CHAPTER 2

THEORY

2.1. Metalworking Fluids

Metalworking [8] is the shaping of a metallic work-piece to conform to a desired set of geometric specifications. Metalworking can be divided into two basic categories cutting and forming. In cutting operations, the blank is shaped by removing unwanted metal in the form of discrete chips. Cutting operations include turning, tapping, milling, broaching, and grinding. Metal-forming processes involve the plastic deformation of the work-piece into a desired shape. Drawing, hot and cold rolling, stamping and forging are examples of metal-forming operations.

In both cutting and forming operations, metal working fluids (MWFs) are used to cool and lubricate the tool and work piece at the time as chips are removed from the cutting zone and rust is inhibited at the new surface. The cooling is most important because much of the energy, more than 95 percent, used in cutting metal is converted into heat. The heat is generated in two ways. First the tool digs in then shears the metal to form a chip. Next additional heat is created by friction as the chip rubs against the cutting face of the tool. The temperature rise very sharply as cutting speeds are increased.

Lubrication can be defined as the reduction of friction between two moving surfaces. In metalworking operations, lubrication can be divided into two types hydrodynamic and boundary or extreme pressure (EP). In hydrodynamic lubrication, the moving surfaces are always separated by a fluid or lubricant. The film thickness and the coefficient of friction are both a function of the parameter ZN/P, where Z is the lubricant's dynamic viscosity, N

represents the relative velocity of the moving surfaces and P is the applied load per unit area. The coefficient of friction will also increase because of a rise in viscous drag. Conversely, increasing the load or pressure will decrease the film thickness and the coefficient of friction as long as hydrodynamic conditions are maintained.

Boundary or EP lubrication is necessary when the pressures experienced are great enough to cause contact between the moving metal surfaces. The purpose of boundary or EP additives is to minimize the wear experienced when the surfaces rub against each other.

Boundary lubricant additives are polar compounds like fatty alcohols, acids and esters, which absorb onto the metal surfaces forming thin, low-shear-strength films. These solid films help prevent metal-metal contact and thus reduce friction and wear.

The EP lubricity additives used in metalworking operations are usually organic compounds that contain phosphorus, chlorine or sulfur. During the metalworking process, these additives react with the metal surfaces, forming organic or organometallic film. These films then act to reduce the force necessary to slide the surfaces past one another, while at the same time minimizing wear.

Cooling is the other critical function of a metalworking fluid. The transfer of heat away from the tool or die is affected by the specific heat of vaporization of the metalworking fluid. The specific heat is the amount of heat required to raise the temperature of 1 g of fluid 1 °C. The larger this value, the more heat the fluid can absorb for an incremental temperature rise, resulting in more efficient cooling. The heat of vaporization is the amount of heat required to vaporize a gram of liquid. A fluid with a high heat of vaporization will also cool efficiently, because it absorbs large amounts of

energy as it transforms from a liquid to a gas. Heat transfer in metalworking can also be affected by the fluid's boiling point, ambient temperature, viscosity, surface energy and application method.

Good lubrication and cooling will prolong tool or die life, improve surface finishes and permit higher production speeds. The cooling and lubricating properties of a metalworking fluids must be matched to the operation being performed. In high-cutting-speed operations that involve heavy cuts or large deformations, the lubricating properties of the metal working fluids are critical.

In addition to providing adequate lubrication and cooling, metalworking fluids must protect the machine and the work-piece from corrosion and remove chips from the cutting zone. It is also important that the metalworking fluids be benign and nonirritating to the operator.

A wide variety of metal working fluids have been formulated and produced by optimizing many operational factors, such as metal type, tool type and design, thermal and biological stability, and health and safety. The metalworking fluids are often produced by mixing and heating together individual chemical components obtained from various chemical suppliers. The composition information of a metalworking fluids, reported on its Material Safety Data Sheet (MSDS), is based on that of its individual components. The physical properties of metalworking fluids are far more widely discussed than their chemical composition in both the trade and scientific. Exact chemical compositions of metalworking fluids are considered trade secrets by metalworking fluids manufacturers.

There are four major classes of metalworking fluids include straight oil, soluble oil, synthetic and semisynthetic metal working fluid [9]. The detail of metalworking fluids as follow:

2.1.1. Straight oil metalworking fluids (neat oil or insoluble oil):

Straight oil metalworking fluids consist primary of highly refined mineral oil or reprocessed oils from various sources. Many straight oils are simply mineral oils without additives. Mineral oil is the most commonly used straight oil due to its low cost and familiarity. To a much lesser extent, animal, marine, and vegetable oils and synthetics oils such as polybutenes and polyols could be used as base oils or added to a base mineral oil to increase wetting action and lubricity.

