

ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

DEPARTMENT OF CHEMICAL ENGINEERING



**Deinking of Black Toner Ink from Laser Printed Paper by using
Anionic Surfactant**

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**Deinking of Black Toner Ink from Laser Printed Paper by using Anionic
Surfactant**

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A Thesis Submitted to

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Presented for partial fulfillment of the Requirements for the Degree of Masters of
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SCHOOL OF CHEMICAL AND BIO ENGINEERING

This is to certify that the thesis prepared by Mehari Abraha, titled Deinking of black toner ink from laser printed paper by using Anionic Surfactant and submitted in partial fulfillment of the requirements for the degree of Masters of Science in Chemical and Bio Engineering (Environmental Engineering Stream) complies with the regulations of the University and meet the accepted standards with respect to originality and quality.

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Declaration

I declare that the thesis for the M.Sc. degree at the University of Addis Ababa, hereby submitted by me, is my original work and has not previously been submitted for a degree at this or any other university, and that all reference materials contained therein have been duly acknowledged.

Mehari Abraha (Candidate)

Date

This is to certify that the above declaration made by the candidate is correct to the best of my knowledge

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Acronyms

ABS	Alkyl benzene sulfonates
AS	Alkyl sulfates
AE	Alcohol ethoxylated
ANOVA	Analysis of variance
APE	Alkyl phenol ethoxylated
APG	Alkyl polyglycoside
B.P	Boiling point
CCD	Central composite design
CI	Cubic inch
CMC	Critical micelle concentration
COD	Chemical oxygen demand
CSF	Canadian standard freeness
DIP	Deinked pulp
DOE	Department of Energy

EA	Ethoxylated amine
EAD	Ethoxylated amide
ERIC	Effective Residual Ink Concentration
ERIC _{DP}	Effective residual ink concentration for deinked pulp
ERIC _{UNP}	Effective residual ink concentration for unprinted
ERIC _{UP}	Effective residual ink concentration for undeinked
FWA	Fluorescent whitening agents
HLB	Hydrophile-lipophile balance
IAF	Induced Air Flotation
IE	Ink removal efficiency
ME	Methanol
MEE	Methyl ester ethoxylated
ODF	Oven dried fiber
OMG	Old magazine
ONP	Old newsprint
PAO	Polyalkylene oxide

PLC	Private limited company
Quats	Quaternary ammonium compounds
RSM	Response surface method
TAPPI	Technical Association of the Pulp and Paper Industry
UP	Undeinked pulps
UV	Ultraviolet

Abstract

The purpose of this research was to synthesize one type of natural anionic surfactant (fatty acid soap) from renewable material (natural oil) and use of this surfactant for ink removal from waste printed paper via flotation deinking in paper recycling process. The work included the preparation of the castor seed raw material, extraction of castor oil, preparation of fatty acid soap surfactant and deinking flotation of waste printed paper. Foamability and foam stability, critical micelle concentration and hydrophilic lipophilic balance (HLB) of the surfactant were determined to evaluate its fundamental surface active properties for the purpose of deinking flotation. HLB value was determined by calculating the ration of hydrocarbon chain (composed of carbons and hydrogens and the carboxylic acid group on one end which is ionic bonded to a metal ion of the surfactant. The hydrophilic-lipophilic balance (HLB) of the fatty acid soap of 19.48, average foamability height of 49cm and critical micelle concentration (CMC) of 0.0065M was obtained. Lab scale flotation deinking process was done and the basic flotation parameters like flotation time, fatty acid soap dosage and pH were optimized for evaluating deinking efficiency. The flotation deinking efficiency was probed by measuring the residual ink concentration of the hand sheet via Perkin Elmer spectroscopy before and after deinking flotation. Differences in flotation efficiency could be explained based on flotation operation parameters, foaming and surface active characteristics of the surfactant. The experimental design selected for this study was the Central Composite Design (CCD).The individual and interaction effects between the basic parameters were studied by using design Expert Software 6.0.8. For the deinking flotation, the maximum ink removal efficiency was determined to be 78.0219 % at the flotation time of 90min, fatty acid soap dosage of 1.5% and pH of 9. The minimum ink removal efficiency was also found to be 49.3715% at flotation time of 150min, fatty acid soap dosage of 3% and pH of 3. Increasing flotation time from 30min up to 90 min and decreasing fatty acid dosage from 3% to 1.5% and increasing of pH from 3 up to 9 were found to have increased the ink removal efficiency.

Key words: Anionic Surfactant, Waste Paper, Flotation Deinking, Hand Sheet, Effective Residual Ink Concentration

1. Introduction

Paper is basically a sheet of fibers with a number of added chemicals that affect the properties and quality of the sheet. The paper recycling process is a way to wash, remove, and bleach unwanted particles from collected printed paper so that it can be sold as an alternative to virgin paper. The use of recycled wastepaper can have several benefits with respect to environmental, operating costs and energy consumptions compared to the various papers that produced directly from pulp. It has been estimated that for every ton of paper, which is made from 100% recycled wastepaper, 24 trees is saved. One ton of pulp made from deinked and bleached wastepaper requires 60% less energy than to manufacture a ton of bleached virgin Kraft pulp (Thompson, 1992).

As the consumptions of paper increased from time to time, the need for a cheap resources grows radically, and the recycling of waste paper increased. The first step for recycling waste paper is the removal of inks from the printed paper because it affects the quality and brightness of paper. Deinking flotation is one of the techniques used for the removal of ink from printed waste paper. This is a process to selectively separate the hydrophobic ink particles from the hydrophilic fiber particles. Paper recycling is becoming active part of the paper industry because it has a dual purpose of developing environmental concerns and economic reasons.

In modern paper recycling plants, the process of removing unwanted particles from the pulp can take as much as three times the amount of steps that it does in the mineral processing industry due to the fact that a higher quality product is needed to compete with the virgin paper. The quality of the paper would have affected at different steps of recycling process and these steps change the quality of the paper. This problem is minimizing by controlling the operation parameters Such as pH, flotation time, amount of chemicals and surfactants in pulping and flotation process, types and properties of ink, property of paper and pulping temperature etc. (Drelich, *et al*, 2004). Many current research activities around the world concentrate on more efficient flotation machines and cells, and improvements in the design of solution chemistry that promotes agglomeration of ink particles and/or reinforces changes in the shape of ink particles (Doshi, *et al.*, 1998).

A mixture of old newsprint (ONP) and old magazine (OMG) is the primary furnish used in most recycling mills. Usual ONP/OMG deinking chemistry uses sodium hydroxide in combination with a variety of other chemicals including sodium silicate, hydrogen peroxide and surfactants. This high pH and chemical-intensive process causes several major problems to the process and recycled paper quality, including a high degree of fragmentation of large sticky contaminants, darkening of pulp fiber, increasing COD in process waters and the need for substantial amounts of acid for neutralization. These adverse effects have hindered the further development of alkaline deinking processes (Biermann, 1996).

Deinking old newsprint under neutral or weakly acidic conditions has shown potential to improve the negative impact of alkaline deinking process. The two main colorants found in printing inks are pigments and dyes. Flotation can remove effectively an ink that contains pigment as the colorant, because pigments, such as carbon black, are insoluble powders that are trapped among pulp fibers and can be removed by the chemicals, surfactants and mechanical actions employed by the flotation process (Hache, *et al*, 1992). One of the earlier broad reason of the problems and hopes for the waste paper industry is found in the supplement 'Waste Paper Recovery' of Municipal Engineering (Borchardt, 1993).

The waste paper could meet price competition and quality requirements of the consumers, there was an essential for research and development into new methods of collection, handling and cleaning the waste papers (Tatkin, 1982).

Deinked pulp (DIP - waste paper from which printing ink has been removed) is an important fibrous raw material in the production of printing papers. To produce bright deinked pulp, manufacturers use printed graphic papers, mainly white grades which have to go through the deinking process to remove printing ink. Printing inks cannot be entirely removed without the application of specific bleaching/deinking processes, which is why this pulp grade has a slightly grayish shade. The grayness of deinked pulps can be reduced by bleaching, but their fluorescence poses a serious problem. The fluorescence is developed by fluorescent whitening agents (FWA) added to white publication and office papers to raise their whiteness.

Recent recycling methods cannot remove fluorescent whitening agents entirely from the pulp, which is why all deinked pulp based papers show fluorescence. Even gray sanitary papers of the poorest quality demonstrate fluorescence in UV light. The presence of fluorescent whitening agents in deinked pulp poses a serious problem connected with metamerism, especially in the case of dyed papers (Doshi, 1995). The fluorescence level of recycled pulps is variable and depends on the grade of paper they are made of. For this reason it is difficult to maintain identical colour (both white and chromatic) in large manufacturing batches (*Earl, 2000*).

In deinking of wastepaper there are several operations including pulping, screening, centrifugal cleaning, washing, flotation and bleaching. In the flotation process, air is bubbled through the low consistency pulp stock. Hydrophobic particles, such as ink, attach to the bubbles and are lifted away from the stock. A foaming agent is added to create foam. The foam is scraped away as a reject stream, producing cleaner fibers in an accept stream. The process in industrial practice is continuous, having a constant feed, accepts and rejects flow rate (Richard, 2012). Flotation deinking is a common practice for removing ink from wastepaper, and is becoming a key process in many recycling paper mill. The application of flotation was successfully introduced to the paper recycling industry in the 1980s, and its applications in wax removal, sticky control, and fiber fractionation have attracted great research interest and the chemistry of the flotation process has been reviewed (Borchardt, *et al*, 1997).

The earliest work on utilization of froth flotation for de-inking of wastepaper dates back to the 1930s. The first flotation de-inking patent was filed by Hines in 1933. However, it was not until 1952 that the first commercial flotation de-inking system was installed at a paper mill in the USA, and the first European installation was at a tissue mill in Greece in 1959. Up to 1970 (Jiang, *et al*, 2000), the growth of flotation de-inking technology was relatively slow, however, in the past 20 years, the market has grown extremely rapidly. The worldwide flotation capacity for de-inking of waste papers has increased from 0.2 million tons in 1965 to about 25 million tons in 1995 (Jiang, *et al*, 2000).

1.1. Statement of the Problem

It is well known that recycled fiber is an important source of raw material for the paper and paper board industry. Besides, recycling materials have low source of fiber cost for paper and board manufacturing, it preserves forest resources, reduce environmental pollution and conserve water and energy consumption (Bagpai, *et al*, 1998). Both printers and papermakers are trying to be more “green”, and thus the recycling of post-consumer waste is becoming an essential In recycling all kinds of mixed waste to recycling facility. Therefore, recycling facilities have to be flexible and be able to remove macro and micro contaminants.

In most technologies the surfactants which have been used for flotation deinking are petrochemical but those are hazardous substances to environment and difficult to treat after they discharge in to the environment. Natural surfactants are obtained from sugar based, protein based materials. They are environmental friendly and they are easy to treat when they discharge in to the environment since they are biodegradable materials.

In Ethiopia, both the locally produced and the imported paper met the demand of the society. However, due to the existence of only one paper and pulp factory in the country, i.e. Ethiopian Pulp and Paper Factory located at Wonji, the majority of the supply is from import. During 1998/99- 2004/05 E.C, the best supply offered by the domestic manufacturer was 12,685 tons while the yearly average consumption during the same period was 146,296 tons (Temesgen, 2014). To avoid this shortage of paper in the country, it is necessary to recycle the waste paper by removing its ink and other dirties from the fiber.

Other benefits of wastepaper recycling are associated with reduced capital and operating costs, reduced cost of purchase of raw material, reduced cost of energy and chemical used and reduced extension of municipal landfill life. In the near future, it is expected that a significant amount of wastepaper recovered from municipal solid wastes will be used for this purpose, and the printed wastepaper will increase in value as a raw material for better grade of paper, if the deinking technology is sufficiently developed.

1.2. Objective

1.2.1. General objectives

The general objective of this research was deinking of laser printed paper that is printed by toner black powder ink by using anionic surfactant.

1.2.2. Specific objectives

The specific objectives were:

- Preparation of natural anionic surfactant from natural oil /castor seed oil
- Characterization of natural anionic surfactant
- Separation of inks using flotation process from the printed paper using deinking flotation
- Study the effects of pH, fatty acid soap dosage and flotation time on the deinking efficiency of the surfactant
- Optimize the ink removal efficiency of the surfactant

1.3. Significance of the Study

Paper recycling is becoming active part of the paper industry because of growing environmental concerns and economic reasons. The paper industry depends on the proper balance of virgin and recycled fibers. To increase recycling rates above today's levels helps to maintain the sustainability of the paper value chain. Recycling helps to reduce energy usage, reduce the consumption of fresh raw materials, reduce air pollution and water pollution (from land filling) by reducing the need for "conventional" waste disposal and also reduces greenhouse gases emissions. Before taking the bold step of recycling, it is crucial to understand the good and bad involved in this process. The deinking of paper is used to recycle the paper and minimize the environmental waste because:

1. Recycling Paper which helps the Environment.
2. Recycling paper is economically responsible.
3. Recycling paper reduces waste.
4. Recycling paper promotes a clean, green image.

1.4. Scope of the Study

The thesis work generally covers castor oil extraction, refining of castor oil, castor oil characterization, Sodium stearate anionic surfactant synthesis by using saponification process, characterization of produced Sodium stearate anionic surfactant, repulping of waste printed paper, deinking flotation of laser printed waste paper from toner ink by using anionic surfactant and evaluation of ink removal efficiency of the surfactant by probing the ERIC of the pulp before and after deinking flotation by measuring effective residual ink concentration of the pulp via PerkinElmer spectroscopy.

2. Literature Review

2.1. Natural Surfactant and Types of Natural Surfactant

2.1.1. Natural Surfactant

The word “Surfactant” is an abbreviations of the three words “Surface Active Agents.” Surfactants are materials that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. In the general sense, any material that affects the interfacial surface tension, can be considered as surfactant, but in the practical sense, surfactants may act as wetting agents, emulsifiers, foaming agents, and dispersants. In respects of deinking flotation of waste paper surfactants play an important role in reducing the surface tension between the fiber of the paper and the printing ink and facilities ink removal from the waste printed paper.

The term ‘natural surfactant is taken directly from a natural source. The source may be of either plant or animal origin and the product should be obtained by some kind of separation procedure such as extraction, precipitation or distillation (Holmberg J., 2001). A surface-active agent has a capacity to lower surface tension of material. Example of natural surfactants are soaps and detergents. It is worth remarking that all surfactants do not display such activity; in effect, only the surfactants with more or less equilibrated hydrophilic and lipophilic tendencies are likely to migrate to the surface or interface. It does not happen if the surfactants molecule is too hydrophilic or too hydrophobic, in which case it stays in one of the phases (Jean-Louis, 2002).

2.1.1. Types of Natural Surfactant

Natural Surfactants are classified based upon the nature of the hydrophilic "head-groups" as:

- Anionic surfactant
- Nonionic surfactant
- Cationic surfactant
- Amphoteric surfactant

2.1.1.1. Anionic Surfactant

Anionic surfactants possess a negative charge on their hydrophilic head end. This charge helps the surfactant molecules to interact with both the paper fibers and ink particles; in lifting and suspending inks in bubble-like arrangements. This is because the negatively charged head group is repelled from the fiber surfaces, which also tend to be slightly negatively charged the reverse action to a cationic surfactant, where the positively charged head group is adsorbed onto a surface, giving an antistatic and conditioning effect. Anionic surfactants are used in greater volume than any other groups due to their easy and low cost of manufacture. The great majority of anionic surfactants will generate significant foaming in solutions above their critical micelle concentration (CMC), which is a desirable attribute in most flotation and cleansing applications, but can restrict the use of anionic surfactants in areas where foam is a problem (Farn ,2006).

When reading the ingredient list on different products, it possible to identify anionic surfactants as those that have the following in their names:

- Sodium
- Ammonium
- Magnesium
- Sulfate
- Sulfonate
- Gluconate

(For example, sodium laurel sarcosinate, sodium stearate, magnesium laurel sulfate, and sodium gluconate...)

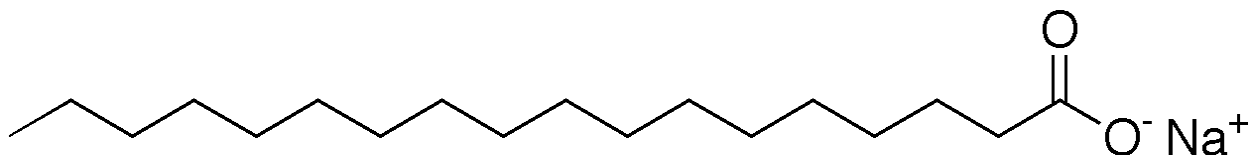
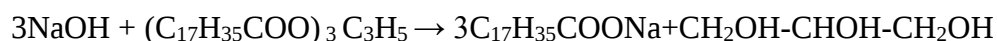


Figure 2. 1.Sodium stearate anionic surfactant

The first anionic surfactant is soap, which is made from a fatty acid such as animal fat or vegetable oil that is allowed to react with an alkali. The preferred counter ions of the anionic surfactants are sodium, potassium, lithium, ammonium and alkyl ammonium soaps (Yangxin, *et al*, 2008).

Soaps are prepared by saponification of triglycerides from vegetal or animal source. For instance with a triglyceride containing 3 stearic acid (C18:0) units, the reaction with sodium hydroxide produces 3 moles of sodium stearate and 1 mole of glycerol (Jean-Louis L., 2002).



Soap is obviously a sustainable surfactant and shows excellent performance under the appropriate conditions. Natural alkyl sulfates were first introduced in laundry detergents around 1932. Then, the low-cost surfactant called alkyl benzene sulfonates became the work-horse among synthetic surfactants. Originally, branched-chain alkyl benzene sulfonates (ABS) were used in detergent compositions, but microbes could not break down ABS and thus they left foam in flotation. They were replaced by linear alkyl benzene sulfonates (LAS) such as sodium dodecyl benzene sulfonate and sodium xylene sulfonate, which are readily biodegradable. In today's market, LAS is still a key low-cost surfactant and alkyl sulfates (AS) are simultaneously in use (Jonson , *et al*, 1998).

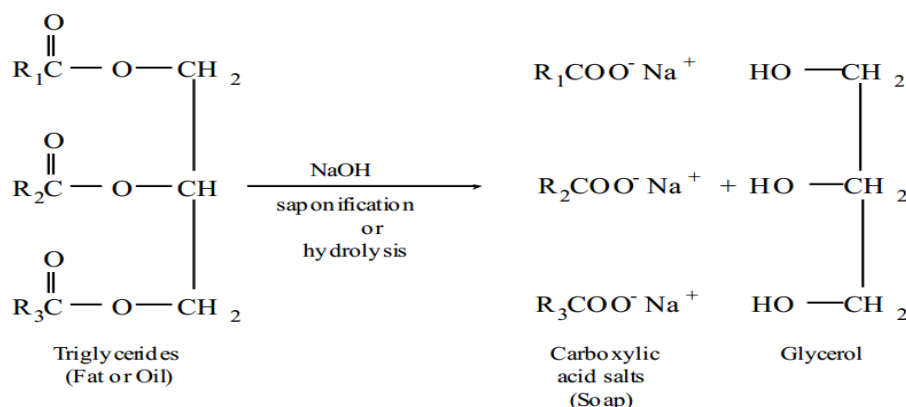


Figure 2.2.Saponification process

Soaps are used in the formation of shaving foams which helps as foaming agent on deinking flotation and are anionic surfactants since it has both hydrophobic tail group and hydrophilic head group. The head group contains a negative ion.

