per 6 gm of fresh, regenerated and reused alumina was set forth in the following table.

Working solution treated with	Initial THAQE (gpl)	Final THAQE (gpl)	Initial THAQE (gm)	Final THAQE (gm)	THAQE conversion (%)
Fresh alumina	83.6	61.90	16.72	12.38	25.95
Regenerated alumina	83.6	67.80	16.72	13.56	18.90
Reused alumina	83.6	72.10	16.72	14.42	13.75

Deactivated alumina disposal to the environment from Hydrogen peroxide plant