2.1.2. Soluble oil metalworking fluids (oil/water emulsion):

Soluble oil metalworking fluids contain once-processed or reprocessed mineral oil as their base oil. Soluble oil metalworking fluids concentration generally contain 60 to 69 % mineral oil. These concentration are mixed with water (in about a 1 to 20 ratio) to form an oil in water emulsion. In general, the greatest challenge with soluble oil is maintaining the emulsion. Binding of the emulsifying agent by mineral in hard water and biological degradation of the emulsifier are typically responsible for breaking the emulsion. Chelating agents and biocides are added to the concentrate in an attempt to minimize the impact of these processes and prolong useful coolant life. Recently, there have been attempts to use vegetable oils instead of mineral oil, which may result in more environmentally friendly metalworking fluids due to their improved biodegradability, but may present additional challenges in maintaining useful coolant life.

2.1.3. Synthetic metalworking fluids

Synthetic metalworking fluids do not contain mineral oil, but instead used chemically synthesized organic compounds such as hydrocarbon-based polyalphaolefins, polyethylene/polypropylene glycols or ester oils as their basis. Three types of synthetics predominate: simple (i.e., organic and inorganic salts dissolved in water); complex (i.e.,

the simple formulation plus synthetic lubricants); and emulsifiable (i.e., complex formulation plus water-soluble organic compounds such as esters to improve lubrication). Simple and complex synthetic metalworking fluids are not oil-in-water emulsion-instead, the chemical are highly soluble in water. Other advantages of synthetic metalworking fluids include heat removal and bioresistance, the latter posing difficulties for wastewater treatment. Disadvantages reportedly include poorer lubrication by some synthetic metalworking fluids, the inability to recycle such fluids on site and a tendency for foaming.

2.1.4. Semisynthetic metalworking fluids

Semisynthetic metalworking fluids concentration typically contain 5 % to 30 % mineral oil along with many of those compounds used in synthetic metalworking fluids. The lower oil content of semisynthetic metalworking fluids also makes cleanup after machining operations easier than the straight or soluble oils. However, like synthetics, semisynthetic metalworking fluids tend to easily foam, a characteristic that may also present a difficulty for biological treatment.

2.2. Component of metalworking fluids

The two main components of metalworking fluids are base oil and additive [9]. The detail of two components discussed as follows:

2.2.1. Base oil

Base oil are most commonly mineral oils. The mineral oils are typically hydrotreated (hydrogenated) petroleum distillated, ether a heavy or light fraction, and naphthenic or paraffinic mature. Soluble oil and semisynthetic metalworking fluids tend to contain

naphthenic mineral oils, whereas straight oils are generally ether paraffinic or naphthenic mineral oils.

Mineral oils contain a collection of hundreds or thousands of different hydrocarbons, which are paraffinic, naphthenic, aromatic and combinations. Alkenes and alkynes are generally not present in mineral oil. A hydrocarbon molecule is generally classified as "aromatic" it is contains at least one aromatic group, "naphthenic" if it contains no aromatic groups but at least one cycloalkane group, or "paraffinic" if it contains only normal and branched alkane groups. The relative amounts of paraffinic, naphthenic and aromatic hydrocarbons in mineral oils depend on sources of crude oils and production processes. Mineral oils are classified similarly. Paraffinic mineral oils contain approximately 70 to 75 % paraffinic, 20 to 25 % naphthenic and 5 % aromatic hydrocarbons. Naphthenic mineral oils contain 35 to 40 % naphthenic, 50 to 55 % paraffinic and 8 to 10 % aromatic hydrocarbons.

The configuration of cycloalkane and aromatic ring structures in mineral oil hydrocarbons is thought to be relatively straightforward. The rings contain five or six carbon atoms and are fused together in a single cluster. The total number of ring is generally four or less. The hydrogenation process typically leaves only a small fraction having more than two aromatic rings per molecule. Aromatics are typically substituted with many small side chains, whereas chyloalkanes tend to have fewer, longer side chains.

Although the hydrocarbons in mineral oils represent a range of molecular weight, the average molecular weight for mineral oils used for metalworking fluids are approximately 425 for paraffinic mineral oils and 310 for naphthenic mineral. These molecular weights correspond to average carbon number of C_{30} and C_{23}, respectively. The hydrocarbons in

HF mineral oils are larger than those in metalworking fluids typically having carbon number in the C_{20} to C_{40} chains.

2.2.2. Additives

Most major additives are organic and vary widely in terms of hydrophobicity, polarity and water solubility. Some may be included in the O&G fraction, depending on the analytical method used. Relative contributions of individual additives to the overall organic content range from the less than 0.1 % to as much as 30 % (wt). The purity of additive types are emulsifiers and surfactants, extreme pressure agents and anti-weld agents, corrosion inhibitors, friction reduction and wettability agents biocides and alkaline reserve and are discussed below.