2.1.1.2. Nonionic Surfactant

Nonionic surfactants have been extensively used in the area of the laundry detergent, flotation purposes and personal-care formulations in combination with anionic surfactants. The nonionic surfactants are represented mostly by linear alcohol ethoxylates, with the alcohols being derived from either petrochemical raw materials or natural resources.

Non-ionic surfactants are the least deinking agent surfactants and they are not usually used because they do not foam well as others. The structures of main nonionic surfactants used in deinking flotation are different from anionic surfactants, because the deinkability composition containing nonionic surfactants is not sensitive to hard water since no precipitation occurs in the presence of divalent ions. Furthermore, nonionic surfactants can be used to cleanse animal fibers such as silk and wool, to avoid the ionic adsorption of surfactant on the amino groups in the fibers since electrostatic force does not work for nonionic surfactants (Yangxin, *et al*, 2008).

APEs such as nonylphenol ethoxylates are efficient, cost effective versatile products which have been used widely in detergent compositions for over forty years. They have a better detergency performance than alcohol ethoxylates (AE). They meet the primary biodegradability but the metabolic products resulting from the degradation process do not readily degrade further and may have undesirable side effects on aquatic life (Motson, 1999).

2.1.1.3. Cationic Surfactant

The majority of cationic surfactants used in detergent compositions are based on the nitrogen atom carrying positive charge. In general, the preferred solubilizing cation is a halide or methosulfate ion. Quaternary ammonium compounds (quats), especially dioctadecyl dimethyl ammonium chloride are used as antistatic agent due to its high antistatic activity. The quaternary ammonium and ethoxylates quats, are used as a common fabric softener (Kennedy R., *et al*, 2008). It works by reducing the friction between fibers, and between fibers and the skin, and thus it can also be used as hair conditioners (Kennedy, *et al*, 2008). It has been found that addition of ethoxylated quats to floor and stone cleaners enhances the spreading and drying abilities and, the lime soap dispersing and emulsification properties. This made the cleaners more effective on slip resistant surfaces, leading to a reduced time consumption for washing those floors and stones (Richter, *et al*, 2003).

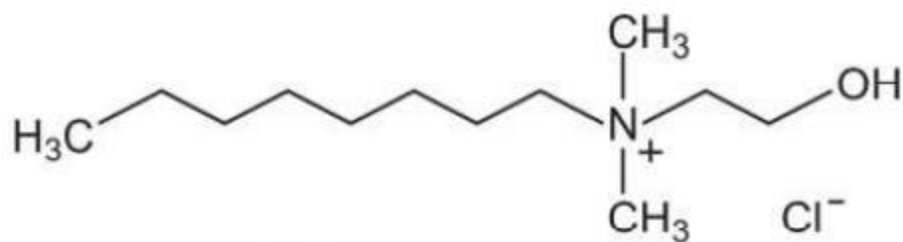


Figure 2. 3. Structure cationic surfactants

Cationic surfactant is used with the amphoteric. However, the amphoteric surfactants are generally mild, with lower skin and eye irritation when compared with the commonly used anionic and nonionic surfactants. They can be incorporated into detergent composition in order to thicken the composition without using a thickener, provide excellent temperature stability, and improve the mildness on the skin.

2.1.1.4. Amphoteric Surfactant

Amphoteric (or zwitterionic) surfactants are so called because the head-group carries both a negative and positive charge so that the hydrophilic portion of the molecule has internally neutralized positive and negative charges. True amphoteric surfactants are those that exhibit a varying charge, from positive, to zwitterionic to just negative, on the hydrophilic depending on the pH of the solution in which they are found.

The classic amphoteric surfactants, such as amphotacetates, are anionic, cationic or zwitterion at various points in the pH spectrum. The class of ‘amphoteric’ surfactants includes betaines, sultaines and sulfonated amphoterics (Richard, 2000). The amphoterics, due to their ability to support both positive and negative charges, usually have large ‘head groups’, the hydrophilic portion of the molecule that exhibits an affinity for the aqueous phase. This property makes them desirable secondary surfactants because they have the ability to modify micellar structure.

Amphoterics are generally used in formulations with anionic or nonionic surfactants to modify the solubility, micelle size, foam stability, detergency and viscosity of various cleansing systems and emulsions. Being internally neutralized, the amphoterics have minimal impact on the biocidal activity of quaternary ammonium salts.

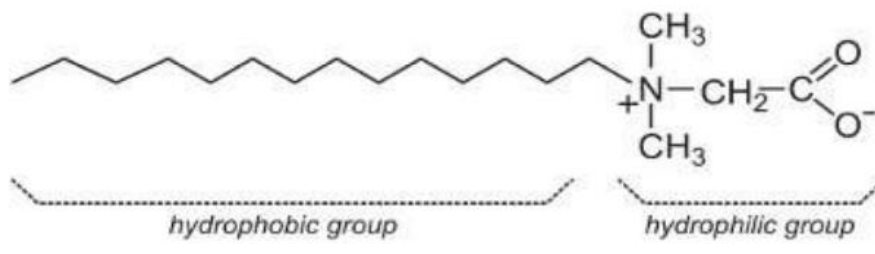


Figure 2. 4. Amphoteric surfactant /an alkyl betaine

2.2. Raw Materials for Natural Anionic Surfactant

2.2.1. Natural Oil and Fats: Triglyceride

Most oils and fats from animal or vegetal origin are triglycerides, i.e., triesters of glycerol and fatty acids, as for instance the structure indicated in the following formula.

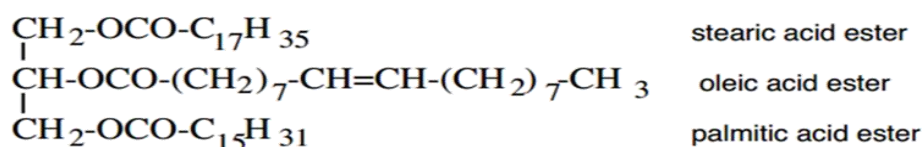


Figure 2. 5. 2-oleyl-palmityl-stearine.

In some cases esterification is incomplete this leading to mono and diglycerides. Natural triglycerides contain the five most common fatty acids in various proportions (Scheibel, 2004):

- palmitic acid (C16:0, i.e. 16 carbon atoms, no double bound)
- Stearic (C18:0), 18carbon atoms , no double bound)
- oleic (C18:1), 18carbon atoms, 1 double bound)
- linoleic (C18:2) , 18carbon 2 double bound)
- And linolenic (C18:3),(18 carbon atoms 3 double bond)

Fatty acids in the C12-C18 range, particularly those from natural origin, are quite important in the manufacture of soap and personal care specialties, because they carry a lipophilic group which is completely biocompatible and well adapted to the preparation of surfactants for deinking flotations.

Other sources of lipophilic materials such as petroleum refining were considered in order to lower the cost, particularly for detergents. Such substances are found in light cuts (gasoline and kerosene) coming from atmospheric distillation and catalytic cracking. It is also possible to make such a chain by polymerization of short chain olefin, particularly in C3 and C4 (Scheibel, 2004).

2.2.2. Other Natural Substance

Some trees like pine and other conifer species contain esters of carboxylic acids and glycerol (or other alcohols In a typical conifer wood digestion), fatty acids accounts for about 50%, while other acids are more complex substances such as Abietic acid and its derivatives (Salager , 2002).

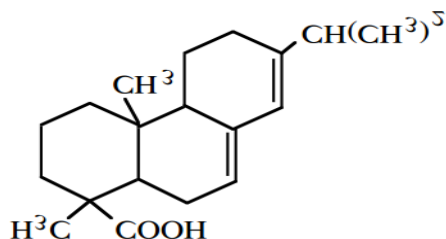


Figure 2. 6.Abietic acid

2.2.3. Castor Oil

Castor oil is pale amber viscous liquid derived from the seeds of the plant *Ricinus ommunis*, sometimes known as ricinus oil (Marter, 1981). Castor oil is one of the few naturally occurring glycerides that approach being a pure compound, since the fatty acid portion is a crude. Castor oil is a pale straw colour but turns colorless or slightly yellowish after refining and bleaching (Weise, 1983). The crude oil has distinct odour, but it can easily be deodorized in the refining process. Like any other vegetable oils and animal fats, it is a triglyceride, which has a glycerol molecule with each of its three hydroxyl group esterified with a long chain of fatty acid.

Its major fatty acid is the unsaturated, hydroxylated 12-hydroxy, 9-octadecenoic acid, known familiarly as Ricinoleic acid. The fatty acid composition of a typical castor oil contains about 87% of ricinoleic acid (Akpan, 2006).The functional group causes ricinoleic acid to be unusually polar, and also allows chemical derivatization that is not practical with most other seed oils.

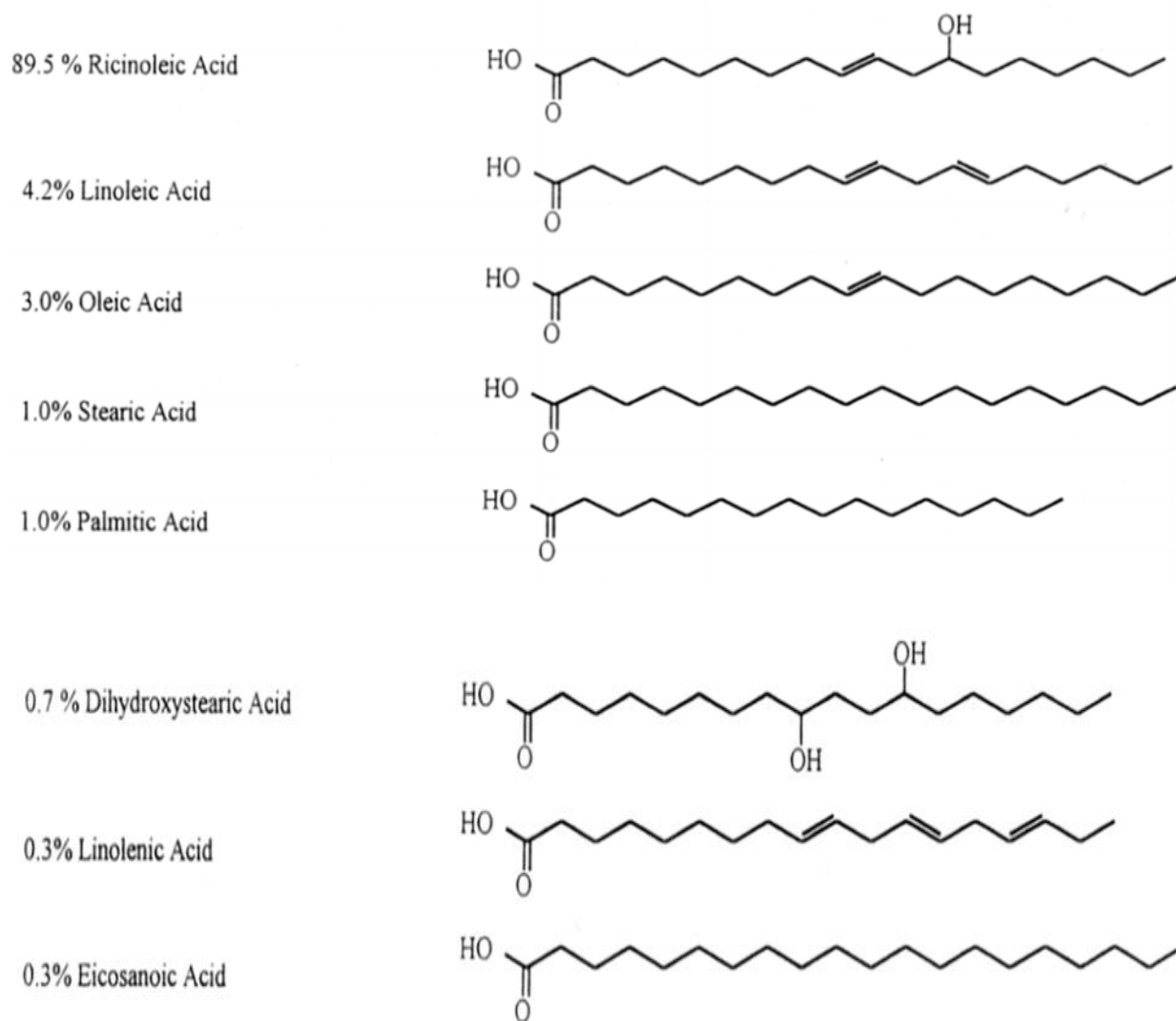


Figure 2. 7.Composition of castor oil fatty acids

Castor oil has been used for coating fabrics and other protective coverings, in the manufacture of high-grade lubricants, transparent typewriter and printing inks and as the raw material for the production of anionic surfactant for foaming agent in deinking flotation and uses for different detergent and cosmetics as surface active agents.

2.3. Characterization of Natural Anionic Surfactant

2.3.1. Hydrophilic to Lipophilic Balance (HLB)

To be surface active, the surfactants must have a hydrophilic (water loving) and hydrophobic (water hating) group. For an aqueous solution, these are usually called hydrophilic and hydrophobic groups (Zhao, 2005). From this comprehensive definition, any chemical that have both a hydrophilic and a hydrophobic portion should have surface activity (reducing the surface energy of liquid or solid) and can be called a surfactant in general. By this definition, defoamers, dispersants, foaming agents, and collectors used in flotation deinking are all surfactants.

The hydrophile-lipophile balance (HLB) value has gained acceptance in the paper industry for characterizing surfactants (Ferguson, 1992). HLB value is a helpful tool in predicting water-soluble properties of an anionic surfactant. The hydrophilic-lipophilic balance (HLB) of an anionic surfactant affects the deinking flotation efficiency. HLB values describe how the surfactant interacts with water soluble and water repellent substances. The higher the HLB value, the higher the foaming ability, and the lower the ink collection ability. An effective anionic flotation surfactant usually possesses the properties of good ink collection and adequate foaming.

Anionic surfactants with low HLB value, the impact from the hydrophobic component(ink) of the molecule is greater than from its hydrophilic portion(fiber),while with the high HLB the situation is opposite (Göttsching, *etal.*, 2000). HLB value is the ratio of weight percentages of hydrophilic to hydrophobic groups in the structure. An effective anionic flotation surfactant usually possesses the properties of good ink collection and adequate foaming. In deinking flotation it has been suggested that anionic surfactants with an HLB value of 14-20 are optimal for deinking of printed paper mixtures (Turai, *et al.*, 1977).

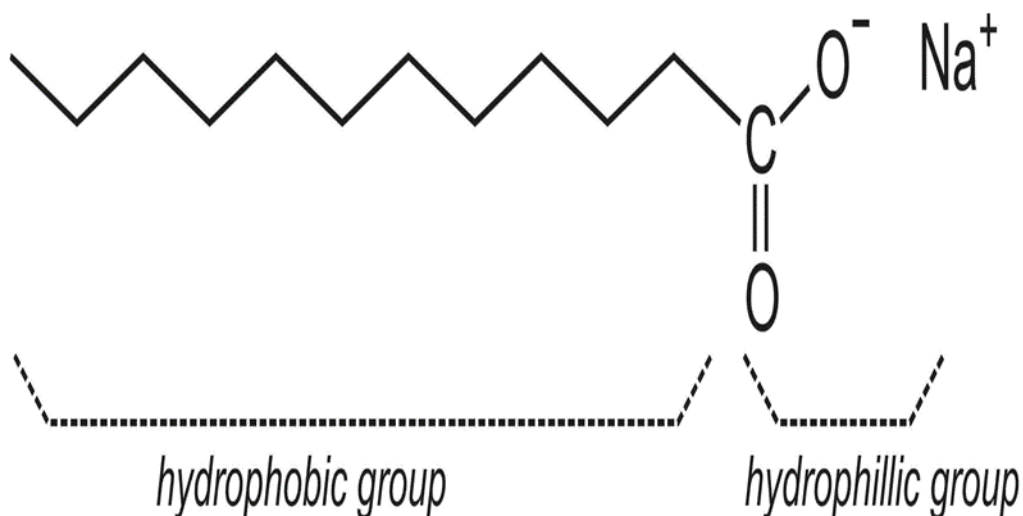


Figure 2. 8. Schematic representation of surfactant

2.3.2. Critical Micelle Concentration (CMC)

Critical micelle concentration (CMC) is the lowest concentration at which micelles first appear for the micelle formation. At the CMC the surface tension is not further lowered with increased concentration, and the formation of micelles from the free monomers in the solution starts.

Critical Micelle Concentration (CMC) is the concentration in water at which individual surfactant molecules start to aggregate. A high CMC value indicates that the surfactant is hydrophilic and vice versa. The CMC of natural surfactants decreases with increasing temperature. Since surfactants are designed as amphiphilic molecules, which interact with both hydrophobic and hydrophilic interfaces. Surfactants have limited aqueous solubility, which needs to reach the level of the CMC of the surfactant to allow maximum performance (Peter, 2002).