2.2.2.1. Emulsifiers and surfactants

Emulsifier and surfactants (e.g., petroleum sulfonates and ethoxylate products) are added to water-base fluids to disperse oil drops in the fluid and to reduce the fluid's surface tension. When sufficient emulsifier is present, it forms spheres or "micelles" with the hydrophobic ends of these molecules at the core and the hydrophilic ends at the other surface in contact with water, and allows for a fully dispersed oil-water mixture. The concentration of emulsifier needed to initial the formation of micelle is defined as the critical micelle concentration (CMC). Because oil is hydrophobic, it partitions into the hydrophobic center of the micelle. Petroleum sulfonates, however, reportedly do not exhibit typical CMC behavior, instead increasing apparent solubility of oil with no CMC threshold.

Petroleum sulfonates typically make up a significant fraction (up to 30 %) of most soluble oil metalworking fluids concentration. Petroleum sulfonates reportedly have a condensed ring structure with one or two aromatic rings and one to three cycloalkane (5

or 6 carbon) rings. The sulfonate group is believed to be attached to an aromatic ring. Methyl groups are present on both ring types and a larger linear alkyl group may be attached to a cycloalkane ring.

Currently, petroleum sulfonates are wildly used as emulsifiers in soluble oil metal working fluids. However, there has been ongoing concern that this material (a byproduct of white oil refining process) will eventually by unavailable to metalworking fluids manufacturers. As a result, metalworking fluids suppliers are investigating alternative emulsifiers.

2.2.2.2. Extreme pressure agents and anti-weld agents

Extreme pressure agents and anti-weld agents (e.g., sulfur, chlorine, phosphorus or lead compounds) are used to guard against welding of the work piece with the metal tool in heavy duty machining. Extreme pressure agents are chemically active compounds that react with metal surface at high temperature and pressure to create a protective layer. This layer has lower shear strength than the base metal and is preferentially sheared. The use of short-chain chlorinated alkanes (C_{10} to C_{13}) has been reduced due to their suspected carcinogenicity, however, long chain chloroalkanes (C_{14} to C_{30}) remain in use.

2.2.2.3. Corrosion inhibitors

Corrosion inhibitors (e.g., fatty acid salts, sulfonates, amines, amides, borates, silicates, phosphates and nitrates) form films on metal surfaces consisting of polar organic compounds or inorganic oxides to prevent attack by acid and peroxide. Such compounds are added to water-base fluids and are retained in the oil phase to inhibit their loss through evaporation. Bacterial tend to preferentially degrade corrosion control compounds such as fatty acids. Amines are also found to be easily biodegraded.

2.2.2.4 Friction reduction and wettability agents

Friction reduction and wettability agents (e.g., animal and vegetable oils fatty esters and amides, fatty acids and alcohol) contain a small polar group that is attracted to the metal surface and a larger hydrocarbon group that dissolves in the oil phase to produce a mono-molecular protective film.

2.2.2.5. Biocide

Biocides are intended to control the proliferation of bacteria, fungi, yeast and mold in the fluid. US EPA lists more than 70 chemical preservatives (antimicrobial agents) and over 200 material preservatives used in metalworking fluids. Several biocides have been identified as source of skin sensitization in humans.

2.2.2.6. Alkaline reserve

Alkaline reserve (e.g., sodium hydroxide, ethanolamines) are used to keep a metal working fluids alkaline (pH between 8.5 to 9) to control bacterial growth (which is favored at natural pH), maintain rust protection, retain emulsion stability and aid cleaning. Ferrous metals tend to corrode at pH below 8.5, while nonferrous metals corrode at pH above 9.

2.2.2.7. Other additives

Other additives include coupling agents, dispersants, viscosity index improvers, oiliness agents plasticizers, chelating agents, anti-foaming agents, passivators, anti-miss agents, odorants and dyes.

2.3. Chitin and chitosan

Chitin $(C_8H_{13}O_5N)_n$ [10] is a long-chain polymeric polysaccharide of beta-glucose that forms a hard, semitransparent material found throughout the natural world. Chitin is

the main component of the cell walls of fungi. It is also a major component of the exoskeletons of arthropods, such as the crustaceans (e.g. crab, lobster, and shrimp), and the insects (e.g. ants, beetles, and butterflies) and of the beaks of cephalopods (e.g. squids, and octopus). Chitin has also proven useful for several medical and industrial purposes.

Chitin is a long, unbranched molecule consisting entirely of N-acetyl-D-glucosamine units linked by β-1,4 bonds. It may be thought of as cellulose in which the hydroxyl groups on the second carbon are replaced with $NHCOCH_3$ groups. Chitin is considered to be synthesized in nature by an enzyme which is capable of effecting a glycosyl transfer of the N-acetyl-D-glucosamine from uridinediphosphate-N-acetyl-D-glucosamine to a preformed chitodextrin acceptor, forming the polysaccharide. This stepwise enzymic transfer results in the production of the long chain of β-N-acetyl-D-glucosamine units, which is insoluble chitin. Figure 2.1 shows chemical structure of chitin.
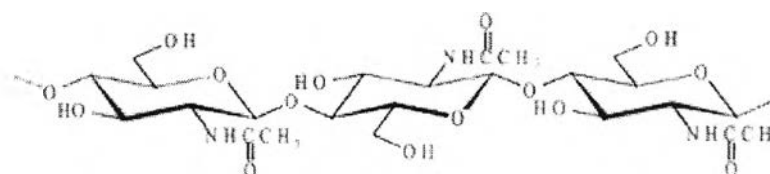

Figrue 2.1 Chemical structure of chitin

Chitosan is a linear polysaccharide composed of randomly distributed ß-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It has a number of commercial and possible biomedical uses. Chitosan is produced commercially by deacetylation of chitin , which is the structural element in the exoskeleton of crustaceans. The degree of deacetylation (%DA) can be determined by

NMR spectroscopy, and the %DA in commercial chitosans is in the range 60 to 100 %.
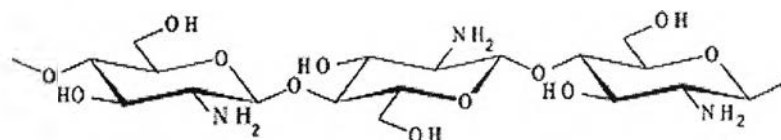
Figure 2.2 presents chemical structrue of chitosan.

Figrue 2.2 Chemical structure of chitosan

The amino group in chitosan has a pKa value of ~6.5, thus, chitosan is positively charged and soluble in acidic to neutral solution with a charge density dependent on pH and the % DA-value. In other words, chitosan is bioadhesive and readily binds to negatively charged surfaces such as mucosal membranes. Chitosan enhances the transport of polar drugs across epithelial surfaces, and is biocompatible and biodegradable. Purified qualities of chitosans are available for biomedical applications.

2.3.1. Physiscochemical properties of chitosan

Chitosan is a collective name given to a group of polymers deacetylated from chitin. The difference between chitin and chitosan lies in the degree of deacetylation. Generally, the reaction of deacetylating chitin in an alkaline solution cannot reach completion. The deacetylation degree usually ranges from 70 % to 95 %, depending on the method used. Treating chitin with solid potassium hydroxide for 30 minutes at 180°C, results in the highest removal 95% of acetyl groups. Most publications use the term chitosan when the degree of deacetylation is more than 70%.

Commercial chitosan is mainly produced by deacetylating chitin and obtained from seashell materials. The quality and properties of chitosan products, such as purity, viscosity, deacetylation, molecular weight and polymorphous structure, may vary widely

because many factors in the manufacturing process can influence the characteristics of the final product.

The degree of deacetylation is one of the most important chemical characteristics of chitosan. This determines the content of free amino groups in the polysaccharide. Methods for checking the removal of acetyl groups in chitosan include infrared spectroscopy, titration, gas chromatography and dye adsorption.

The molecular weight of chitin is usually larger than one million while commercial chitosan products fall between 100,000 and 1,200,000. During the manufacturing process, harsh conditions can lead to degradation of the chitosan product. The molecular weight of chitosan can be determined by methods such as chromatography, light scattering and viscometry. Among these, viscometry is the most simple and rapid method for determination of molecular weight.

The viscosity of chitosan solution is influenced by many factors, such as the degree of polymer deacetylation, molecular weight, concentration, ionic strength, pH and temperature. In general, as the temperature rises, the viscosity of the polymer solution decreases. However, a pH change in the polymer solution may give different results depending on the type of acids employed. With acetic acid, the viscosity of chitosan tends to increase when the pH is lowered.

Chitosan is insoluble in water, alkali and organic solvents but is soluble in most solutions of organic acids when the pH of the solution is less than six. Acetic and formic acids are two of the most widely used acids for dissolving chitosan. Some dilute inorganic acids, such as nitric acid, hydrochloric acid, perchloric and H_3PO_4, can also be used to prepare a chitosan solution but only after prolonged stirring and warming.

2.3.2. Application of chitosan

The major applications of chitosan are centered on sludge dewatering, food processing, and metal ion chelation. The present trend in industrial applications, however, is toward producing high value products, such as cosmetics, drug carriers, feed additives, semipermeable membranes and pharmaceutics.

The chitosan is polymer for their ability to chelate transition metal ions. Chitosan is an excellent coagulating agent and flocculant due to the high density of amino groups on the polymer chin that can interact with negatively charged substance, such as proteins, solids and dyes. The chelating ability of chitosan can be improved by homogeneous hydrolysis, cross-linking, controlled N-acetylation and complexation with other polymers like glucan

Applications of chitosan in cosmetics can help to remove leftover starch contained in shampoos. Its used also have the effect of conferring shine and strength to hair due to interactions between the polysaccharide and hair proteins. Recently, more reports have been published on the use of chitosan and its derivatives in cosmetic products.

Chitosan has many potential applications in agriculture because the polymer is essentially naturally occurring and biodegradable. Therefore, it used not cause pollution problems. One application that is widely employed at present is seed coating

In addition to directly treating plants with chitosan, the polysaccharide has also been employed for improving soil properties and preparing hydroponic fertilizer.