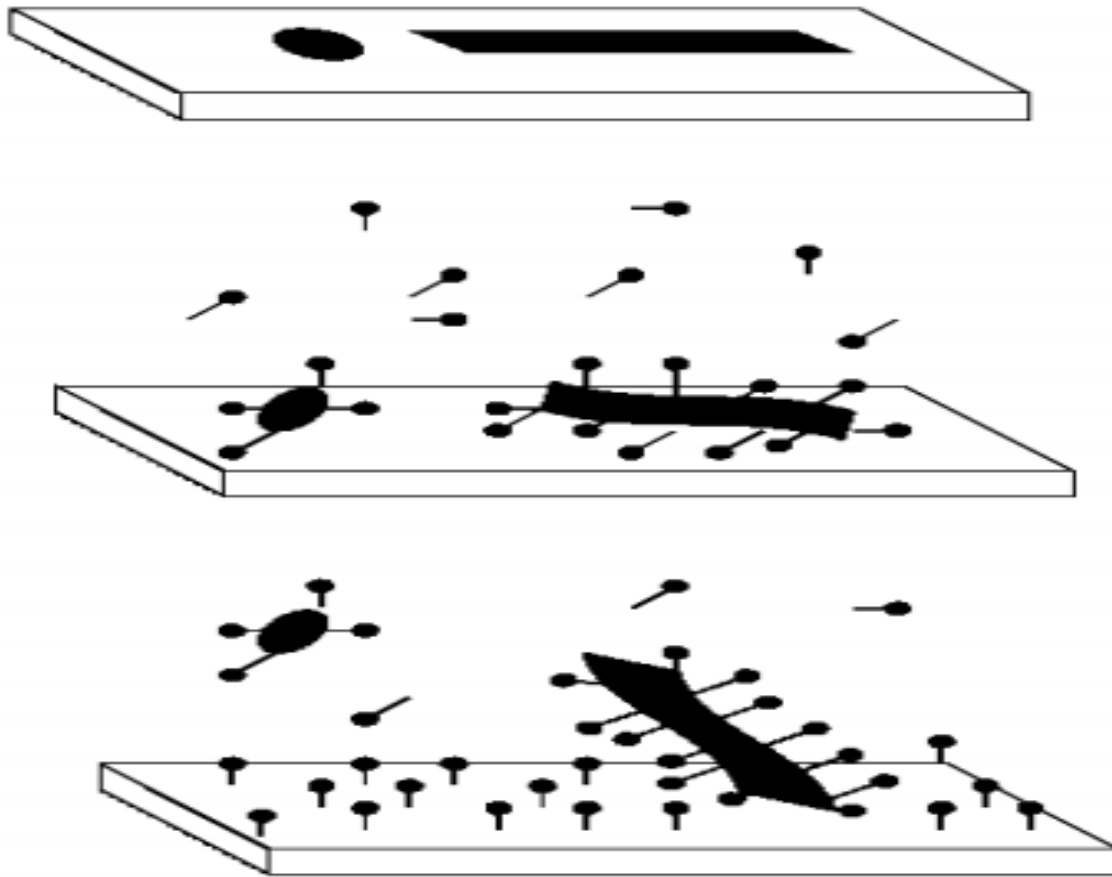


Figure 2. 9. Deinking with the use of surfactants.

Source: (Lasheva, *et al*, 201)

2.3.3. Surfactant Foamability and Foam Stability

Foamability and foam stability are of main concerns in foam displacement for enhanced deinking flotation of waste printed paper in paper recycling. Foams are typically formed in regular hexagonal texture as a result of gas dispersion through a continuous surfactant solution.

Foams are generally described in terms of:

- Foamability: defined as the capacity of the surfactants to form foam irrespective of the special foam properties.

- Foam stability: defined as the variations of foam height or volume with time, immediately after foam generation.

The two terms are interrelated and the more stable the foam films the greater is the solution's hexagonal texture. And thin liquid films to prevent bubble foamability, It is thermodynamically unstable and they are stabilized by surfactants to prevent bubble coalescence.

2.4. Types and Properties of Printing Ink

Before the advent of synthetic colorants, inks were based on two substances, carbon black and the iron gall complex. Generally the raw materials for ink production are vehicles, binders, colorant (pigment or dyestuff) and variety of additives (Kirth-Othmer, 1981). The vehicle is a solvent that dissolves the binder and disperses the pigment. The binder is a polymeric material that on drying it forms a film on the surface of the paper, thereby enveloping and adhering the pigments to the substrate. The colorants impart colour to the ink. The dominant pigment is carbon black as most inks are black, although coloured pigments (greenish-blue, purplish pink and yellow) are used in colour printing. The compositions of printing ink is vary, as printing inks are formulated according to the printing process used (Dobias, *et al.*, 1992). There are different types of printing inks.

2.4.1. Letterpress Ink for Paper (Black Toner Ink)

Copier toner is a chemical solution used to develop xerographic images; put simply, it's the solution that allows laser printers to print. Many industrial laser-based printers and photo copiers in office environments use toner, which comes in a large plastic cartridge.

Fine powder and pigment compose the core elements of toner, though many other ingredients accent these basic components. Each toner cartridge contains varying ratios of ingredients, as per the individual needs of the copier.



Figure 2.10.black tonner ink

Source: (Heise, 1996)

This types of ink has the following compositions:

Table 2.1.composition of black tonner ink

Components	Amount (%w/w)
Carbon black (black pigment)	13.00
9 poise mineral oil (wetting agent)	68.00
0.5 poise mineral oil (wetting agent)	10.00
Asphaltum solution	5.00
280-320oC petroleum distillate (solvent)	4.00

Source :(Sharif Ahmed, 2007)

2.4.2. Lithographic Ink for Paper

It has the following composition:

Table 2.2.composition of Lithographic ink

Components	Amount (%w/w)
Organic pigment (colour)	18.00
Quickset varnish	40.00
Gloss varnish	15.00
Fast setting varnish	15.00
Polyethylene wax paste (prevents damage To the film against rubbing)	5.00
Anti-set-off paste	3.00
Cobalt/manganese driers (catalyst for Drying oil oxidation)	1.00
280-320°C petroleum distillate (solvent)	3.00

Source :(Sharif Ahmed, 2007)

2.4.3. Flexographic Ink for Polyethylene Film

It has the following composition:

Table 2.3.composition of Flexographic ink

Component	Amount (%w/w)
Titanium dioxide (white pigment and opacifier)	35.00
Alcohol soluble nitrocellulose (resin)	5.00
Alcohol soluble polyamide (resin)	15.00
Dibutyl phthalate (plasticizer)	1.00
Polyethylene wax (prevents damage To the film against rubbing)	1.00
Amide wax (prevents damage To the film against rubbing)	1.00
Ethanol (low B.P. solvent)	30.00
N-propyl acetate (low B.P. solvent)	8.00
N-propanol (low B.P. solvent)	4.00

Source :(Sharif Ahmed, 2007)

2.4.4. Gravure Ink for Paper

It has the following composition:

Table 2.4.composition of Gravure ink

Component	amount (%w/w)
C.I.pigment red 57:1(red pigment)	10.00
Alcohol soluble nitrocellulose (resin)	20.00
Ketone resin (resin)	10.00
Dioctyl phthalate (plasticizer)	2.00
Polyethylene wax (prevents damage To the film against rubbing)	1.00
Ethanol (low B.P. solvent)	30.00
N-propyl acetate (low B.P. solvent)	20.00
Ethoxy propanol (low B.P. solvent)	7.00

Source :(Sharif Ahmed, 2007)

2.4.6. For Letterpress Printing on Corrugated Boxes (Water reducible red)

It has the following composition:

Table 2.5.composition of letterpress printing on corrugated boxes

Components	Amount (%w/w)
Balance Fixe (CI Pigment White 21)	10.00
Rutile titanium white (CI Pigment White 6)	5.00
Lake red C	14.00
Varnish	54.00
Diethylene glycol	8.00
Wax paste	5.00
Amine	4.00
High acid value	
Maleic resin	50.00
Glycol	40.0
Amine	10.0

Source :(Sharif Ahmed, 2007)

2.5. Deinking Flotation Cell Set-Up and Flotation Conditions

The flotation column has two main regions:

1. A collection region, where the pulp slurry is in contact with gas bubbles,
2. And aeration region, where the pulp is recirculated in tangential Venturi aerators where the gas flow is regulated by using a mass flow meter.

The froth generated at the top of the flotation column is removed by using an adjustable reverse funnel connected to a vacuum pump. The pulp level in the cell and the froth retention time before removal can be modified by adjusting the position of the overflow system and of the reverse funnel, respectively (David Beneventi, *et al*, 2010). The pressurization deinking flotation system generally consists of a pressurization pump, a retention tank, and a gas supply.

The pump increases pulp suspension pressure while the retention tank provides adequate time for gas to transfer into liquid and also for excess gas applied to the system to be released.

An Induced Air Flotation (IAF) Deinking cell uses the principle that foam extraction is proportional to the surface area and not the volume of the foaming machine. Therefore, a large surface with a low depth (80 cm) is used, and large amounts of foam are easily produced in an inexpensive foaming tank (Krofta, *etal*, 1989). The IAF cell is specifically designed for deinking of wastepaper. It removes ink from wastepaper by producing foam artificially. This foam collects ink, and when the foam is extracted, the ink is separated from the wastepaper (Somasundaran, *et al*, 1999). Normally in most deinking operations, the deinking chemicals (surfactants) including dispersant, collector, and frothing agent are added directly to the pulp suspension prior to air flotation.

According to the US Department of Energy (DOE), this can cause adverse effects, including the following:

1. Contamination of fibers by froth.
2. Decrease in surface hydrophobicity and removal efficiency of the ink particles.
3. Poorer control of froth stability.

Based on laboratory work and scaled-up pilot investigations, the following results have been obtained for the newly developed Surfactant Spray during the air flotation as compared to the normal method of the addition of all the deinking chemicals to the pulp suspension prior to flotation:

1. Increased deinking efficiency.
2. Higher recycle fiber quality with brightness gain of 10%.
3. Improved paper machine run ability.
4. Reduced air flotation fiber losses by up to 50% compared with conventional technology.
5. Higher capital effectiveness.
6. Minimized environmental impact through reduced water and deinking chemicals.

The construction of an IAF cell should be designed for low power and space requirements as well as for simple operation and low equipmental cost. The froth (foam) removes ink preferentially and the subsequent washing can be made in stages that can result in a brighter pulp. The paper slurry is diluted at the entrance with recycled clarified water to approximately 0.75–1.50% consistency and foaming chemicals /surfactants are added at this location (Lawrence, *et al*, 2010). Flotation is possible only when the surface of the particles to be floated is hydrophobic. When the surface of the particles is completely wetted by water, they are not floated. A number of both organic and inorganic solids exhibit varying degrees of hydrophobic character when their surfaces are freshly formed. These include hydrocarbons, waxes, coals, graphite, tars, bitumen, sulfur, talc, molydenite, printing inks and various synthetic plastics.

The typical industrial flotation cell, schematically shown in Fig.2.11. Below is referred to as a mechanical cell. In addition to the collectors and frothers, a number of inorganic and organic reagents are employed as ‘modifying’ or ‘regulating’ agents in flotation of complex multi-componential ores. These ensure that some of the components are hydrophilic, or reinforce the action of a given collector. These are termed depressants, activators or deactivators.

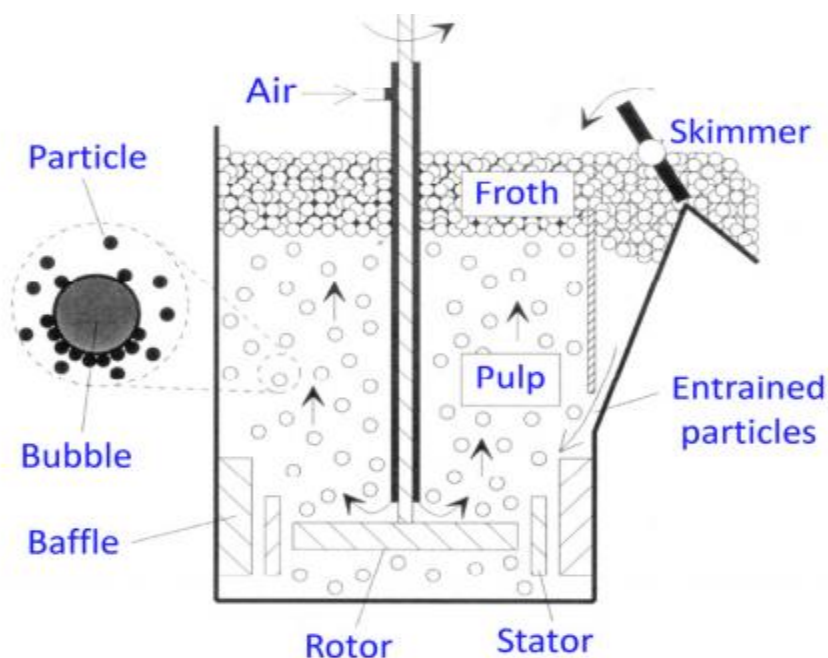


Figure 2. 11.An agitation-type flotation cell.

Source: (Pallab Ghosh, 2012)

In general, surfactants play three roles in flotation deinking (Ferguson, L.D., *et al*, 1992):

- a) As a dispersant to separate the ink particles from the fiber surface and prevent the redeposition of separated particles on fibers during flotation deinking;
- b) As a collector to agglomerate small ink particles to large ones and change the surface of particles from hydrophilic to hydrophobic; and
- c) As a foaming agent to generate a foam layer at the top flotation cell for ink removal.

Although surfactants play important roles in deinking, they can also have some adverse effects on ink removal, fiber quality, and water reuse. For example, the adsorption of dispersant and frothers on fiber surfaces may reduce fiber-fiber bonding and create foaming problems in paper machines (Dorronsoro, *et al*, 1998). The impeller or agitator, also referred to as the rotor, is considered to be the heart of a mechanical flotation cell as it provides the energy to perform the following functions necessary for the flotation process (Gorain, *et al*, 2000):

1. Suspension of solids in the cell tank.
2. Dispersion of air into bubbles.
3. Creation of micro turbulence for effective bubble-particle collision.
4. Suction of air into the cell in self-induced type cells.

2.6. Process Descriptions of Flotation Deinking of Waste Paper

The deinking process is referring to the removal of printing ink from a slurry of wastepaper in the recycling process. The ink is about 0.5-2% of the mass of the waste paper (Biermann, 1996). Generally, the de-inking process is based on the separation between hydrophobic inks and hydrophilic paper fibers. When there is a mix of papers, printed by conventional and digital printing systems, the de-inking process does not work properly (Hpala, et al, 2005).

The industrial process for removing wastepaper contaminants involves re-pulping, screening, cleaning, washing and flotation. But the laboratory deinking trials commonly include four successive stages, namely sample preparation, pre-washing, pulp treatment and fiber/ink particles separation. Each stage contributes to the overall effectiveness of deinking (Heise, et al, 1996; Knudsen O, et al, 1998). Conventionally, two general approaches have been employed to remove ink in order to produce the deinked fiber after repulping. These two approaches are flotation and Wash deinking. Both flotation and Wash deinking can be referred to as combination deinking processes (Terrence Cotter, *et al*, 2022). The underlying chemical and physical requirements to successfully deink are different for Wash, flotation, and combination deinking processes.

The deinking chemistry and the physicochemical interactions among air bubbles, fibers, and ink particles are very complex. Existing technologies and process designs of flotation deinking are based on the experiences obtained from mineral flotation processes. Limited process control mechanisms are available. Many problems remain unsolved such as high fiber and water losses, fiber contamination by deinking chemicals, adverse chemistry modification due to surfactant low efficiency in removal of small ink particles etc. Therefore, innovative technologies based on the mechanistic understanding of flotation processes are greatly needed to solve or alleviate the above problems. Because of the significant variability in the supply of secondary fibers in recycling practices, process control in flotation deinking is very important to improve recycling operations (Ferguson, *et al*, 1992).

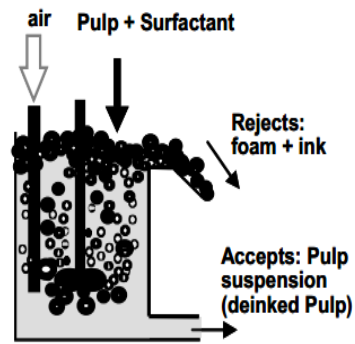
The surfactants used in mineral flotation may not be necessary in flotation deinking. For instance, some ink particles, such as Xerox toner, are hydrophobic in nature and no collector is necessary. But the dispersant is necessary because the ink particles cannot be removed from fibers by other chemicals, such as sodium silicate, sodium hydroxide, or by mechanical actions, such as magnetic and electrical fields, and ultrasonic irradiation. Traditionally, the frothers and other surfactants are added into the pulp suspension during repulping. However, the surfactant present in pulp slurry will not only contribute to the foam stabilization, but also adsorb onto ink particle surfaces and cause a decrease in the hydrophobic of ink particles (Jiang, *et al*, 2000). Furthermore, the mechanical control of froth stability is very difficult if the surfactant is directly added into the pulp slurry because the properties of wastepaper may vary significantly.

Because the foams are stabilized by surfactant only on the top of the flotation cell, it is of interest to develop a feasible method to directly add the frothers to the top of the flotation cell rather than in the pulp suspension. As a result, a separate control of the addition of various surfactants to improve the performance of deinking processes can be achieved.

Table 2.6. General Characteristics of Pulp Components of Flotation Systems Used in Processing of De-inking of Paper

Parameter	De-inking Flotation
Components of pulp	Cellulose fibers, ink, and mineral filler particles
Skimmed fraction	Always reject (ink and mineral filler particles)
Concentration of pulp	1.0-1.2 wt.% solids
Concentration of solids to be floated	<< 0.1 wt. %
Hydrophobicity of particles	most of the ink particles are hydrophobic
Typical size of particles	ink particles: 20-200 μm ; cellulose fibers: a few millimeters
Shape of particles	often flat-like ink particles with the aspect ratio of >2:1; substantial difference in size and shape of ink particles and cellulose fibers; ink particles have smooth surface with rounded irregularities
Density of particles	1.3-1.4 g/cm ³

Source : (J. Drelich, *et al*, 2001)



Source: (Venditti, et al)

Figure 2. 12. Simple flotation of deinking of waste paper

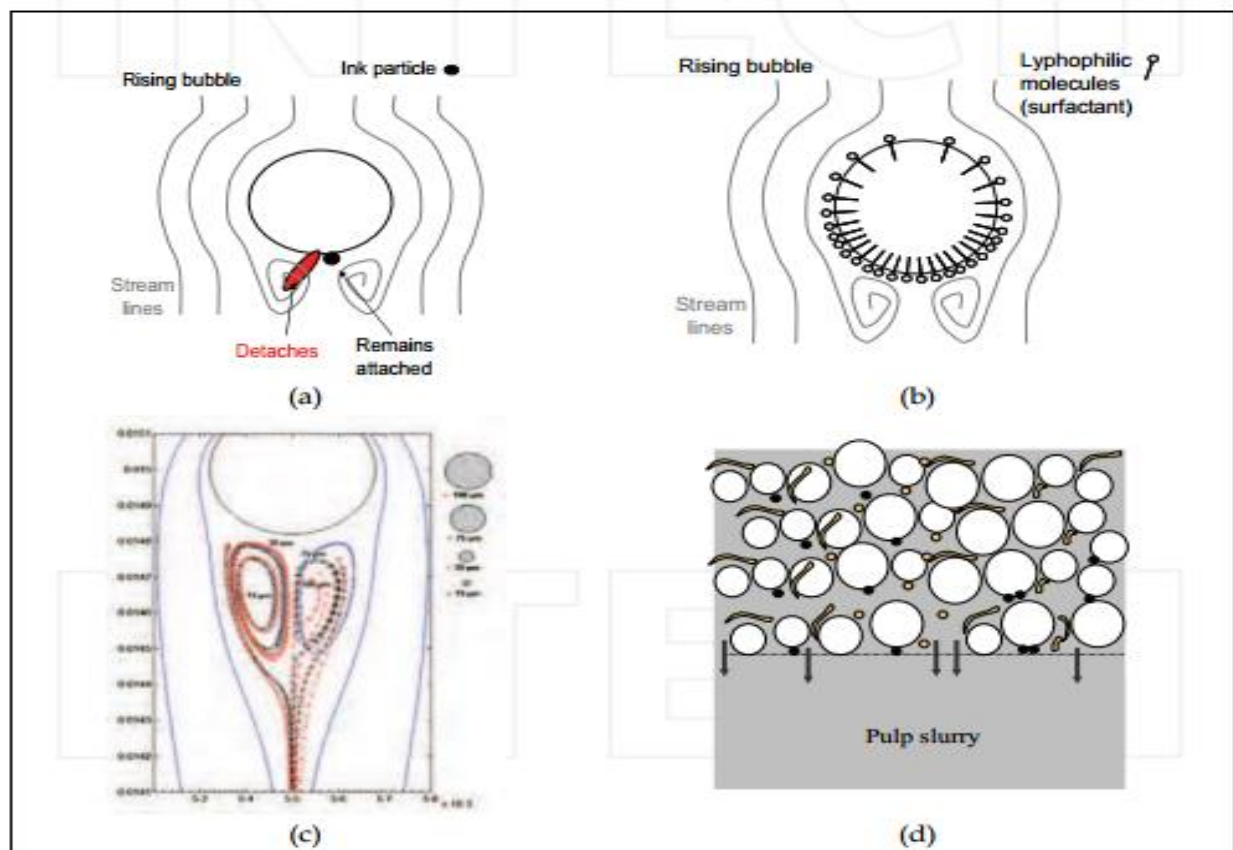


Figure 2. 13. Transport mechanisms of flotation deinking process

Source: Source: (Venditti, et al)

(a) Particle attachment and flotation, (b) lipophilic molecules adsorption, (c) influence of size on the path of cellulose particle in the wake of an air bubble (d) water and particle drainage in the froth.

In flotation deinking system, the gas and the solid phases are excellently dispersed in water as bubbles and particles with size ranging between $\sim 0.2 - 2$ mm and $\sim 10 - 100$ μm , respectively (Beneventi, et al. 2007). The collision between bubbles and hydrophobic particles can induce the formation of stable bubble/particle aggregates which are conveyed towards the surface of the liquid by convective forces (Fig. 2.13a). Similarly hydrophobic molecules adsorbed at the air/water interface are removed from the pulp slurry by air bubbles (Fig. 2.13b).

During the rising motion of an air bubble in water, a low pressure area forms in the wake of the Bubble inducing the formation of vortexes with size and stability depending on bubble size and rising velocity. Both hydrophobic and hydrophilic small particles can remain trapped in vortex streamlines (Fig. 2.13c) and they can be subsequently entrained by the rising motion of air bubbles. Particles and solutes entrainment is correlated to their concentration in the pulp slurry and to the water upward flow in the froth (Zheng, et al., 2005).

At the surface of the aerated pulp slurry, a froth phase is formed with water films dividing neighboring bubbles and solid particles either dispersed in the liquid phase or attached to the surface of froth bubbles (Fig. 2.13d).

The process for reusing waste paper to make new paper involves a flotation step to remove foreign substances like ink from the paper pulp. Usually soap is used to stabilize the air bubbles that adsorb at their interfaces hydrophobic substances like inks. Due to their low density, the air bubbles rise with the ink to the top where they can be separated. Foam is a colloidal dispersion in which a gas is dispersed in a continuous liquid phase. Foam bubbles usually have diameters greater than 10 μm and may be larger than 1000 μm (Drelich, et al, 2001).

2.7. Effect of Flotation Parameters on Deinking Efficiency

2.7.1. Concentration of Surfactant

Ink removal efficiency increases with an increase in froth stability, so that there is an increase in surfactant concentration in conventional flotation systems. Unfortunately, the increase in surfactant concentration in the pulp suspension will also increase the adsorption of surfactant onto ink particles, resulting in a reduction of the surface hydrophobicity of ink particles and ink removal efficiency (Ferguson, *et al*, 1992). Practically, it is difficult to optimize the surfactant concentration in a paper recycle mill because of the variability in the secondary fiber sources. This indicates that good control of surfactant concentration and its distribution within a flotation cell can significantly improve the flotation deinking operation (McCool, *et al*, 1993).

Based on the above fundamental understandings of flotation deinking, it is clear that effective controls of the key process variables can increase ink removal and reduce fiber and water losses. Surfactant spray technology that was proposed and tested in early research can separately control foam properties (the foam stability and the height of foam layer in a flotation cell) from other variables. As a result, the surfactant consumption, concentration and its distribution, froth structure and stability, and fluid dynamics in the froth can be controlled.

2.7.2. Flotation Time

It was determined that the type of recycled paper had the greatest influence on final brightness, followed by bleaching conditions, flotation cell residence time and flotation consistency. The residual ink concentration and yield were largely determined by residence time and consistency in the flotation cell (Pauck, 2011). Flotation method was obtained by disintegrating mixed wastepaper on the mill, and provided as high consistency pulp slurry. In order to evaluate the pre-washing stage contribution to deinking, a preliminary washing step was conducted immediately after the sample preparation: a “washed” mixed wastepaper was obtained. To avoid redeposition, the released ink was immediately separated from the fibers. The fibers were finally recovered for testing.

2.7.3. pH

Alkaline pH causes fiber swelling and subsequent ink release. Nonionic surfactants are essentially independent of flotation cell, however, anionic surfactants like sodium stearates, or soft soaps, are highly affected because of their ionizable nature (blaint, 1992). Bubbles tend to be too large for efficient flotation when the pH is 5 or below. Low pH levels also convert acids at the fiber surfaces to their unionized forms, making the fibers more hydrophobic and hence, more susceptible to flotation (BLAI T, 1992). Also, beyond a pH of 11 the bubbles tend to be extremely small have been shown to increase fiber yield loss (BLAINT, 1992).

2.7 .Yield of a Recycling Waste Paper Process

Recovery from pulping waste paper is commonly expressed as the percentage, by oven-dry weight, of pulp obtained from the original waste paper. One of the most important aspects of paper recycling is the yield from the process. The yield is defined as the % of the solids in the incoming wastepaper that are in accept of the recycled pulp. For instance, if 100 tons per day of solid wastepaper entered a process and 60 tons per day of recovered solids were produced, the yield of the process would be 60%. The yield depends on the wastepaper furnish, the types of operations in the recycling process (e.g., screening, washing, flotation, etc,) and the conditions under which those recycling sub-operations are run.

Removal efficiencies of contaminants are typically higher when the fraction of the feed to reject is larger. However, all separation processes have significant amounts of fiber in the reject screens so the improved contaminant removal is accompanied by lower fiber loss. There is always a conflict between making cleaner pulp and maintaining high fiber yield (Richard, 2002).

In screening, openings in baskets allow good fiber to go to the Accepts side but block large contaminants. The industrial screening operation can be simulated in the lab by simply screening a dilute pulp stream with a sieve (a simple colander with openings of about 1-2 mm typically used to wash foods will also work). In lab, a paper envelope will be pulped, screened and then made into a hand sheet.

Solid material can be lost in the screening operation and also in the making of a hand sheet (in which small particles are “washed” through the paper machine wire). By weighing the dry envelope before processing and the generated pulp after, a process yield can be determined. A number of analytical tests can be performed on pulp samples. Some measure chemical characteristics while others measure physical attributes. The most common tests are described below. Many of the following descriptions will relate to TAPPI (Technical Association of the Pulp and Paper Industry) standard test procedures. It is important to recognize, however, that there are many European standards which are equally applicable and, in some cases, more widely practiced (Sherbrook, 2001).

Consistency test measures the dry solids concentration of a suspension of fiber in water. A representative sample of pulp is collected, it is filtered to remove free liquid, and then oven dried to remove all remaining water. In stock preparation refining systems, consistency is normally between 2% and 6%. This permits relatively easy pumping of the slurry using conventional centrifugal pumps. Sheet properties are tested by diluting and forming the pulp into hand sheets using a sheet mold and a very specific forming procedure.

From the hand sheet mold the wet sheets are carefully removed and pressed under standard conditions. Pressing is done on a number of sheets at a time, with thin highly polished steel plates among them. The pressed sheets are stored in a temperature and humidity controlled room after adhering in to the steel plates which are placed on separator rings. When the hand sheets are dried and conditioned they are peeled from the polished plates and set sideways for physical testing. One very important factor to remember when using hand sheet test results to predict machine made paper is that hand sheets are fully restrained by the polished plates during the drying process (Sherbrook, 2001).

2.8. Effective Residual Ink Concentration (ERIC) as a Measurements of Ink Removal Efficiency

The ERIC (Effective Residual Ink Concentration) measurement has become a standard in paper industry for the measurement of residual ink in recycled pulp and paper. The ERIC measurement takes advantage of a fortuitous situation of all the various components that are found in recycled pulp. Ink and only ink absorbs light at 950nm. ERIC is a measure of the darkening effect of the remaining ink in a paper sample, not the actual amount of ink. Subvisible ink particles have a large effect on the visual appearance of paper because the number of particles can be quite numerous and the surface area of these particles are maximized, which causes the ink particles to become very effective absorbers of light energy.

Ink removal efficiency of a recycling operation is characterized by the brightness increment of the final paper over that of feed stock. Final paper brightness has been used as a product specification of recycled papers. However, the brightness measurement has deficiencies in quantifying ink-removal efficiency and the amount of residual ink in deinked pulp because paper brightness depends on additional factors, such as pulp refining, pressing, calendaring, and formation. Jordan and Popson developed a near-infrared reflectance technique to measure residual ink concentration in paper made of deinked pulp using Kubelka-Munk theory (Kubelka, *et al.*, 1930). The technique measures reflectance at an infrared wavelength (950 nm) from a paper sample over a black backing, R_0 , and reflectance from a thick stack of paper from the same sample, R_∞ . The Kubelka-Munk constant k , the specific absorption coefficient of the sample, can be calculated from the two measured reflectance values, R_0 and R_∞ .

It is directly related to the residual ink concentration in the paper sample when measured at a near-infrared wavelength where the absorption from lignin and dyes can be ignored (Jordan B., *et al*, 1994). Residual ink concentration was measured using a UV-Vis reflectance spectroscopy at 950nm wave length. The hand sheets from the pulping and flotation stages were made using a Technical Association of the Pulp and Paper Industry (TAPPI) Standard sheet machine. Reflectance measurements of each hand sheet, black-backed and self-backed, were made at 950 nm using a UV-Vis reflectance spectroscopy from which the absorption (k) and scattering coefficients (s) were determined from Kubelka-Munk theory (Karen stack, *et al*, 2005).

Two reflectance values from deinked (DIP) and undeinked (UP) pulp samples by using of UV-Vis reflectance spectroscopy are measured. Absorption coefficient, K , is expressed as function of S by using Kubelka-Munk equation. K of recycled paper includes two parts, K_{paper} and K_{ink} . Thus, K is regarded as a direct index of ink influence. Black ink is defined with an absorption coefficient of $10,000 \text{ m}^2/\text{Kg}$ (Jordan D., *et al*, 1994). It's very useful to treat it as default value and then compare with Obtained from recycled paper samples. Their ratio between K_{paper} and K_{ink} is defined as effective residual ink concentration (ERIC), with a unit of ppm.

2.9. Environmental Impact of Deinking

Environmental effects of de-inking is generated during the major de-inking operations starting from the raw material up to the final operation .use of recycled fiber material for the production of paper and paperboard has a significant share in solving problems related to environmental protection and conservation of energy resources. When considering papers from a cradle to grave perspective, they can have a potential impact on the environment at a number of points in their use cycle.

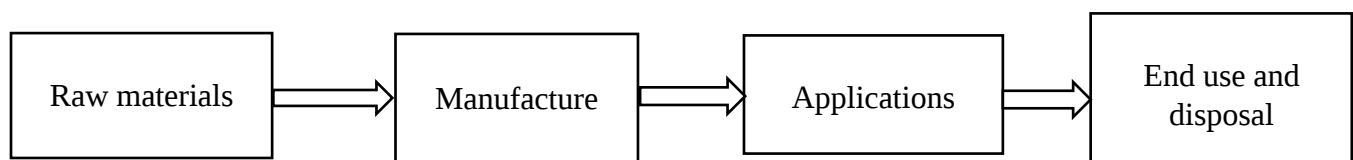


Figure 2. 13. Life cycle of paper

We will look at the impacts associated with each stage in the life-cycle shown above. The paper industry has undertaken a study to evaluate the carbon footprint of paper manufacture. The values obtained vary widely from site to site as electricity is the primary source of energy used in the manufacture of paper and materials; the actual carbon footprint of electricity varies depending on the percentage of low carbon footprint electricity production methods such as nuclear or hydroelectric power. A fundamental change in society's attitudes to the use of the natural resources, and to the production of excessive amounts of waste through careless use and consumption is observed.

The society now sees the waste stream produced by the modern life styles as a high cost problem that must be solved and as a long term threat to the viability of the environment and the present lifestyle (Krofta, *et al.*, 1989). Utilization of waste paper is bound to have an impact on environmental cleaning in a big way and this will reduce deforestation and help in preserving the ecology of the forest. The pressure to conserve natural resources and reduce solid waste from the community has led to an increased trend toward recycling of old newspapers, periodicals and magazines, and office wastes (Richardson, *et al.*, 1992). Recycling reduces the requirement for virgin fiber and energy and can lower the environmental impact of paper manufacture (Frederick, *et al.*, 1996)

Recycling paper manufacturing creates major environmental benefits, including preventing the overuse of natural resources, production of greenhouse gases, release of toxic emissions, impacts on regions and communities, disposal of waste, and others. Separating the fibers for papermaking takes far more resources when derived directly from trees than when recovered from recycling. On average, more than four tons of trees are required to make one ton of chemical pulp for virgin copy paper (Susan, 2012).

Half the weight of trees is water and less than half the weight of dried trees results in papermaking fiber. Deinking of waste paper has the following environmental advantages.

- It helps preserve forests, because it reduces demand for wood;
- It conserves resources and generates less pollution during manufacturing, because the fibers have already been processed once; and
- It reduces solid waste, because it diverts usable paper from the waste stream

3. Materials and Methods

3.1 Materials and Chemicals

The raw material used during this experimental work was castor seed. Castor seed was purchased from Addis Ababa merkato shop center. The chemicals in the study sodium hydroxide, sodium sulfide, hydrochloric acid, distilled water, sulfuric acid, potassium hydroxide, N-hexane, phenolphthalein, Sodium chloride and ethanol were purchased from Atomic educational materials supply in Addis Ababa, Ethiopia. All chemicals were reagent grade.

3.2 Equipments

The Equipments used during the experimentations includes laboratory autoclave, PerkinElmer spectrophotometer (AAU17 5839), aeration apparatus unite for deinking flotation (Ch-EL254),Magnetic stirrer hot plate (AAiT-101-4531-08-CHD-1516),Ranger RD compact scale (Ch-EL 283), Laboratory Pulper (EPP-3-01-5),Soxhlet extractor, Printer, Pulp disintegrator machine(EPP-3-01-6),Pressing machine(EPP-3-01-10),Condenser, water bath(SBS40), separating funnel, refrigerator, oven, sheet forming machine (EPP-3-01-9), pH meter (350S), beating machine (EPP-3-01-05) ,conductivity meter (hand held) and different size of conical and Erlenmeyer flasks, beakers, measuring cylinders, burette, zipper bags. Raw material preparation (fatty acid soap) and deinking flotation of the printed paper was done at Addis Ababa institute of technology, School of Chemical and Bio Engineering Laboratory, Addis Ababa. Pulping of waste papers and pulp hand sheet were done in the laboratory of Ethiopian Pulp and Paper Share Company, Wonji. Effective residual ink concentration analysis of paper hand sheet was done at Addis Ababa University College of natural science department of chemistry Laboratory, Addis Ababa. The overall structure of the experimental works is shown in Figure (3.2).

3.3. Experimental Methods

3.3.1. Castor Seed Preparation

The raw materials for preparation of natural surfactants are Natural Oil and Fats: Triglycerides. The natural oil was extracted from castor seeds. The castor seeds was undergone various processing in the course of its preparation for extraction.

The unit operations involved are:

1. **Clearing:** The castor beans had some foreign materials and dirties which were separated by hand picking.
2. **Drying:** The cleaned beans were sun dried in the open air, until the covering splits and sheds the seeds. The beans were further dried in the oven at 60°C for 7hrs to a constant weight in order to reduce its moisture content.
3. **Winnowing:** The separation of the shell from the nibs (cotyledon) were carried out using tray to blow away the cover in order to achieve very high yield.
4. **Grinding:** It is the process of size reduction by crushing the beans in order to weaken or rupture the cell walls to release castor seed for extraction and then dried for about 15 days.

3.3.2. Castor Oil Extraction

The dried powders of castor been had subjected to Soxhlet extraction using n-hexane as a solvent, to do this: Normal Hexane was poured into round bottom flask and the dried powder of castor been was placed in the thimble and inserted in the center of the extractor. The Soxhlet was heated at 60°C. When the solvent was boiling, the vapour rises through the vertical tube into the condenser at the top. The liquid condensate drips into the filter paper thimble in the center, which contains the solid sample to be extracted. The extract leaches through the pores of the thimble and fills the siphon tube, where it flows back down into the round bottom flask. This allowed to continue for 3hours.

The extract was then removed from the tube. Further extraction was carried out repeatedly until the required amount of oil was obtained. At the end of the extraction, the resulting mixture containing the oil was heated to recover solvent from the oil.

3.3.3. Characterization of castor oil

3.3.3.1. Determination of the Percentage of Castor Oil Extracted

10 g of castor seed was placed in the thimble and 180 mL of *n*-hexane poured into the empty round bottom flask. The solvent was heated to 60°C and allowed to heat for 3 h continuously while extracting the oil by using Soxhlet apparatus. Different weight of the castor seed, 12 g, 16 g and 20 g were added in the apparatus at 3 h intervals, solvent was evaporated and the percentage of oil determined using known procedures.

$$\text{Yield of Oil} = \frac{\text{mass of oil}}{\text{mass of castor seed}} \times 100\% \quad (3.1)$$

3.3.3.2. Determination of Saponification Value

2 gram of castor oil was weighed into a 250 mL glass conical flask, and then 10 mL of ethanol ether mixture (2:1) was added to the same flask followed by 25 mL of 0.5 N ethanolic potassium hydroxide. The flask was then fitted to a reflux condenser and refluxed using a boiling water bath for 30 min with occasional shaking. To the warm solution were added 3 - 4 drops of phenolphthalein indicator and the warm solution was titrated against 0.5 M HCl to the end point. The same procedure was used for other samples and blank. The expression for saponification value (S.V) is given by equation:

$$SV = \frac{v_0 - v_1}{w} \times N \times M \quad (3.2)$$

Where, v_0 = the volume millimeter of HCL solution (for the blank space)

v_1 = the volume millimeter of HCL solution (for the oil)

N = normality of HCL

M = molecular weight of KOH

W=mass of sample solution oil

3.3.3.3. Determination of Acid Value

2.0 g of the castor oil was placed into 250 mL conical flask followed by 25 mL of ethanol and add 3 drops of phenolphthalein indicator. The mixture was heated in a shaking water bath for 5 minutes. While hot, it was titrated against 0.1 N KOH until pink color appeared. Vigorous shaking was done when approaching the end point to ensure thorough mixing. The volume of 0.1 N KOH consumed by an acid was recorded. The acid value was calculated as reported in the literature.

$$AV = \frac{V \times N_b \times M}{W} \quad (3.3)$$

Where V is the volume of alkali added in mL until it changes the color to red, N_b is the normality of KOH.