Concerns about the environment have aroused great interest in the excessive use of agrochemicals, such as fertilizers, herbicides and pesticides. To reduce environmental damage caused by agrochemicals, the use of chitosan in controlled-release systems was been investigated. Table 2.1 presents application of chitosan in many fields.

Table 2.1 Application of chitosan [10]

Agriculture	Defensive mechanism in plants
	Stimulation of plant growth
	Seed coating, Frost protection
	Time release of fertilizers and nutrients into the soil
Water & waste treatment	Flocculant to clarify water (drinking water, pools)
	Removal of metal ions
	Ecological polymer (eliminate synthetic polymers)
	Reduce odors
Food & beverages	Not digestible by human (dietary fiber)
	Bind lipids (reduce cholesterol)
	Preservative
	Thickener and stabilizer for sauces
	Protective, fungistatic, antibacterial coating for fruit
Cosmetics & toiletries	Maintain skin moisture
	Treat acne
	Improve suppleness of hair
	Reduce static electricity in hair
	Tone skin
	Oral care (toothpaste, chewing gum)
Biopharmaceutics	Immunologic, antitumoral
	Hemostatic and anticoagulant
	Healing, bacteriostatic

2.4. Adsorption

Adsorption [11-13] is the physical and/or chemical process in which a substance is accumulated at an interface between phases. For the purposes of water treatment, adsorption from solution occurs when impurities in the water accumulate at a solid-liquid interface. The adsorbate is the substance being removed from the liquid phase to the interface. The adsorbent is the solid phase onto which the accumulation occurs. Adsorption from dilute aqueous solution is said to occur when the concentration of the adsorbent in water is small enough to allow assumptions of ideality. In this limiting case, Henry's Law holds: the partial pressure of the adsorbate is proportional to its mole fraction and the ratio of the activity of the adsorbate to its concentration (the activity coefficient) equal to unity.

2.4.1. Mechanisms of adsorption

Adsorption of substances onto adsorbents takes place because there are forces to that attract the absorbate to the solid surface from solution. Alternatively, one can view this thermodynamically as a case where adsorbate has a lower free energy at the surface than in solution. During equilibration, the adsorbate is driven onto the surface to the lower energy state, which it "prefers" in keeping with the second law of thermodynamics. The specific forces or mechanisms by which adsorbate is attracted to the solid solution interface can be physical or chemical.

2.4.2. Physical Adsorption

Electrostatic force is the basic physical principle that describes interactions between molecules of adsorbate. Electrostatic attraction and repulsion based on Coulomb's Law. Other physical interactions among molecules, based on the electrostatic force, include dipole-dipole interactions, dispersion interaction and hydrogen bonding.

A molecule is said to have a dipole moment when there is a net separation of positive and negative charges within it. Molecules such as H_2O and NH_3 have permanent dipoles because of coagulation of atoms and electrons within them. They are polar compounds. When two dipoles are near each other, they tend to orient their charges to lower their combined free energy negative charges of the other. When electrostatic forces among the charge of the two molecules are summed, the net dipole-dipole interaction is an attraction between the two. Polar molecules tend to attract each other. Hydrogen bonding is a special case of dipole–dipole interaction in which the hydrogen atom in a molecule has a partial positive charge and attracts an atom on another molecule that has a partial negative charge.

When two neutral molecules that lack permanent dipoles approach each other, a weak polarization is induced because of quantum mechanical interactions between their distribution of charge. The net effect is the disperion interaction or the London-van der Waals force.

In water treatment there is often interest in the adsorption of an organic adsorbent from a polar solvent (water) onto a nonpolar adsorbent (activated carbon). In general, attraction between adsorbate and polar solvent is weaker for adsorbates of a less polar nature due to a nonpolar adsorbate is less stabilized by dipole-dipole or hydrogen bonding to a water nonpolar compound therefore adsorb more strongly to nonpolar adsorbents. This is known as hydrophobic bonding hydrophobic ("disliking water") compounds will adsorb on carbon more strongly. For example, adsorption of fatty acids on carbon from an aqueous solution is stronger as the length of the molecule increases, because the longer hydrocarbon chain is more nonpolar.

2.4.3. Chemisorption

Chemical adsorption or chemisorption, is also based on electrostasic forces. The differenec between physical adsorption and chemisorption is not distinct; the former is less specfic for which compound sorb to which surface sites, has weaker forces and energies of bonding, operates over longer distances, and is more reversible. In chemisorption, the attraction between adsorbent and adsorbate approaches that of a covalent or eletrostatic chemical bond between atoms, with shorter bond by chemisorption to a surface generally cannot accumulate at more than one molecular layer, or monolayer, because of the specificity of the bond between adsorbate and surface. The bond may also be specific to particular sites or functional groups on the surface of the adsorbent. These properties have modeling implications.