3.3.4. Refining of Castor Oil

The refining was needed to remove gum from the extracted oil. Distilled water was added to the oil and the mixture stirred for 2 mins and allowed to stand in the separating funnel. The aqueous layer was then removed. The de-gummed oil was collected and stored for use. The procedure was repeated to ensure removal of most gums.

3.3.5. Preparation of Natural Anionic Surfactant (Sodium Stearate) from Natural Oil

Sodium stearate of the molecular formula $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-\text{Na}^+$ is anionic surfactant used for flotation deinking purpose. To manufacture this surfactants: 76.2g of extracted refined oil was weighted into a 1000 mL glass beaker, and then 1000mL of ethanol water mixture (1:1) was added to the same beaker followed by 25.4g of sodium hydroxide. The beaker was then fit to a boiling water bath with a temperature of 60°C for 30 min with occasional shaking. After being heated for about 30 min, the odor of alcohol was disappeared, indicating the completion of the saponification reaction.

A stock mass containing a mixture of the soap, glycerol, and excess sodium hydroxide was obtained. Use a refrigerator to cool the beaker with its contents. To precipitate or "salt out" the soap, 150 mL of a saturated sodium chloride solution was added to the soap mixture while stirring vigorously. This process increases the density of the aqueous solution; therefore, soap was floated out from the aqueous solution and after this time it was put on filter paper to dry up.

The next step was acidification process of the stock to give sodium stearate fatty acid soap by using sulfuric acid. A mass of stock was carried out on an experiment in order to transform it in to sodium stearate. The stock was dissolve in water until it contained about 75% water by volume. The water solution was further treat with the solution of 4N H₂SO₄ at 90°C until the pH =6. then they was washed with water until the pH of rinsed water reaches 7.

3.3.6. Characterization of Natural Anionic Surfactant

The surfactant was characterize to the Hydrophile-Lipophile balance (HLB) value, critical micelle concentration (CMC) and foamability stability.

3.3.6.1. Determination of Hydrophile-Lipophile Balance (HLB)

Calculation of HLB value of surfactant is very important in product quality and yield points of view. HLB values was calculated theoretically or may be determined by experimentally. Formulas for calculating HLB values may be based on either analytical or composition data. For most polyhydric fatty acid soap (surfactants) the values of HLB was calculated with the formula:

$$HLB = \frac{E+P}{5} \quad (3.4)$$

Where,

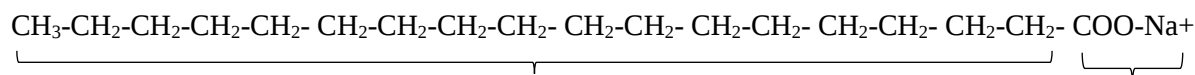
E= weight percentage of carboxylate head

P= weight percentage of hydrocarbon tail

A soap is a salt of a compound known as a fatty acid. A soap molecule consists of a long hydrocarbon chain (composed of carbons and hydrogens) with a carboxylic acid group on one end which is ionic bonded to a metal ion, usually a sodium or potassium.

The hydrocarbon end is nonpolar and is soluble in nonpolar substances (such as fats and oils), and the ionic end (the salt of a carboxylic acid) is soluble in water.

The structure of a soap molecule is represented below:



Non-polar hydrocarbon chain ionic end (soluble in nonpolar substances) (soluble in water)

3.3.6.2. Critical Micelle Concentration (CMC)

There are more different methods used to determine CMC. From these conductivity method is the one by the relationship between conductivity of ionic surfactant solution and concentration of the anionic surfactants on which the turning point was CMC.

30ml of 0.05M aqueous stock solution was prepared. 25ml of deionized water was pipetted in to a 200ml beaker and 1ml of the stock solution (surfactant) was added in to water and stir. The electrode was cleaned by ethanol after each determination and rinse rapidly with deionized water and dry. Then draw the graph between molar conductivity Vs concentration of anionic surfactant. Then, the conductivity was recorded.

3.3.6.3. Surfactant Foamability

Foams are typically formed in regular hexagonal texture as a result of gas dispersion through a continuous surfactant solution. It is thermodynamically unstable and they are stabilized by surfactants to prevent bubble coalescence. Foams are generally described in terms of their foamability defined as the capacity of the surfactants to form foam irrespective of the special foam properties, and foam stability describing the variations of foam height or volume with time, immediately after foam generation. The most widely valued property of the surfactants in aqueous solution is their ability to inspire the formation of foam and froths.

These activities could be endorsed to the physical nature and bubble development. In present case, the concentration of fatty acid soap was varied to investigate the effect on the foamability. to taste the foamability of the surfactant by using the following procedures:

4g of the anionic surfactant was dissolved in 60ml of distilled water in a 100 ml measuring cylinder and shaken vigorously for 3 min. It was allowed to stand for 20 min after which the height of the foam was determined. This was repeated thrice for each soap sample and the mean computed.

3.3.7. Preparation and Pulping of Waste Paper

540 sheets of unprinted white paper was printed with black powder ink and used in this study for waste paper furnishes. The paper was printed on one side only. The paper was cut into 20 to 30mm squares and stored in opaque plastic bags at room temperature for one month. To know the amount of ink used, weight measurement was used between 540 sheets of printed and 540 sheets of unprinted papers. Pulping was carried out on process at room temperature and printed oven dried paper were used in this experiment.

The oven dried paper was soaked with a 5% sulfuric acid solution for 30 min, and then washed to a neutral pH with deionized water. Subsequently, it was soaked again with 5% caustic soda solution at the same concentration and temperature for another 30 min, and then washed to a neutral pH with deionized water. A screen was employed to estimate yield. The repulping yield (Y) of waste paper can be calculated by the following formula in equation (3.2):

$$Y = \frac{X}{X+Y} \times 100\% \quad (3.5)$$

Where X=Oven dry weights of waste paper and Y=waste paper suspension including water, respectively.

3.3.8. Experimental Design for Deinking Flotation and Deinking Optimization process

Experimental data analysis was done using Design- Expert 6.0.8 software. The experimental design selected for this study was three-level-three-factor face-centered central composite design (CCD) and the response variable measured was the ink removal efficiency of hand sheet. In addition the hand sheet preparation was done at Ethiopian pulp and paper factory PLC, Wonji.

The ink removal efficiency analysis of the hand sheet was done at Addis Ababa University College of natural science department of chemistry. Design of the experiments were set up to see if the independent variables (flotation time, amount of surfactants and pH) affect the efficiency of the deinking flotation. Flotation time was used in flotation deinking with three levels of 30, 60 and 90min. three level pH of 3, 6 and 9. Dosage of surfactant were 1.5%, 2.5% and 3% based on oven dried fibers. These parameters was used to check the optimum deinking efficiency of the surfactant during flotation deinking process.

Three-level-three-factor face-centered CCD was used in the optimization study which requires 15 experiments to be conducted. The twenty experiments were done and the data was statistically analyzed using Design-Expert Software 6.0.8 to obtain a suitable model equation for the ink removal efficiency of hand sheet as a function of the independent variables.

Table 3.1.Independent variables and levels used in the CCD for the deinking flotation

variables		units	levels		
	Code factor		-1	0	+1
Flotation time	X1	min	30	60	90
Amount of Fatty acid soap (based on ODF)	X2	%	1.5	2.5	3
pH	X3	-	3	6	9

Table 3.1 lists the range and levels of the three independent variables studied. The lower and higher levels are chosen by considering the operating limits of modified deinking flotation process conditions.

Table 3. 2.the complete experimental design matrix

Coded Factor				Actual factor		
Run	X1	X2	X3	Flatation time(min)	Fatty acid soap Based on OD fiber(%)	pH
1	0	0	0	60.00	2.25	6.00
2	0	+	0	60.00	3.51	6.00
3	+	+	+	90.00	3.00	9.00
4	-	+	+	30.00	3.00	9.00
5	-	+	-	30.00	3.00	3.00
6	+	-	+	90.00	1.50	9.00
7	+	-	+	90.00	1.50	3.00
8	-	-	+	30.00	1.50	9.00
9	0	-	0	60.00	0.99	6.00
10	+	0	0	110.45	2.25	6.00
11	-	-	-	30.00	1.50	3.00
12	-	0	0	9.55	2.25	6.00
13	0	0	-	60.00	2.25	0.95
14	0	0	+	60.00	2.25	11.05
15	+	-	+	90.00	3.00	3.00

3.3.9. Experimental Flotation Deinking Process

Toner ink separation and removal from the fiber net was carried out in a flotation column cell. This cell is 36cm tall and 3.5cm in diameter with an aeration system. An air flowmeter for flow rate control was used. The working flow rate of air was 2L/min. as the pulp treatment was accomplished, each sample was diluted with the surfactants.

The pulp was charged into column and floated in the presence of surfactants. The ink particles were attached to the air bubbles due to their relatively high hydrophobicity and were floated to the surface of suspension, and the hydrophilic fibers were remain in the water phase. A scraper was used for foam removal over the course of flotation.

The removed foam was collected in a reject tank. The yield of the flotation was calculated once the reject was dried and was deducted from the original floated slurry weight. The role of surfactants was as agglomeration and flotation agents, which act to separate the ink particles in the froth flotation deinking cell. In fact, it has been shown from both laboratory de-inking experiments and fundamental surface force measurements that surfactant particles are produced from the precipitation of these long chain anions with sodium ions. These soap particles then function as collectors by a co-agglomeration process between the soap and ink particle forming larger mixed hydrophobic flocs which become attached to the air bubbles.



Figure 3.1. Aeration apparatus of flotation process

3.3.10. Pulp Hand Sheet Preparation

Dry waste paper pulp produced from deinking flotation condition was used for sheet preparation procedures. 138g of oven dry pulp was mixed with 23 liters of water to make pulp slurry with consistency of 0.6%. Pulp slurry was added in to a beating machine and beat up by circulating it. Freeness of slurry was checked out at each ten minutes beating interval. This was done by taking 333ml of slurry from the beater (this contains 2gm of moisture free fiber) and then dilute to 1000ml with distilled water and measured freeness value.

When the freeness of pulp is 30CSF, 800ml sample was taken from beater and diluted to 2liters of water (0.17% consistency) and disintegrated at 1500rpm for five minutes. The beated and disintegrated pulp suspension was taken from the disintegrator and diluted to 4liters of water and agitated well by hand.

404ml from the diluted suspension was taken 60gm/m² was prepared by sheet forming machine. Once the sheets are prepared two stage pressing was followed by applying 0.47MPa pressure for four minutes by pressing machine. Then the stocks are removed from the press and attached to the drying plates in order to dry by oven at 130°C for 45 minutes. The prepared sheets were then tested for the residual ink concentration.

3.3.11. Evaluation of Deinked Pulp

The comparison of the blank hand sheet with those from the flotation runs allowed for determining the percentage of deinking efficiency. Deinking efficiency can be evaluated by measuring Effective Residual Ink Concentration (ERIC) of hand sheets made from the recycled paper before and after deinking. Increases in Effective Residual Ink Concentration (ERIC) values indicate an efficient deinking flotation process. For each experiment, three hand sheets (60gsm) were prepared for each trial according to accepted procedure (TAPPI Standard) at Ethiopian pulp and paper industry located at Wonji. Hand sheets were prepared for measuring ink concentration of sheet.

Select the 950 nm filter position or modified spectral equivalent. Place the hand sheet on the instrument and read and record the reflectance of the sheet (R_{∞}). Place the sheet on the instrument and back it with the black cavity, Read and record its reflectance (R_0). The scattering coefficient (S) of the sample at 950 nm was calculated by:

$$S = \left[\frac{R_{\infty}}{W(1-R_{\infty}^2)} \right] \ln \left[\frac{1-R_0R_{\infty}}{1-\frac{R_0}{R_{\infty}}} \right] \quad (3.9)$$

Where w = grammage (g/m²) and where R_0 and R_{∞} are expressed as decimals. Their ratio between K_{paper} and K_{ink} is defined as effective residual ink concentration (ERIC), with a unit of ppm.

$$K = S \frac{(1-R_{\infty})^2}{2R_{\infty}} \quad (3.4)$$

$$\text{ERIC} = \frac{K_{\text{sheet}}}{K_{\text{ink}}} \times 10^6 \text{ (ppm)} \quad (3.5)$$

Black inks have been shown to have an absorption coefficient of about 10,000 m²/kg (Carre, et al, 1995). This was considered to be a default value for this method (i.e. $k_{ink} = 10,000 \text{ m}^2/\text{kg}$). Deinking efficiency of the paper hand sheet could be calculated as follow:

$$IE \% = \frac{ERIC_{UP} - ERIC_{DP}}{ERIC_{UP} - ERIC_{UNP}} \times 100\% \quad (3.6)$$

Where, $ERIC_{UP}$ and $ERIC_{DP}$ are the residual ink concentration for undeinked hand sheet (pulp) and deinked hand sheet (pulp) and $ERIC_{UNP}$ is unprinted paper.

3.3.12. Experimental Setup

In this experimental setup, there were two main types of production units. one was the synthesis of anionic surfactant (Fatty acid soap) from castor seed oil. And the second was flotation deinking of printed paper for ink removal using this fatty acid soap. For fatty acid soap production, Mixture of castor oil, sodium hydroxide and methanol was heated on a water bath equipped with a motor stirrer. For saponification reaction a 1000 ml glass reactor equipped with agitator was used in all experiments. The saponification reaction system was employed for sodium soap (fatty acid soap) production and this was used for flotation deinking as foaming agent. The overall experimental setup was shown in the following diagram.

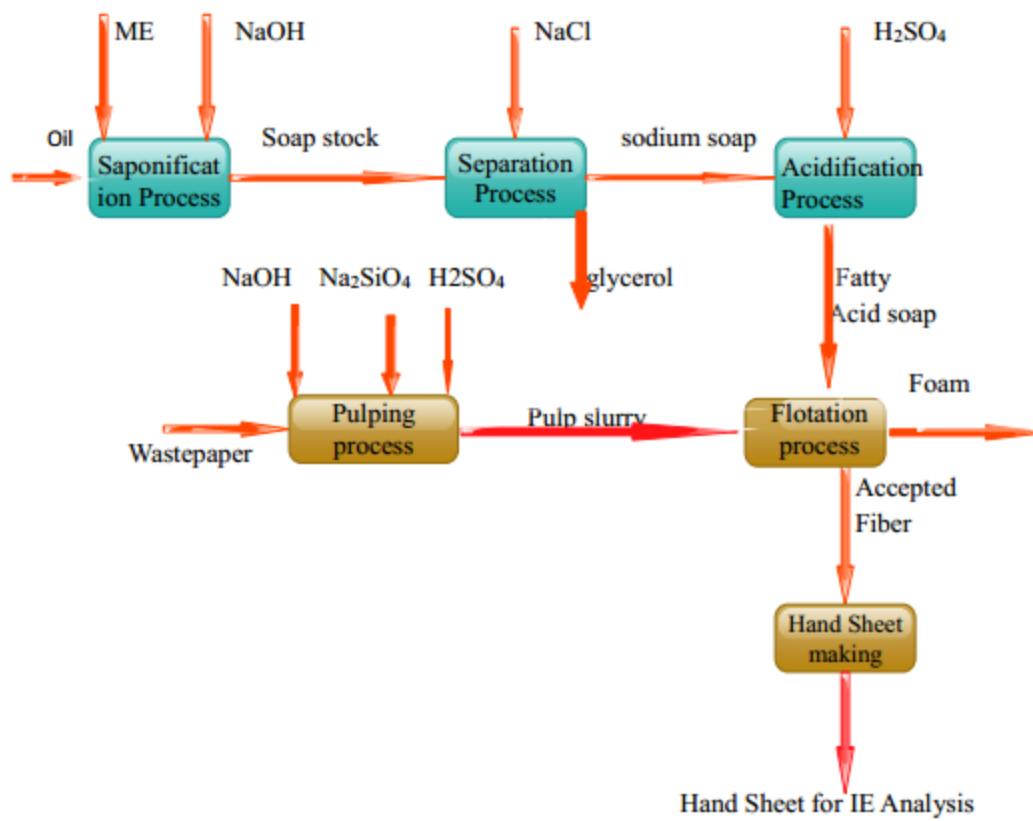


Figure 3.2.Experimental set up flow diagram

4. Results and Discussion

4.1. Castor Seed Preparation, Oil Extraction, Purification and Characterization

4.1.1. Castor Seed Preparation and Processing

About 8kg of castor seed was purchased for this research work. The seed was cleaned from different impurities and dirties by processing in different unit operations.



Figure 4. 1.Castor Seed Sample.

4.1.2. Castor Oil Extraction

Solvent extraction method was used for oil extraction. From 1824.82g castor seeds 500g crude castor oil was extracted using Soxhlet extractor machine.

4.1.5. Refining of Castor Oil

The total amount of crude oil obtained from solvent extraction was 500g. From this crude oil 86.5g was removed during the purification process. About 165ml distilled water was used for degumming purpose.

4.2. Castor Oil Characterization

4.2.1. Determination of the Percentage of Castor Oil Extracted

Percentage of oil extracted was determined by calculating the yield of Soxhlet extractor machine using equation (4.1) below.

Table 4.1. percentage yield of castor oil extracted

Determination	Value (g)
Weight of empty flask	108.9
Weight of empty flask +oil	125.35
Weight of oil	16.45
Percentage of oil extracted (%)	27.42

$$\text{Yield of Oil} = \frac{\text{mass of oil}}{\text{mass of castor seed}} \times 100\% \quad (4.1)$$

Yield of oil = 27.42%

4.2.2. Determination of Saponification Value

Saponification number indicates the number of fatty acid chain length of triglycerides. The products of castor oil was titrated with 0.1M HCL. The saponification number was determined by using the equation (4.2).

$$SV = \frac{V_0 - V_1}{w} \times N \times M \quad (4.2)$$

Where, V_0 =the volume millimeter of HCL solution (for the blank space) =0.051L

V_1 = the volume millimeter of HCL solution (for the oil) =0.038L

N =normality of HCL=0.1M

M=molecular weight of KOH=56g/mole

W=mass of sample solution oil =2g

$$S_v = \left(\frac{0.0892 - 0.028}{2} \right) \times 0.1 \times 56 = \frac{171.36 \text{mgKOH}}{\text{goil}}$$

4.2.3. Determination of Acid Value

The fatty acid value was determined by using the equation (4.2).

$$AV = \frac{V \times N_b \times M}{W} \quad (4.3)$$

Where V is the volume of alkali added in mL until it changes the color to red, N_b is the normality of KOH.

✓ $V=2.5\text{mlKOH}$

✓ $N_b=0.1\text{mol/l}$

✓ $M=56\text{g/mol}$

✓ $W=2\text{g}$

$$AV = \frac{1.28 \times 0.1 \times 56}{2} = \frac{3.584 \text{mgKOH}}{\text{goil}}$$

$$FFA = \frac{AV}{2} = \frac{3.584}{2} = \frac{1.792 \text{mgKOH}}{\text{goil}}$$

4.3. Preparation of Natural Anionic Surfactant from Natural Oil

From 200g of refined castor oil 620.65g of sodium stearate (anionic surfactant) was gained and 15g of glycerol was removed by saponification process.



Figure 4. 2. Sodium stearate (anionic surfactant)

4.4. Characterizing of Anionic Surfactant

4.4.1. Determination of Critical Micelle Concentration (CMC)

CMC was determined by using the relationship between conductivity of ionic surfactant solution and its concentration on which turning point was CMC. The conductivity of surfactant concentration were listed on appendix B.

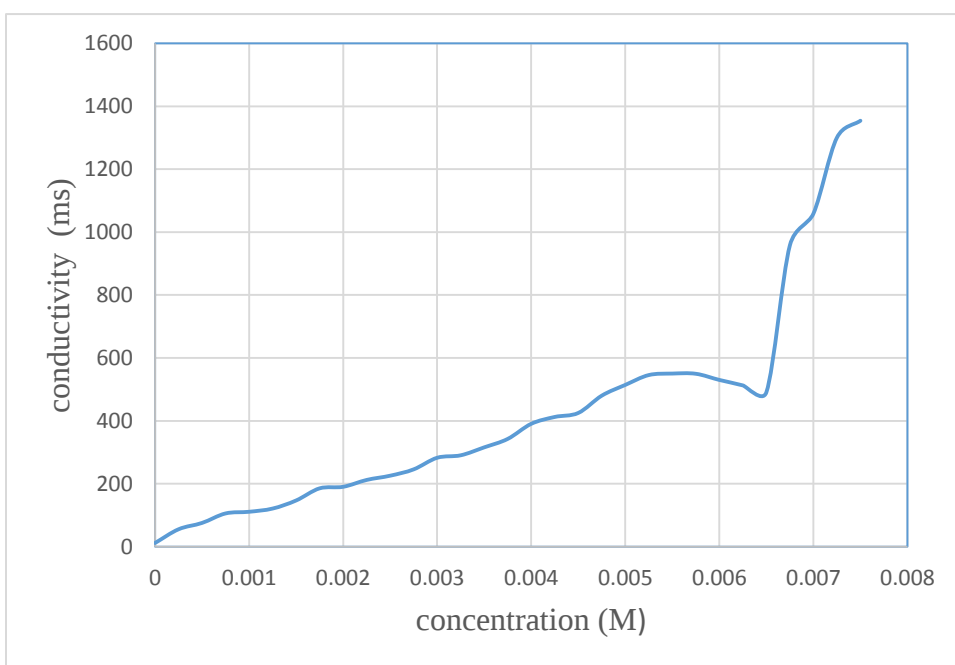


Figure 4. 3.CMC curve

From the above graph the first turning point was at (0.0065, 490.7), therefore the CMC was 0.0065 with conductivity of 490.7ms.

4.4.2. Determination of Hydrophile-Lipophile Balance (HLB)

HLB values was determined by experimental and theoretical work. Formulas for calculating HLB values may be based on either analytical or composition data. For most polyhydric alcohol fatty acid esters and surfactants, the values of HLB was calculated with the formula in equation (4.4):

$$HLB = \frac{E+P}{5} \quad (4.4)$$

Where, E= weight percentage of hydrocarbon tail ($3C_{17}H_{35}$) =78%

P= weight percentage of carboxylate head ($3COONa$) =21%

$$HLB = \frac{78 + 21}{5} = 19.48$$

The hydrophilic-lipophilic balance (HLB) of a surfactant affects the flotation efficiency. HLB values describe how the surfactant interacts with water soluble and water repellent substances. In deinking flotation it has been suggested that surfactant with an HLB value of 14-20 are optimal for deinking of paper and magazine mixtures (Turai, *et al*, 1977).

4.4.3. Surfactant Foamability and Foam Stability

Foams are generally described in terms in to two terms. The one is foamability and the other is foam stability. Foamability is defined as the capacity of the surfactants to form foam irrespective of the special foam properties. Foam stability is defined as the variations of foam height or volume with time, immediately after foam generation. The two terms are interrelated and the more stable the foam films the greater is the solution's hexagonal texture. And thin liquid films to prevent bubble foamability.

The increasing of fatty acid soap concentration enhanced the dense foam production with increased depth. At higher concentration of fatty acid soap, a very thick high quality foam was observed. From the table 4.2, the maximum foam height was 49cm at 17min time. After 17min it begins to decrease to some value.

Table 4. 2. Foamability height

Foam height (cm)	0	6.5	18	26.5	49	18	9.5	9.5	0.8
Time(min)	1	5	9	13	17	21	25	29	33

Table 4.3.Characteristics of surfactants

Sr. No	Parameter	Values
1	Critical micelle concentration(M)	0.0065
2	hydrophile-lipophile balance (HLB)	19.48
3	Foamability height (cm)	49

4.5. Preparation and pulping of Waste Paper

4.5.1. Physical properties of Unprinted and Printed Paper

To know the amount of ink used, weight measurement was used between 540 sheets of printed and 540 sheets of unprinted papers.

Table 4.4.properties of printed and unprinted paper

Paper sample	Un Printed	Printed
Size	A4 (210mmX297mm)	A4 (210mmX297mm)
Color	White	White
Thickness(mm)	0.11	0.11
Weight of 540 sheet (g)	2700	2711.7
Weight of ink (g)	-	11.7

The moisture content was also determined by the following formula in equation (4.5).

$$\text{Misture content (\%)} = \frac{M_1 - M_2}{M_1} \times 100 \quad (4.5)$$

Where,

M1 = mass of waste paper before drying

M2 = mass of waste paper after drying

The weight was measured at every 2 hours interval. Weight measuring was continued until constant weight was obtained.

4.5.2. Preparation and Pulping of Waste Paper

To know the amount of ink used on the printed, weight measurement was used between 540 sheets of printed and 540 sheets of unprinted papers. The total weight of the 540 sheet unprinted paper was 2700g and the printed 540 sheets was weighted 2711.7g. from this the total amount of printing ink was 11.7g.



Figure 4. 4. Pulp slurry

4.6. Deinking Flotation Process

The pulp was charged into flotation column cell and floated by using anionic surfactants by controlling parameters from the previous analysis which are: flotation time, Amount of surfactants (based on ODF), and PH.

After flotation a scraper was used for foam removal over the course of flotation. The removed foam was collected in a reject tank and the remaining pulp was collected in accept tank. The yield of the flotation was calculated once the reject was dried and was deducted from the original floated slurry weight. The total weight of the oven dried fiber in the feed tank and in the reject foam tank was 150g and 11.5g respectively. The percentage of fiber loss was calculated by using the formula in equation (4.6):

$$\text{fiber loss} = \frac{\text{amount fiber rejected with foam}}{\text{total amount of fiber on feed}} \times 100 \quad (4.6)$$

$$\text{Fiber loss} = \frac{11.5g}{150g} \times 100 = 7.67\% , \text{ Therefore the yield of the flotation cell was } 92.33\%.$$

4.7. Pulp Hand Sheet Preparation

15 hand sheet pulp was prepared which have 60gm/m² amount of fibers .The prepared sheets were then tested for the effective residual ink concentration.

4.8. Statistical Analysis on Factors Affecting Deinking

Flotation Process

The experimental design selected for this study was the Central Composite Design (CCD) and the response variable measured was the ink removal efficiency. Three level-three-factor CCD apply the face-centered cubic design. Having three levels instead of five was cited as desirable because it reduced the preparation time and complexity of the experiment. Three-level-three-factor face-centered CCD was employed in the optimization study and a total of 15 experiments were conducted. The three deinking flotation process variables are flotation time, fatty acid soap dosage (based on ODF) and pH.

Face-centered CCD was selected according to the region of interest and it is very efficient for fitting a second order model. Design-Expert Software 6.0.8 was used in the least squares regression analysis of variance (ANOVA). The statistical software program was used to generate the model equation, interaction effects of the independent variables and surface plots using the fitted equation obtained from the regression analysis holding one of the independent variable constant.

The CCD conditions and their respective responses and the ANOVA are given in Table 4.6 and Table 4.7 respectively. The actual ink removal efficiency which done at different process parameters was determined by using Perkin Elmer spectroscopy to analysis the residual ink concentration on the undeinked and deinked pulp sheet. The detail calculations and results are discussed in sections below and in Appendix B-4.

Table 4.5.experimental and predicted values

Run order	Flotation time (min)	Fatty acid soap (%)	pH	Expermental ink removal efficiency (%)	Pridicted ink removal efficiency (%)	Residual
1	60.00	2.25	6.00	68.4	66.32	2.08
2	60.00	3.51	6.00	58.03	61.04	-3.01
3	90.00	3.00	9.00	62.61	58.41	-0.21
4	30.00	3.00	9.00	60.11	63.26	-0.65
5	30.00	3.00	3.00	72.46	67.91	4.55
6	90.00	1.50	9.00	78.0	78.39	0.943
7	90.00	1.50	3.00	54.86	49.77	5.09
8	30.00	1.50	9.00	60.11	60.65	-0.54
9	60.00	0.99	6.00	53.51	56.78	-3.27
10	110.45	2.25	6.00	52.30	56.03	-3.66
11	30.00	1.50	3.00	53.72	49.06	4.66

12	9.55	2.25	6.00	51.67	54.30	-2.63
13	60.00	2.25	0.95	52.37	61.62	-9.32
14	60.00	2.25	11.05	63.40	76.56	3.04
15	90.00	3.00	3.00	68.1	58.42	4.98

4.8.1. Development of Regression Model Equation

The model equation that correlates the response (ink removal efficiency) to the Deinking flotation process variables in terms of actual value was given below. The predicted model for percentage of Removal efficiency in terms of the coded factors was given in equation (4.7).

$$IE = +66.32 + 0.51 * A + 1.27 * B + 4.44 * C - 3.95 * A^2 - 2.62 * B^2 + 0.98 * C^2 - 4.10 * A * B + 2.71 * A * C - 5.61 * B * C - 1.55 * A * B * C \quad (4.7)$$

Where,

A=flotation time

B=fatty acid soap dosage

C=pH

Final Equation in Terms of Actual Factors:

$$IE = -30.26694 + 0.76917 * \text{Flotation time} + 48.63351 * \text{Fatty acid soap} + 3.97441 * \text{pH} - 4.34953E-003 * \text{Flotation time}^2 - 4.67954 * \text{Fatty acid soap}^2 + 0.10875 * \text{pH}^2 + 0.18217 * \text{Flotation time} * \text{Fatty acid soap} + 0.030125 * \text{Flotation time} * \text{pH} - 2.49278 * \text{Fatty acid soap} * \text{pH} \quad (4.8)$$

4.8.2. Model Adequacy Check

The model was tested for competence by analysis of variance. The regression model was found to be significant with the correlation coefficients of determination of R-Squared, adjusted R-Squared and predicted R-Squared having a value of 0.7928, 0.5625 and -1.3158 respectively. The quality of the model developed could be evaluated from their coefficients of correlation.

The value of R-squared for the developed correlation was 0.7928. It implies that 79.28% of the total variation in the ink removal efficiency was attributed to the experimental variables studied. The graph of the predicted values obtained using the developed correlation versus actual values was shown in Figure (4.5). The results in Figure (4.5) demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points were very close to the line of perfect fit. This result indicates that it was successful in capturing the correlation between the three deinking process variables to the ink removal efficiency. The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in Table (4.7). Based on a 95% confidence level, F – value is a test for comparing model variance with residual (error) variance.

If the variances are close to the same, the ratio will be close to one and it is likely that any of the factors have a significant effect on the response with the P – value less than 0.05. It was calculated by model mean square divided by residual mean square.

Here the model F – value of 3.44 implies the model is significant. There is only a 3.583% chance that a “Model F – Value” this large could occur due to personal error or disturbance.

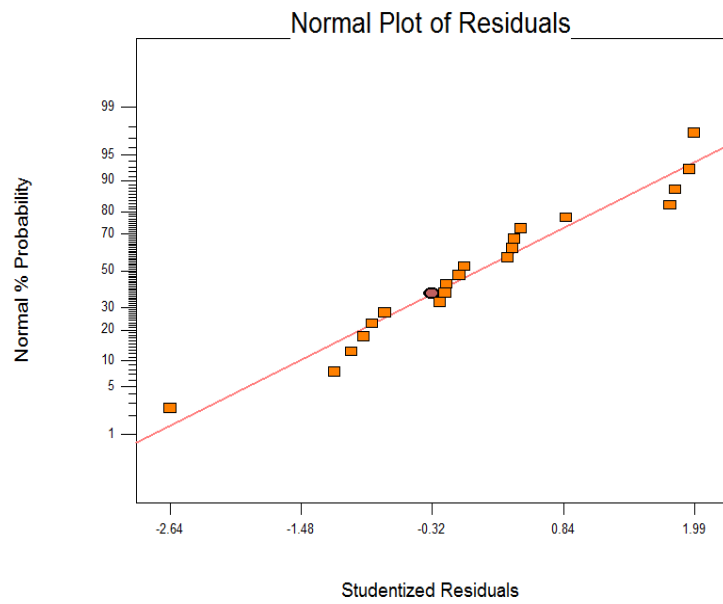


Figure 4. 5. Model Adequacy curve

Table 4.6.ANOVA for the regression model equation and coefficients

Source	Sum of	DF	Mean	F	Prob > F	
	Squares		Square	Value		
Model	1092.06	10	109.21	3.44	0.0383	significant
A	3.62	1	3.62	0.11	0.7434	
B	21.89	1	21.89	0.69	0.4276	
C	269.64	1	269.64	8.50	0.0172	
A2	224.32	1	224.32	7.07	0.0261	
B2	98.89	1	98.89	3.12	0.1113	
C2	13.83	1	13.83	0.44	0.5256	
AB	134.40	1	134.40	4.24	0.0697	
AC	58.81	1	58.81	1.85	0.2064	
BC	251.66	1	251.66	7.93	0.0202	
ABC	19.19	1	19.19	0.60	0.4567	
Residual	285.48	9	31.72			
Lack of Fit	230.10	4	57.53	4.40	0.0647	Not significant
Pure Error	55.38	5	11.08			
Cor Total	1377.54	19				

This shows that the pH, square of flotation time and interaction between fatty acid soap and pH affects the ink removal efficiency significantly. The "Lack of Fit F-value" of 4.40 implies the Lack of Fit is not significant. There is only a 6.47% chance that a "Lack of Fit F-value" this large could occur due to noise. Non Significant lack of fit is good because we want the model to fit.

4.9. Individual Effects of Deinking Flotation Process Variables

Based on the analysis of variance, deinking flotation was significantly affected by square of flotation time and pH. This result demonstrated that the advantage of using face-centered CCD for experimental data analysis in capturing the individual effects of variables that affects the deinking flotation.

4.9.1. Effects of Flotation Time on Deinking Flotation

As shown in Figure (4.6) below the ink removal efficiency was significantly affected by square flotation time. It can be seen from the figure that with increasing flotation time the ink removal efficiency increases up to it reaches 60min and after this point reversing its trend because the pulp brightness can actually decrease somewhat with further increase of flotation time. Additionally, if the flotation time is increasing beyond its maximum point it can lead to lower fiber yield and removal of its whiteness. This long flotation time has an effect on darkening the fiber by removing the bright fillers and pigments. Besides this, when the flotation time is too low, the foam generated would not stable enough and they need enough time to be stable and able attach with air rather they would return back in to the fiber. This low flotation time has a diverse effect ,since more ink needing to be collected means that an optimum flotation time was required to reach the target pulp brightness.

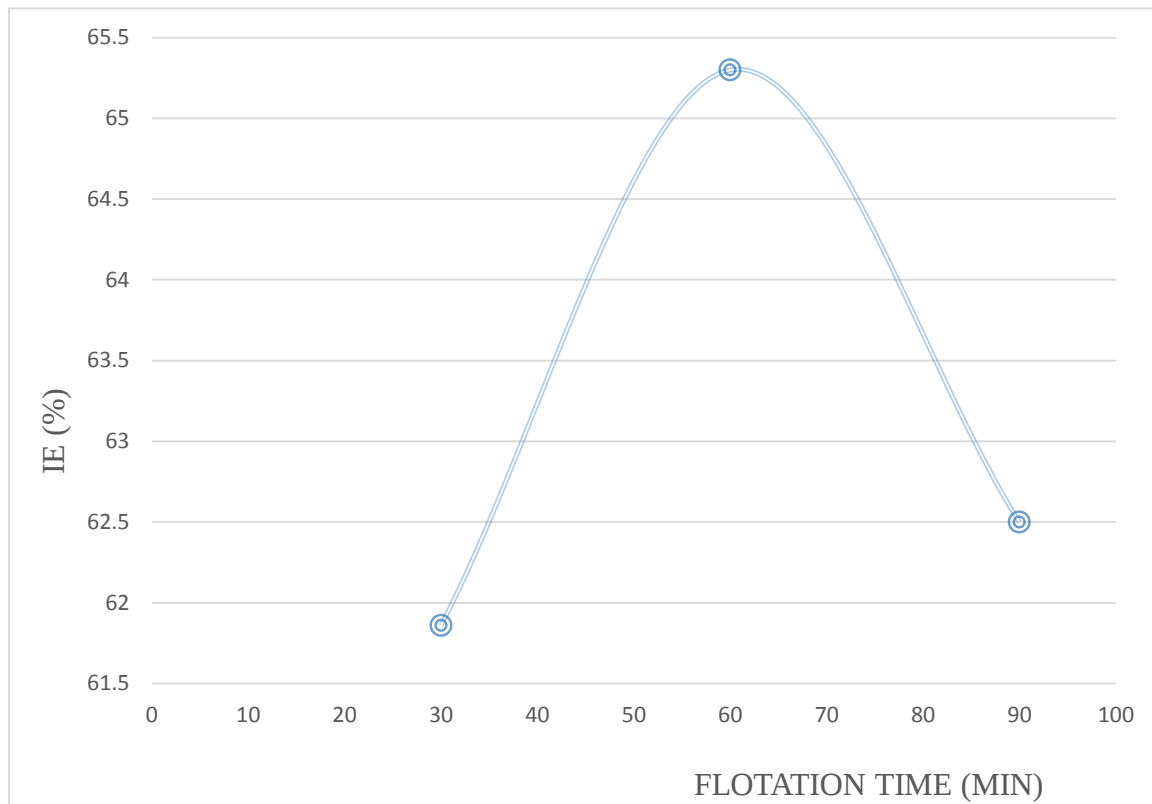


Figure 4. 6.ink removal efficiency Vs flotation time

4.9.2. Effects of Fatty Acid Soap Dosage on Flotation Deinking

As shown in figure 4.7 the ink removal efficiency was increased with fatty acid soap dosage but when it reaches 2.5% (based on ODF) changes its slope downward and this was due to the reasons of increasing their coagulation speed and absorb on the surface of the fiber, this leads to increase the hydrophobicity property of the fiber and This leads to the result of exactly stability of the ink particles and thus a reduced amount of ink attached to the air bubbles in flotation. Therefore the graph concludes excess dosage of fatty acid soap would affect the deinking flotation process. On the other hand, a lower limit for the dosage of fatty acid soap also seems to exist. Optimum fatty acid soap per dry fiber looks to be most favorable in this study.