One class of chemical bonding of adsorbate to specific surface sites is acid-base reactions of a functional group. An example is the reaction of hydrated metal ions from solution with hydroxide sites on metal oxides:

$$ROH(aq) + SOH \leftrightarrow SOR + H_2O \ (aq) \qquad (2.1)$$

where R is metal ion adsorbate and S is metal oxide adsorbent .

The bond energies of the various mechanisms for adsorption may be approximately ranked from strongest to weakest: covalent or electrostatic chemical bonding (> 10 Kcal/mole), dispersion interactions and hydrogen bonding (2 to 10 Kcal/mole) and dipole-dipole interaction (< 2 Kcal/mole).

2.4.4. Adsorption of Electrolytes

For adsorption of ionic species to surfaces, the most important mechanism is eletrostatic attraction, which is highly dependent on pH and ionic strength. Adsorption of

electrolytes can be used to control heavy metals, fluoride and a few other minerals. The use of synthetic resins has been suggested for specific removal of electrolytes.

The adsorption of acids and bases on nonpolar adsorbents such as activated carbon can depend strongly on pH. While both neutral and ionized forms of these compounds may adsorb to carbon forms of these compounds may adsorb to carbon from water, the ionized forms tend to be stabilized by interaction with polar water. This means that adsorption of neutral forms is generally much stronger and the pH of maximum removal depends on the particular dissociation constant of the acid or base.

2.5. Thermodynamics of adsorption

The adsorption of chemical compounds from solution onto a surface may be viewed as an energetic process driven by thermodynamics [11-13]. At constant temperature and pressure, a system not in equilibrium will spontaneously change to decrease its Gibbs free energy. At thermodynamic equilibrium the system of adsorbent, adsorbate and solvent reaches a minimum free energy level. The future detail is in Chapter 5.

2.6. Adsorption Isotherm

An adsorption isotherm [11-13] specifies the equilibrium surface concentration of adsorbate on adsorbent as a function of bulk concentration of adsorbate in solution. It is called an isotherm because it describes the equilibrium state of adsorbate, adsorbent and solute at a given temperature. Several models can be used for the description of the adsorption equilibrium data. Three widely used forms are the Langmuir, Brunauer, Emmett and Teller (BET) and Freundlich isotherms.

2.6.1. Langmuir isotherm

The basic assumption underlying Langmuir isotherm, which is also called the ideal localized monolayer model, are:

a) The molecules are adsorbed on definite sites on the surface of the adsorbent.

b) Each site can accommodate only one molecule (monolayer)

c) The area of each site is a fixed quantity determined solely by the geometry of the surface.

d) The adsorption energy is the same at all sites. and

f) The adsorbed molecules cannot ingrate across the surface or interact with neighboring molecules.

For adsorption from solution by solid adsorbents, The Langmuir isotherm can be expressed as

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_o} \qquad (2.2)$$

where q_e is the amount of cutting fluid adsorbed per unit weight of adsorbents at equilibrium concentration (mg/g), q_0 is the maximum adsorption at monolayer coverage (mg/g), C_e is the final concentration in the solution (mg/l) and K_L is the adsorption equilibrium constant (l/mg).

The linear form of Langmuir isotherm can be written as

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{K_L q_0} \frac{1}{C_e} \qquad (2.3)$$

Plot of $1/q_e$ against $1/C_e$ a straight line, has slope $1/K_L q_o$ and intercept $1/q_o$.

2.6.2. BET isotherm

The BET adsorption isotherm extends the Langmuir model from a monolayer to several molecular layers. Above the monolayer, each additional layer of adsorbate molecules is assumed to equilibrate with the layer below it; layers of different thicknesses are allowed to coexist. The equilibrium for the adsorption onto the new layers is defined by the law of mass action as for the Langmuir model for the first layer. However, the equilibrium constant is now set equal to, where is the free energy of precipitation of the adsorbate. The process of sorbing a new layer of adsorbate onto old layers is assumed to be identical to the process of condensing adsorbate from solution to solid or liquid. The resulting isotherm has the form

$$\frac{x}{m} = \frac{X_m K_B C_e}{(C_s - C_e)[1 + (K_B - 1)(C_e / C_s)]} \qquad (2.4)$$

where x is the amount of cutting fluids adsorbed (g), m is the weight of adsorbents (g), X_m is the amount of cutting fluids adsorbed in forming a complete monolayer (mg/g), C_s is the saturation concentration of cutting fluids (mg/l), C_e is the concentration of cutting fluids in emulsion equilibrium (mg/l) and K_B is the BET constant.

Rearranging the BET equation yields

$$\frac{C_e}{(C_s - C_e)x/m} = \frac{1}{K_B X_m} + \frac{K_B - 1}{K_B X_m}\left(\frac{C}{C_s}\right) \qquad (2.5)$$

Plotting of the $\dfrac{C_e}{(C_s - C_e)x/m}$ against Ce/C_s should give a straight line having slope $\dfrac{K_B - 1}{K_B X_m}$ and intercept $\dfrac{1}{K_B X_m}$.