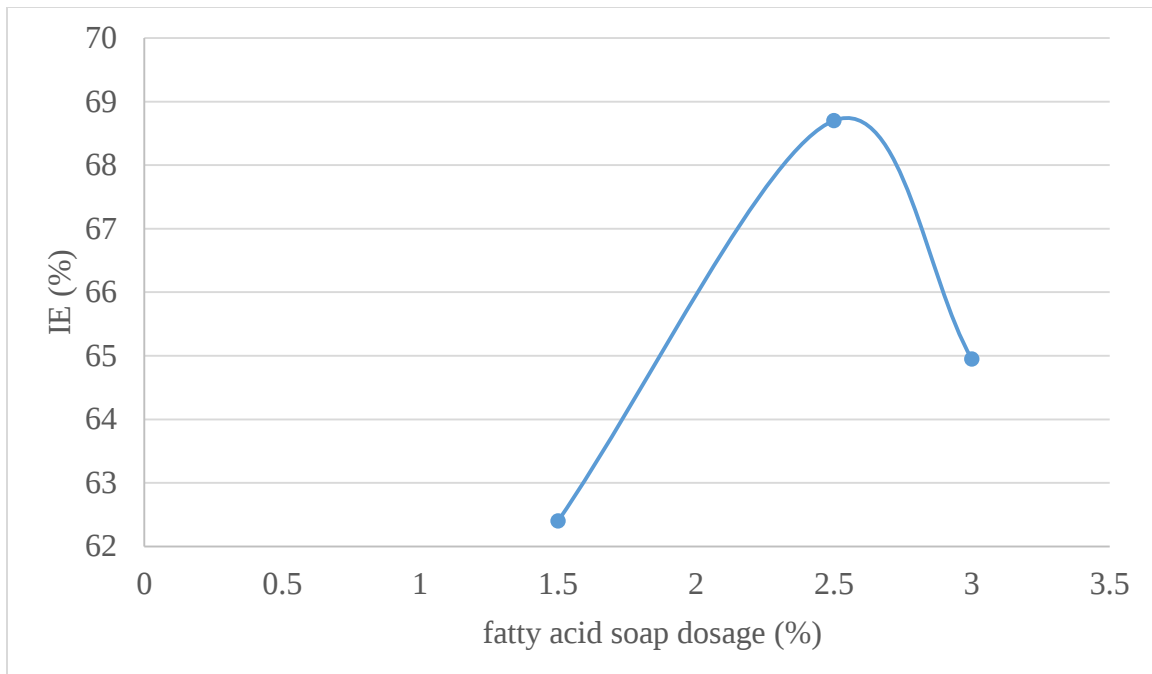


Figure 4. 7.Fatty acid soap Vs ink removal efficiency

4.9.3. Effects of pH on Flotation Deinking

In deinking flotation, the pH of the pulp slurry was important because it helps to determine the extent of ionization, hydrolysis and the charge of surfactants on the surface of the fiber slurry. This in turn influences the possibility of the collector/fatty acid soap to attach on the fiber surface. Therefore, at the various ionized solid/liquid interfaces, pH can either helps or hinders the adsorption of the surfactant and contributing to greater or lesser selectivity of deinking flotation. Acidic medium deinking flotation has a risk to damage the equipment due to their more negative charges imposed on the contaminant and substrate to repulsive each other. The removal efficiency increased with increasing pH up to 9, which means there was higher concentration of sodium hydroxide that was used to swelling up the fiber and helps to detach the ink from the fiber easily. And Low pH levels also convert acids at the fiber surfaces to their unionized foams, making the fibers more hydrophobic and hence, more difficult to flotation.

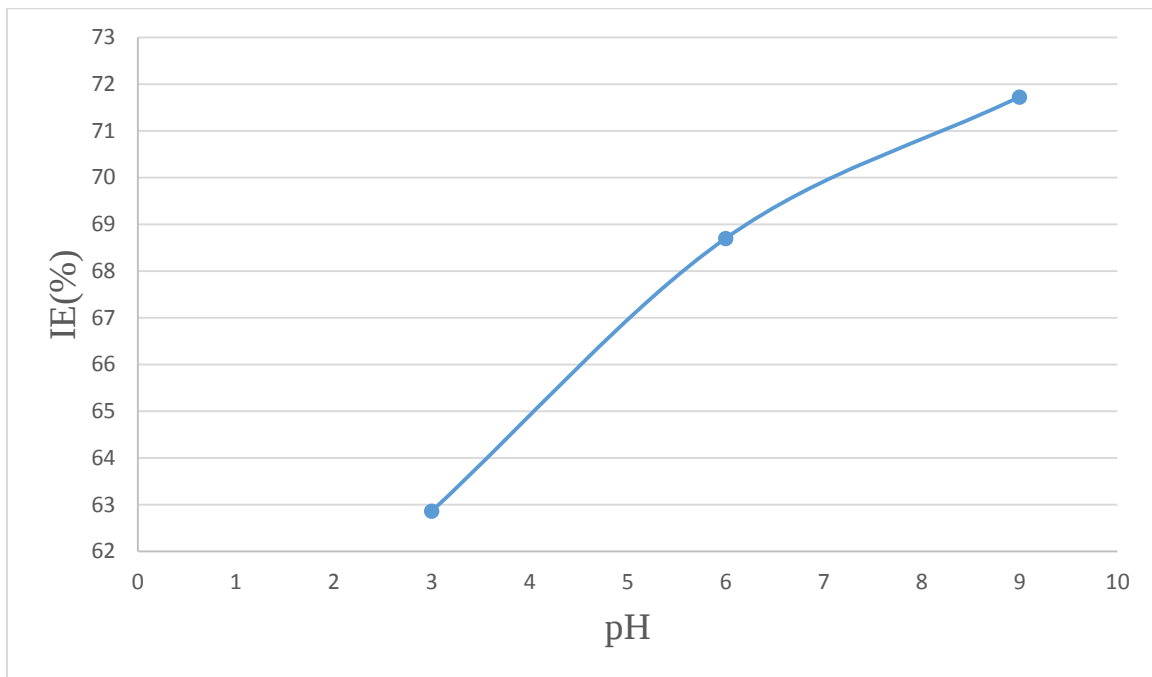


Figure 4. 8.pH Vs ink removal efficiency

4.10. Effect of Interaction between Process Variables

In this study, the optimization of deinking flotation parameters such as flotation time, fatty acid soap dosage and pH was carried out to maximize ink removal efficiency and minimize fiber loss during flotation process. The most common way to summarize the results of a central composite design experiment was in the form of a response surface plot and via response contours plot. The process variables were found to have significant and not significant interaction effects. The interaction between flotation time and amount of surfactant, flotation time and pH have a non-significant interaction on the ink removal efficiency during the deinking flotation. But the interaction between amount surfactant and pH had a significant effect on the ink removal efficiency during the deinking flotation.

4.10.1. Interaction Effects of Flotation Time and Fatty Acid Soap dosage

Response surface method was used to recognize independent variables (flotation time and fatty acid soap dosage) that produce optimum values of the response (ink removal efficiency) at constant pH. Both independent variables were individually increased or decreased in an attempt to find the optimum practical ink removal efficiency. Subsequently, these optimum variables were selected as the conditions for obtaining the best results.

The Fig. 4.9.and 4.10 below shows the 3D response surface and counter plots for the ink removal efficiency generated by the predicted model respectively.in the counter plot, ink removal efficiency increased until the flotation time reached 60min, and then it decreased. And also, increasing the fatty acid soap dosage from 1.5% to 2.5% led to increase in the ink removal efficiency and begins to decrease when the fatty acid soap dosage was further increasing from 2.5% to 3%. Based on the below graphs (figure 4.9 and 4.10), optimal conditions for ink removal efficiency was 66.5% with a desirability of 0.5311 at 2.5 %(based on ODF) and 60min flotation time with constant pH of 6.

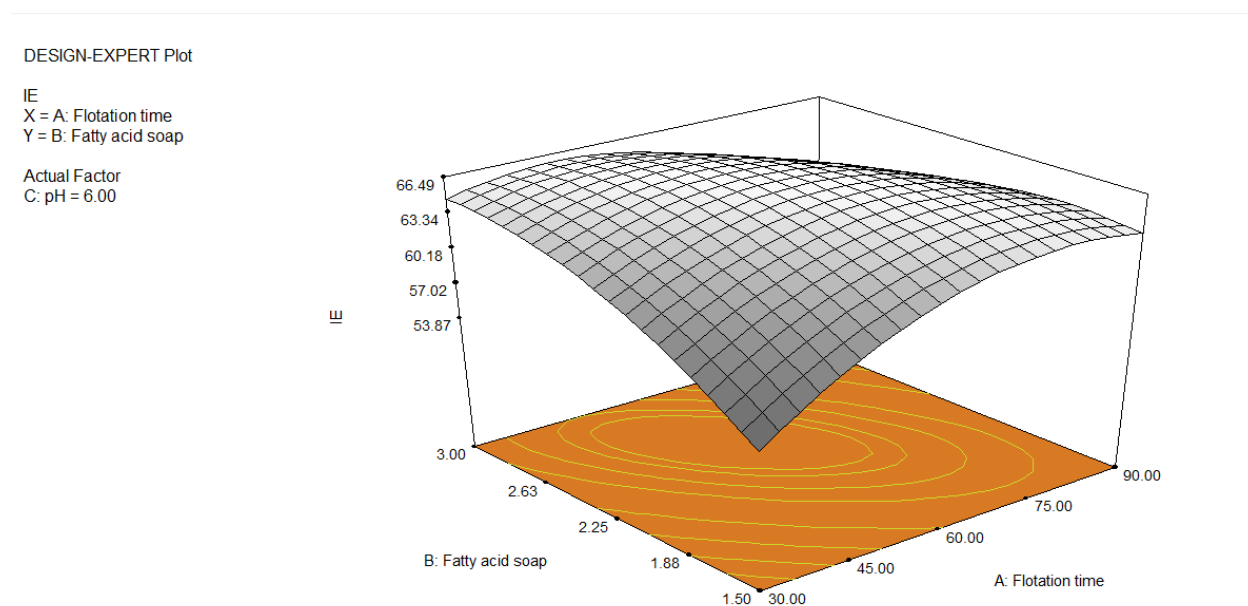


Figure 4. 9.Surface plot of the interaction effect of flotation time and fatty acid soap on ink removal efficiency

DESIGN-EXPERT Plot

IE

◆ Design Points

X = A: Flotation time

Y = B: Fatty acid soap

Actual Factor

C: pH = 6.00

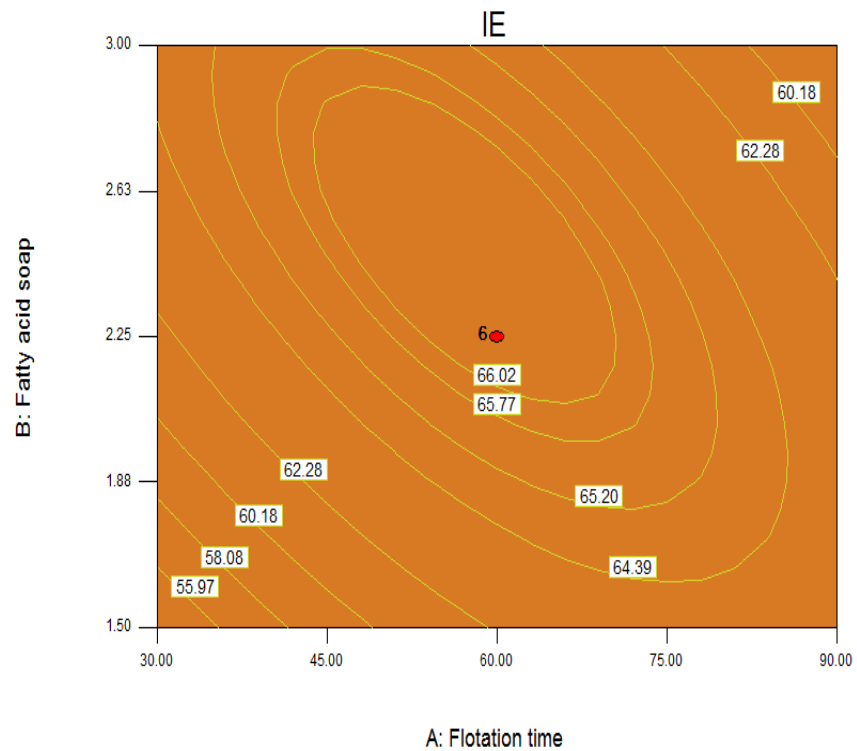


Figure 4. 10. Contour Surface plot of the interaction effect of flotation time and fatty acid soap on ink removal efficiency

4.10.2. Interaction Effects of Flotation Time and pH

The effects of the deinking flotation parameters on the ink removal efficiency were plotted in Fig 4.11 in 3-D surface plot and in fig 4.12 in 2-D contour plots. These figures show the effect of the flotation time and the pH on the ink removal efficiency maintaining the fatty acid soap dosage constant at optimum value (i.e. 2.25%). As can be seen, the interaction effect between the variables (flotation time and pH) was obvious from both the 3-D response surface and the contour-line plots. The increase of flotation time from 30min to 72.3 min leads to an increase of the ink removal efficiency from 61.1% to 72.4% and it begins to decrease when the flotation time was further increasing from 72.31min to 90 min to 56.1%. On the other hand, the effect of the pH was stronger at higher pH. Moreover, the increase of the pH from 3 to 9, increases the ink removal efficiency from 56.7% to 72.4%.

DESIGN-EXPERT Plot

IE

X = A: Flotation time

Y = C: pH

Actual Factor

B: Fatty acid soap = 2.25

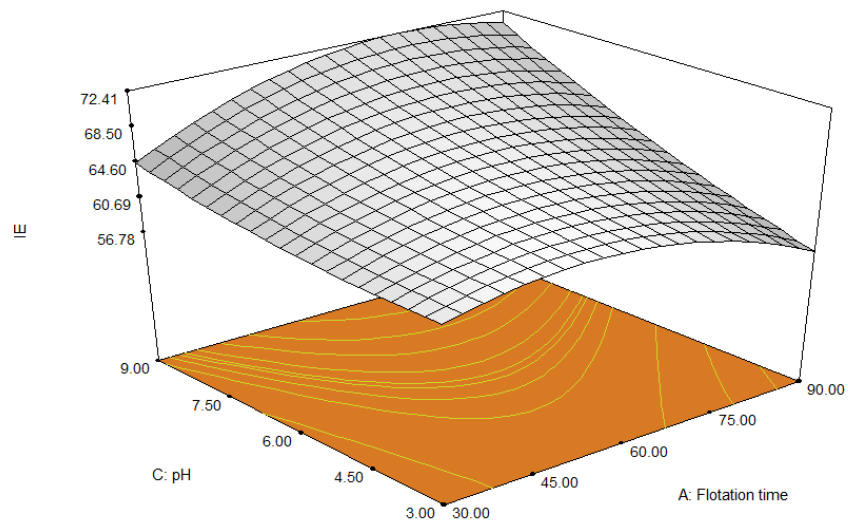


Figure 4.11. Surface plot of the interaction effect of flotation time and pH on ink removal efficiency

DESIGN-EXPERT Plot

IE

◆ Design Points

X = A: Flotation time

Y = C: pH

Actual Factor

B: Fatty acid soap = 2.25

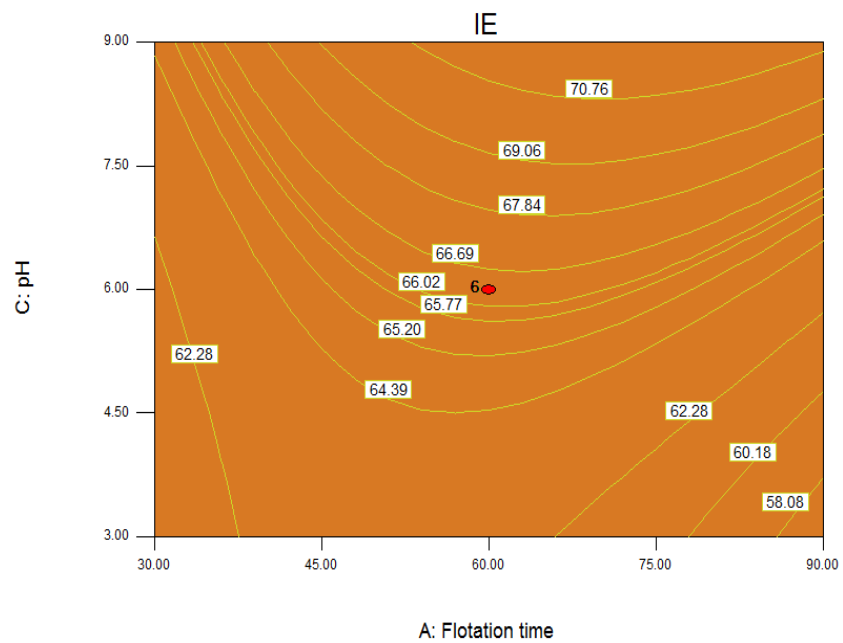


Figure 4. 12. contour Surface plot of the interaction effect of flotation time and pH on ink removal efficiency

4.10.3. Interaction Effects of Fatty Acid Soap Dosage and pH

The ink removal efficiency was increasing when the fatty acid soap dosage increases from 1.5% to 2.65 % then begins to decrease when the fatty acid soap dosage increases further from 2.65% to 3%. The ink removal efficiency was increasing with increasing the pH from 3 to 9.

Therefore the optimum deinking flotation efficiency was at pH of 9 and fatty acid dosage 2.65 % (based on ODF) at constant 60min flotation time.

DESIGN-EXPERT Plot

IE

X = B: Fatty acid soap

Y = C: pH

Actual Factor

A: Flotation time = 60.00

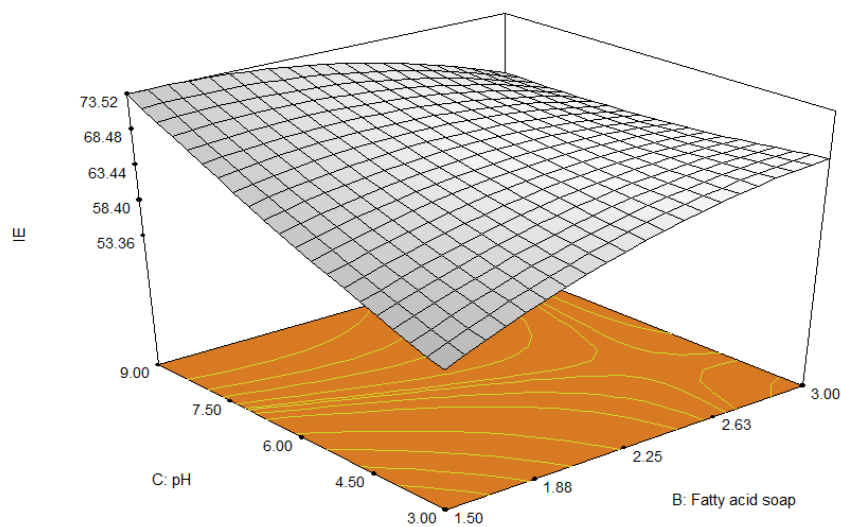


Figure 4. 13. Surface plot of the interaction effect of fatty acid soap and pH on ink removal efficiency

DESIGN-EXPERT Plot

IE

• Design Points

X = B: Fatty acid soap

Y = C: pH

Actual Factor

A: Flotation time = 60.00

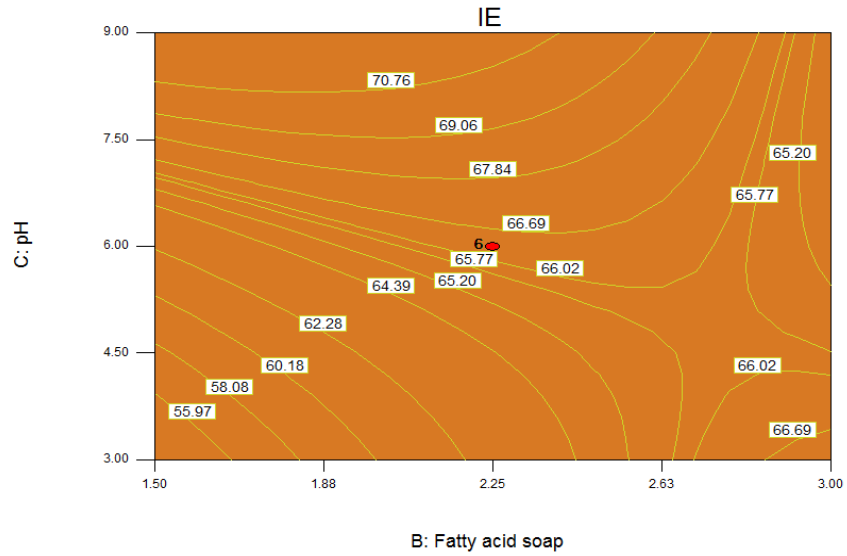


Figure 4. 14. Counter plot of the interaction effect of fatty acid soap and pH on ink removal efficiency

4.10.4. Interaction effects between Amount of Surfactant, Flotation Time and pH

DESIGN-EXPERT Plot

IE

X = A: Flotation time

Y = B: Fatty acid soap

Z = C: pH

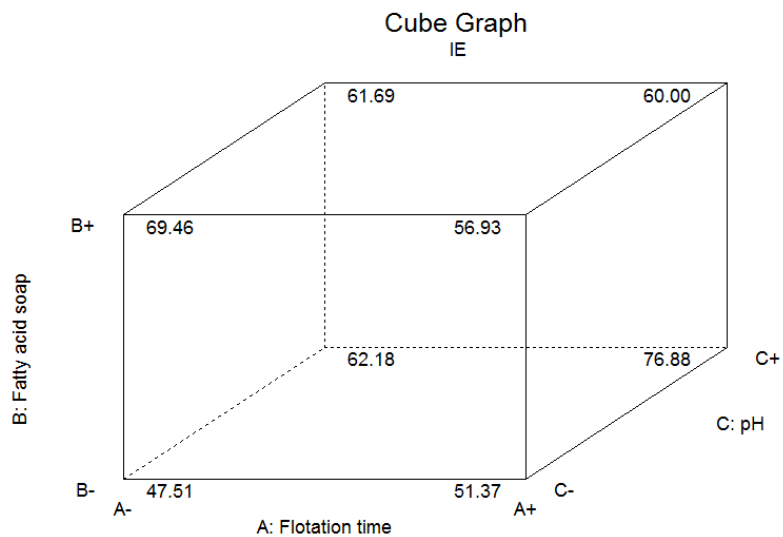


Figure 4. 15. cubic plot of Interaction effects amount of surfactant, residence time and pH on ink removal efficiency

Higher amount of flotation time and higher pH with lower amount of fatty acid soap was found to have higher ink removal efficiency as compared to lower amount of flotation time and pH with higher amount of fatty acid soap. The ink removal efficiency was lower at lower amount of fatty acid soap and flotation time with lower pH.

4.11. Optimization of Process Variables

The results above have shown that the three deinking flotation variables and the interaction among the variables affect the ink removal efficiency. Therefore, the next step was to optimize the process variables in order to obtain the highest ink removal efficiency using the model regression developed. Using the numerical optimization function in Design-Expert, it was predicted that at conditions of 90min flotation time, 1.5% fatty acid soap (based ODF) and pH 9, an optimal ink removal efficiency of 78.39% can be obtained. In order to verify this prediction, experiments were conducted and the results were comparable with the prediction. It was found that the experimental value of 78.02% ink removal efficiency which was well agreed with the predicted value. Therefore, this study shows that Anionic surfactant obtained from castor seed oil can definitely be used for deinking flotation agent for removal of ink from waste paper.

Table 4.7: Model validation

Flotation Time (min)	Fatty acid soap dosage (%)	pH	Ink removal efficiency (%)	
90	1.5	9	Predicted	Experimental
			78.39	78.02

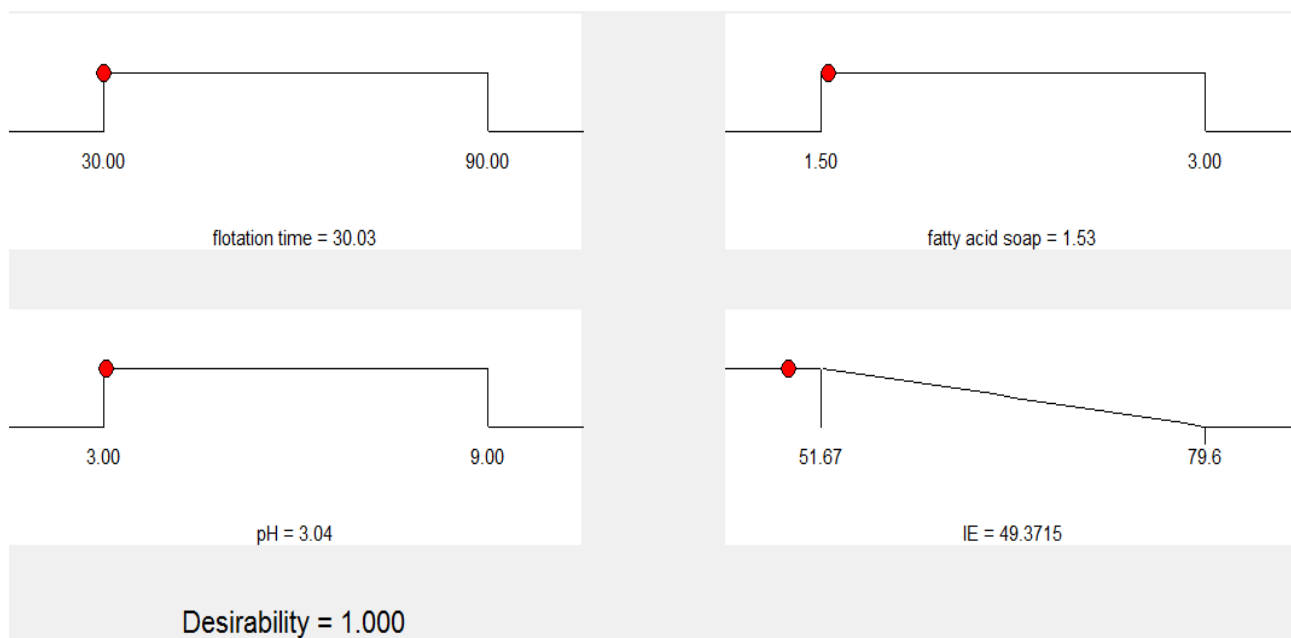
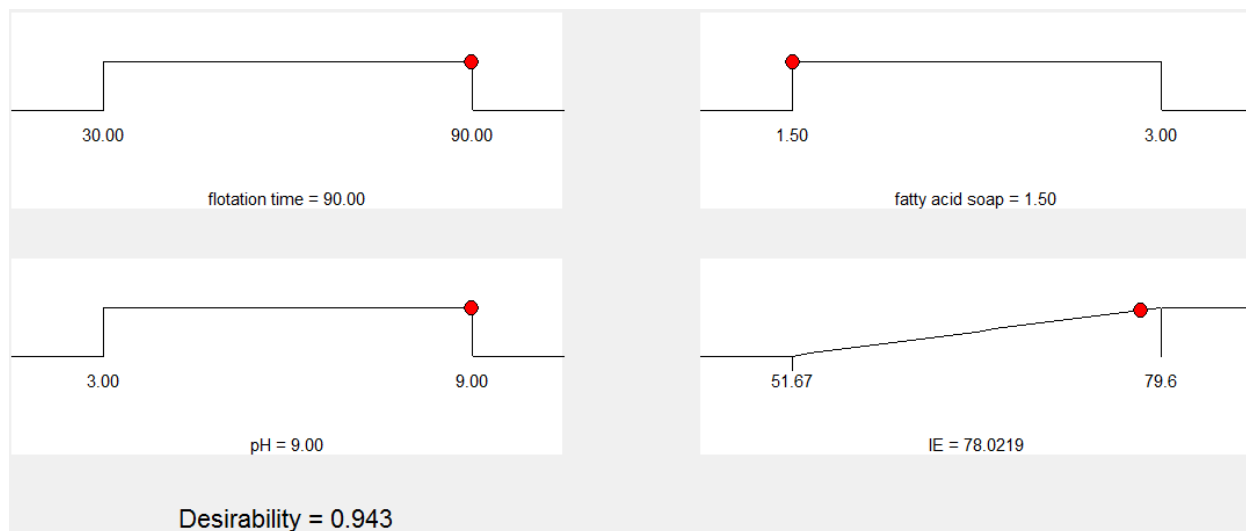


Figure 4.16.numerical Optimization of process parameters

5. Conclusion and Recommendation

5.1. Conclusions

In this research, deinking flotation of waste printed paper by using natural anionic surfactant produced from locally available raw material (*castor* seed oil) as a floating agent in flotation process. Different investigation parameters has been done on deinking flotation process. The three deinking flotation process parameters affecting the ink removal efficiency which are flotation time, fatty acid soap dosage and pH has been studied. The outputs of the experiment conducted have been analyzed by employing Design-Expert 6.0.8, three-level-three-factor face centered CCD, through analysis of residual ink concentration of hand sheet paper before and after deinking.

Based on the analysis of experimental results, it was found that all the three process variables showed an interaction effect on the ink removal efficiency.

A flotation time of 90min, amount of fatty soap of 1.5 %(based on ODF) and pH of 9 results an optimal value of 78.02% removal efficiency. The physicochemical properties determined for the fatty acid soap are HLB, CMC, foaming power & foam stability.

This work investigated deinking efficiency of two steps (pulping /flotation) using flotation cell equipped with aeration apparatus.

The key findings of this study were:

- The use of flotation column in flotation stage resulted in a good ink removal efficiency in the removal of ink from pulp of waste printed paper.
- The existing environmental problems resulting from waste paper in effluent from stationeries and offices could be minimized by recycling them in to paper and other board products. This would result in economical and environmental benefits from the raw materials used in the paper industry.

5.2. Recommendations

- In this thesis deinking flotation of waste printed paper was employed by using natural anionic surfactant which was obtained from castor seed oil using an aeration apparatus of flotation cell. This thesis was mainly focused only with one types of ink i.e. carbon black toner ink powder printed paper. Therefore, I recommended that, a further researcher should also study with different properties of paper and different types of inks which might have diverse effect on ink removal efficiency.
- Flotation de-inking is a separation process of inks and other contaminants from fibers.in Ethiopia ,The paper factory (Ethiopia pulp and paper factory PLC) uses a human resources to separate the printed paper from the other waste paper and they uses the printed paper for manufacturing of cartons and other materials as packing materials, but if they would use the deinking flotation technology linked with their factory, they would produce good quality of pulp and paper from the waste printed paper.
- Ink removal efficiency Should studied be by using different methods like brightness, residual ink concentration (ERIC) and image analysis (dirty count method).but this research was done by measuring residual ink concentration by using Perkin Elmer spectroscopy because the unavailability of brightness and image analyzers equipments. And also the residual ink concentration has its own limitation because if all residual ink particles are agglomerated into a few large dots, its effect on the overall reflectance (i.e. the appearance) of the paper is relatively small and the paper would appear brighter or lighter, resulting in low ERIC readings. The ERIC reading measures the overall darkening effect due to the residual ink, not the actual amount of ink present, therefore further studies should analysis the exact ink concentration by using image analysis using motic electronic microscope.

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Appendices

Appendix A: Compositions of Castor Oil

Table A- 1.Fatty acid composition of castor oil

Fatty Acid	Formula	%
Ricinoleic	C18H34O3	89.5
Palmitic	C16H32O2	1
Stearic	C18H36O2	1
Oleic	C18H34O2	3
Linoleic	C18H32O2	4.2
Dihydroxystearic acid	C18H36O4	0.7
Linolenic	C18H30O2	0.3
Eicosanoic	C24H47NO2	0.3

Source: (wan, 2012)

Table A- 2.Characteristics of castor oil in different situation

Properties	Cold pressed	Solvent pressed	Dehydrate oil
Specific gravity	0.961-00.963	0.957-00963	0.926-0.937
Acid value	3	10	6
Iodine value (Wij)	92-88	80-88	125-145
Saponification value	179-185	177-182	185-188

Source: (Ogunniyi, 2006)

Appendix B: Experimental Data

Table B- 1.Moisture content of castor seeds

Run	Weight of castor seed before drying(W1) gm	Weight of castor seed after drying(W2)gm	(W1-W2) gm	Moisture Content (%)
1	6.64	6.45	0.19	2.94
2	6.15	5.82	0.33	5.7
3	6.02	5.92	0.1	1.68
4	5.89	5.86	0.51	0.51
Average moisture content %				2.7

Table B- 2.Moisture Content of waste paper

Run	Mass of waste paper before drying (gm):M1	Mass of waste paper after drying (gm):M2	M1-M2	Moisture content %
1	63.4	59.94	3.46	5.45
2	58.9	56.07	2.83	4.8
3	57.2	54.56	2.64	4.62
4	55.6	53.23	2.37	4.26
Average				3.83

Table B-3. Conductivity of surfactant at different concentration

Volume of stock solution (ml)	Concentration solution M	Conductivity (ms)
0	0	11.52
1	0.00025	55.2
2	0.0005	75.35
3	0.00075	105.5
4	0.001	110.8
5	0.00125	121
6	0.00135	146.7
7	0.00175	185.3
8	0.002	190.25
9	0.00225	212
10	0.0025	225.5
11	0.00275	245.65
12	0.003	282.6
13	0.00325	290.4
14	0.0035	315.6
15	0.00375	342.5

16	0.004	390.5
17	0.00425	412.3
18	0.0045	425
19	0.00475	480
20	0.005	514.25
21	0.00525	545.5
22	0.0055	550.25
23	0.00575	549.6
24	0.006	530
25	0.00625	512.6
26	0.0065	490.7
27	0.00675	958
28	0.007	1058.7
29	0.00725	1300.3
30	0.0075	1354.23

Table B- 4.Experimental data for ink removal efficiency

sample	Reflectance for DP		Opacity of DP %	Scattering coefficient of DP S (m ² /kg)	Absorption coefficient of DP K _{sheet}	ERIC _{DP} (ppm)	ERIC _{UDP} (ppm)	ERIC UNP (ppm)	IE (%)
	R ₀	R _∞							
1	0.46	0.52	89.2	6.46	1.42	142.27	452.6	0	68.4
2	0.43	0.50	87.2	7.60	1.90	189.97	452.6	0	58.03
3	0.45	0.51	88	7.28	1.69	169.20	452.6	0	62.61
4	0.56	0.62	90.2	15.50	1.80	180.52	452.6	0	60.11
5	0.51	0.56	91.5	7.21	1.25	124.64	452.6	0	72.46
6	0.69	0.72	92.6	18.05	0.98	98.25	452.6	0	78.0
7	0.39	0.46	87.3	6.39	1.98	198.17	452.6	0	54.86
8	0.44	0.51	87.6	7.67	1.80	180.55	452.6	0	60.11
9	0.41	0.49	86.8	7.93	2.10	210.41	452.6	0	53.51
10	0.39	0.46	85.8	6.87	2.14	214.10	452.6	0	52.30
11	0.54	0.61	88.2	16.92	2.11	210.98	452.6	0	53.72
12	0.36	0.44	85	6.10	2.18	218.73	452.6	0	51.67
13	0.37	0.45	85.2	6.23	2.16	215.58	452.6	0	52.37
14	0.45	0.512	88	6.92	1.61	161	452.6	0	63.40
15	0.46	0.52	89.2	6.46	1.42	142.3	452.6	0	68.1

Appendix C: Some Laboratory Work Pictures



Figure C- 1.Fatty acid soap preparation



Figure C- 2. Mixing of pulp slurry



Figure C- 3. Beating pulp machine



Figure C- 4. Laboratory aerated floatation



Figure C- 5. Hand sheet pulper



Figure C- 6.Hand sheet making machine



Figure C- 7.pulp Freeness test



Figure C- 8.pulp Disintegrator

Appendix D: Glossary

Toner:

It is a powder used in laser printers and photocopiers to form the printed text and images on the paper, in general with a toner cartridge. In its early form it was a mix of carbon powder and iron oxide. Then, to improve the quality of the printout, the carbon was melt-mixed with a polymer. Toner particles are melted by the heat of the fuser, and are thus bonded to the paper.

Micelle:

An electrically charged group of molecules: an electrically charged particle formed by an aggregate of ions or molecules in soaps, detergents, and other suspensions.

Laser printer:

Laser printing is an electrostatic digital printing process. It produces high-quality text and graphics (and moderate-quality photographs) by repeatedly passing a laser beam back and forth over a negatively charged cylinder called a "drum" to define a differentially charged image.