The Langmuir and BET models incorporate an assumption that the energy of adsorption is the same for all surface sites and not dependent on degree of coverage. In reality, the energy of adsorption may vary because real surfaces are heterogeneous.

2.6.3. Freundlich isotherm

The Freundlich adsorption isotherm is perhap the widely used mathematical description of adsorption in aqueous solution. The Freundlich isotherm is used for heterogeneous surface (rough surface) and the exponential distribution of sites and their energies. The Freundlich isotherm is expressed as

$$q_e = K_F C_e^{1/n} \tag{2.6}$$

where K_F is Freundlich constant.

The linear form of Freundlich equation is written in logarithmic form

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{2.7}$$

The log-log plot of q_e against C_e for this equation is linear. The slope and intercept are $1/n$ and $\log K_F$, respectively. The value of $1/n$ obtained for adsorption of most organic compounds by activated carbon is < 1. Steep slopes $1/n$ close to 1 indicated that high adsorption capacity at high equilibrium concentration that rapidly diminishes at lower equilibrium concentration covered by the isotherm. Relatively flat slope $1/n \ll 1$ indicated that the adsorptive capacity is only slightly reduced at the lower equilibrium concentrations.

2.7. Literature review

There are many processes to treat cutting fluids from industrial use. The detail of each process to study the treatment of cutting fluids is included in the following review.

Pinotti et al. [14] studied flocculation of food emulsion waste using crab shells of chitosan as polyelectrolyte and found that adding NaCl concentration reduced the dose of chitosan to produce destabilization and flocculation due to the thickness of a double layer. Repulsive forces also decreased and reduced the distance between colloidal particles. The longer the surfactant chain length, the greater the tendency toward polyelectrolyte association.

Ríos *et al.* [15] studied the destabilization of cutting oil emulsion by using $CaCl_2$ and $AlCl_3$ salts as coagulants and found that the addition of an $CaCl_2$ and $AlCl_3$ as inorganic coagulants destabilizes the cutting oil emulsion of Albakool and Smith-Morris oils. The destabilization of Unil-Shell oil emulsion takes place at a temperature higher 40 ^0C, thus the formulation was a major factor in the treatment of cutting oil emulsion. After addition of the salts, most of the emulsion oil was removed in the first five minutes of setting.

Smoluchowsky's model of rapid flocculation explains the coagulation and flocculation processes, especially when macromolecules were adsorbed at the interface and coalescenced between droplets in an aggregate which occured instantaneously. The addition of an electrolyte lowers the zeta potential of the droplets, and destabilization of emulsion was abserved: large droplets were formed with such a diameter that setting according to Stokes's law took place. A creamed layer appeared at the top of bottle. After that coalescence phenomena occurred and separateded in an oil phase.

The result of mechanical, thermal stress and contamination of substances can be the emulsion behavior. The treatment of cutting oil with only inorganic salts showed a higher degree of turbidity, while the dispersed oil was readily removed by ultrafiltration.

Benito *et al.* [16] studied integrated processes of coagulation-flocculation followed by ultrafiltration for removal of emulsified oil from the steel industry. The adding of NaOH or lime can reduce oil and COD by about 90% and 75%, respectively. The oil contents of permeate from the ultrafiltration were 75% lower than the regulatory limits established by the EU countries.

Pinotti and Zaritzky studied effect of aluminum sulfate and cationic polyelectrolytes to destabilization of emulsified wastes [17]. They found that charge neutralization would be more important for chitosan than for polyacrylamide treatment. The increase of NaCl concentration reduces the dose of chitosan, polyacrylamide and aluminum sulfate necessary to produce destabilization and flocculation. The thickness of the double layer and the repulsive forces decrease when ionic strength increases. The polyelectrolytes showed coincidence between the doses to reach zero colloidal charge and minimum turbidity. The resident time to produce clarification was larger for aluminum sulfate than for polyelectrolytes. An increased amount of aluminum sulfate showed a short time for clarification. The pH 6 was optimum for aluminum sulfate. The polyelectrolyte was not affected by the pH. A higher dose of polyelectrolyte was restabilizated and became turbid again. The mechanisms of destabilization action, charge neutralization occurred for the chitosan treatment; polyacrylamide bridging occurred and aluminum sulfate treatment a destabilizing model by hydrolyzed metal ions, in which electrostatic attraction, chemical forces and adsorption were all relevant.

A membrane processes was used to treat cutting fluid. Benito *et al.* [18] used an organic ultrafiltration membrane to treat waste cutting oil. They found that oil rejections were obtained at higher than 99.9% for all tests. The highest fluxes were obtained under the following conditions: rotation speed of 375 rpm, temperature 40^0C and

transmembrane pressure 0.10 to 0.15 MPa. The permeate flux reduction was mainly due to the oil layer formed on the membrane surface. Polysulfone membranes were less hydrophilic than regenerate cellulose membranes, so they were easily wetted with surfactants present in the oily emulsion and fouled. Surfactant droplets covered a large area of the polysulfone membrane as opposed to that on the regenerate cellulose membrane, reducing the surface porosity and pore size of the membrane and allowing pore blocking by the oil droplets.

Benito *et al.* [19] designed and constructed a modular pilot plant which included coagulation/flocculation, centrifugation, ultrafiltration and adsorption processes for treatment oil wastewater. The main advantage of the plant is its versatility, allowing a combination of several of the aforementioned treatments.

Hu *et al.* [20] studied ulftrafiltration behavior of emulsified metalworking fluids and found that the permeate flux was increased by increasing the transmembrane pressure and temperature. The foulant on the used membrane surface was mainly oil. The recovery of membrane permeability can be performed with a micellar solution.

Hilal *et al.* [21] studied treament of waste coolant by coagulation and membrane filtration and found that the coagulation and ultrafiltration processes showed both advantages and disadvantages. Coagulation produces a sub-product that can be used as a fuel. The concentration produced from the ultrafiltration process has to be disposed of as a waste via a cement kiln or an industrial waste incinerator.

Belkacem *et al.* [22] recommended $CaCl_2$ salt and chemical cleaning solutions to limit the problems of fouling and reduce permeate flux. The capillary pressure of the membrane was the main influence for removing cutting oil waste higher than pore size.

Taylor [23] evaluated the potential of biodegradation for disposal of cutting fluid from the machining of uranium. It was found that biodegradation offers the potential to convert this material into forms amenable to disposal as low level radioactive waste. The organic carbon of about 33% was conversed into carbon dioxide. The hydrocarbon of about 90% was biodegraded. Downstream processing of the biotreated fluid by ultrafiltration and adsorption onto activated charcoal, produced a waste stream that would qualify as aqueous radioactive waste.

Lorain *et at.* [24] studied the potential of freezing in wastewater treatment. Using the idea to gradually freeze wastewater and theoretically pure water ice will be produced while pollutant concentration increases in the remaining liquid. This technique proved difficult to achieve pure water removal. Too high a concentration of the wastewater induced pollution of the solid. The technique gives efficiency of about 100% for soluble pollution treatment.

Hosny [25] used electroflotation to separate oil-water emulsions. The flocculant agent enhanced aggregating smaller oil drops into larger oily waste for contact with gas bubbles. Electroflotation can be used to treat diluted emulsion of oily waste. At high oily waste concentrations, a combination of flocculation and electroflotation could be proposed for treating oily wastewater.

Portela *et al.* [26] presented supercritical water oxidation as a more powerful process to treat cutting oil waste. The continuous addition of a H_2O_2 stream at the reactor inlet accelerated the oxidation process and enhanced COD and TOC reduction. Portela *et al.* [27] using wet air oxidation and supercritical water oxidation treated cutting oil waste. It wasfound that wet air oxidation process was not efficient enough due to the moderate temperature used. The supercritical water oxidation was a more powerful process since

operating temperature were high at about 600 ^{0}C. Hydrogen peroxide was used as a source of oxygen and as a source of free radical. The organic material was easily oxidized in both cases for treat cutting oil wastes. More than 90% TOC reduction was achieved within 10 second at 500 ^{0}C.

Domeño and Nerín [28] reported that after the pyrolysis process of industrial waste oil of the PAHs, carcinogenic substances, were obtained and were more toxic than initial residue compounds.

It was found that the literature of the removal of cutting fluids by adsorbents was very slight. Mathavan and Raraghavan [29] studied the treatment of oil-in-water emulsion using peat. They described that cutting oil, refinery oil, crude oil and mineral oil could be adsorbed by peat. The percentage of removals of oil obtained was about 90 to 99% depending upon the type of oil-in-water emulsion. The adsorption isotherm of adsorbent was fitted with BET model. The column was capable of adsorption of oil to an extent of about 90% for more than 8 h.

Solisio et al. [30] used a mixture of Ca and Mg oxides as adsorbent to treat exhausted oils. They found that a mixture of Ca and Mg oxides activated by a concentrated HCl, can reduce emulsified oil and water-insoluble oil 90% and 40 %, respectively. The adsorption isotherm of Ca and Mg oxides was fitted with the Freundlich model. The mechanism of adsorption of exhausted oil occurred due to the apolar fraction of the oil and is mainly adsorbed by Van der Waal force, which was stronger when chlorine atoms were substituted for oxygen atoms. This took place when the adsorbent was activated with an HCl solution.

Cambiella et al. [31] studied treatment of oil-in-water emulsion by using a sawdust bed filter and adding calcium sulphate as a coagulation. The experiments show

that several processes were involved in oil removal, i.e. coagulation, coalescence, adsorption or straining. To remaining pressure drop across the bed was below the 0.5 bar and oil removal ratios greater than 99% were reached.