CHAPTER 1
INTRODUCTION
For a healthy life, unpolluted and pure water is required. The rapid growth of industries is creating a lot of pollution that have the tendency to bring more harmful impact than good such as water, sound and air pollution. Industrial waste effluents have threatened the water resources at present time. Waste water has been affected by the hazardous or dangerous chemicals, toxic heavy metals, dyes, waste residual oil, waste emulsified oil etc. which develops pollution in water.
During various industrial operations such as production of machine parts, reducing work piece, improving surface finish, reducing thermal deformation, protecting tools from abrasive wearmetal working fluids (MWFs) are used. MWFs are liquids used in the metal working industry involving the operations such as cutting, turning, drilling, rolling, quenching, grinding and milling (Anderson et al. 2003). MWFs were first used to increase the life span of an instrument for metal processing. The MWFs mixture for engineering coolant is 5% oil and 95% clean water. The term oil is used to identify a large class of compounds such as mineral, vegetable, animal, essential or edible origin. Oil is a naturally occurring substance which is known to be one of the most important sources of energy in the modern industrial world. Those oil which are employed for metal working purposes are usually derived from the class of mineral oils, petroleum products and lubricants. It is also used as a raw material for many chemical and synthetic polymers worldwide.
In USA, 632 million gallons of lubricants are produced by independent manufacturers, 92 millions of MWFs and 32 millions of grease used for metal deformation (Byers, 1994). However, special attention may be necessary in dealing with the very cost conscious consumer segment that may not be aware of the serious environmental consequences of improper disposal of used oil. According to Kline et al. (2004), the estimated volume that is disposed of improperly, was 348 million gallons in 2004.

1.1 Industrial waste effluent and Regulations
On the basis of commercial premises, there are three types of waste waters discharged into sewer, gutter, farmlands, Rivers. These are domestic sewage type effluent, waste rain water and machining waste effluent. Special attention is paid to machining waste effluent with which the research work is dealing.

1.1.1 Domestic sewage
Waste water/effluents from wash basins, toilets on site of industry, mess for workers known as domestic sewage or foul drainage usually kept separate from machining effluent whilst on industry drainage system, although it further mixed with the main sewerage system. There are usual charges for it from Municipal Corporation.

1.1.2 Rain Water
Rain water contains soil, sewerage, pesticides, toxic metals, chemicals from the rocks causing pollution to river lakes ponds etc. Microorganism present in the rain water causes different types of disease.

Some industries have rain harvesting system but the waste rain water from car parking area, working site area, from roofs also discharge into drainage system known as surface drainage system distinct from foul drainage system and regulated by Environment protection agency. This effluent either discharged directly to the rivers or channeled to the surface drains located in roads after insurance that the effluent is not contaminated by any chemical impurities.

1.1.3 Machining effluent
Machining effluent may be defined as waste liquid that contains suspended particles, heavy metals, oil/water emulsion and which is produced by machining processes, a part of industrial premises. This effluent is separated from domestic sewage. If machining effluent disposed into the sewers then it will be charged by local water corporation according to their laws and rules. All industrial waste waters (machining effluents) are subjected to discharge to public sewerage system under either the Water Resources Act 1991 or the Water Industry Act 1991 with a prior consent of Water Corporation. Water Corporation provides effective treatment to waste effluent by imposing special restrictions and disposed it as treated effluent. Treatment of
effluent provided by Water Corporation depends upon the various restrictions such as Hazardous vs. Non-Hazardous regulatory classification of the waste (from Resource Conservation and Recovery Act, administered by U.S. EPA, RCRA), connecting sewers size waste water treatment works capacity, daily waste volume and its flow rate, nature and composition of waste water, pH and temperature etc. By measuring all the mentioned quality parameters of waste effluent Water Corporation allow it to treat and disposed of into Rivers.

1.1.4 Regulations

In order to protect environment, as well as employee and society, from the potential safety and health problems that can occur during disposal operations, one should follow the manufacturer's instructions for disposal as well as relevant government regulations. Government regulates the laws that where and how to dispose machining effluents. Disposal of fluid may vary according to restrictions. The Environmental Protection Agency (EPA), regulates emissions and disposal of polluting substances under the Clean Air, Water Act and the Resource Conservation and Recovery Act. The regulations on the protection of environment can be found in the Waste Water Frame Work Directive (2000/60/EC) that aiming to achieve a better status of all water by 2015 (Cheng et al. 2005). Publicly owned treatment works (POTWs) also have their own discharge regulations for disposing the local small industrial effluent. The National Center for Manufacturing Sciences' Metal working Fluids Optimization Guide (NCMS Guide) describes the important factors to consider when selecting metal cutting fluids. The EPA agency determined that used oil being recycled should not be listed as a hazardous waste under Resource Conservation and Recovery Act (RCRA). The EPA stated in the November 1986 decision that the agency intended to issue recycled used oil management standards and was conducting studies necessary to determine appropriate standards under § 3014 of RCRA and to determine whether used oil being disposed of should be listed as a RCRA hazardous waste, or regulated under other statutes (Hazardous Waste Management System et al. 1992). The regulations allow for recycling and burning used oils for heating purposes as long as volume is limited to self-generation activities, but prohibits combustion in
heating systems in excess of 500,000 Btu/hr or collections of used oil from others for
the purpose of space heating on the basis that the volumes can increase to the point
where they become environmentally significant. Mines, military installations, and
service station garages where space heaters can be used are examples of where these
regulations would be most applicable. The objective was not to impose a significant
burden on small garage/mine operators who have long standing practices of utilizing
used oil as an economical heating fuel. Some federal statutes and regulations dealing
with used oil management including:
• Resource Conservation and Recovery Act (RCRA) Used Oil Management
Standards
• Toxic Substances Control Act (TSCA)
• Clean Air Act (CAA) National Emission Standards for Hazardous Air Pollutants
(NESHAP)
• Clean Air Act Offsite Waste Rule
• Clean Water Act Centralized Waste Treatment (CWT) Point Source Category
• The Spill Prevention Control and Counter measures (SPCC) plan requirements
• The Comprehensive Environmental Response, Compensation, and Liability Act
(CERCLA)
The Emergency Planning and Community Right to Know Act
• The Nuclear Regulatory Commission used oil regulations
• Coast Guard used oil regulations dealing with releases of used oil to navigable
waters and shipboard management of used oil
• Hazardous Materials in Transportation Act (HMTA) (U. S. Department of energy et
al. 2006).

1.2 Impacts of waste Metal Working fluids on Environment
The original and spent MWFs were formed of base oil refined from crude oil which
contained a large amount of poly-aromatic hydrocarbons (PAHs) that are now known
to be carcinogens. The problems caused by oil mists and MWFs were so significant
for industrial health that they were even one of the priority chosen by the US
Occupational Safety and Health Administration (OSHA) in 1996. Generally, they are composed of oil and organic compounds mixed with water. Once the mixture has been used for a period of time, it degrades and generates a toxic liquid waste. The used and waste MWFs or lubricants or coolants or metal cutting oil contains sharp metallic particles during processes which are sufficiently small to enter the hair follicles of the skin and block up the openings to the sebaceous glands, produce irritation, abrasions and favorable environment for pus-forming bacteria. Both mineral-based and synthetic oils have low acute oral and dermal toxicity (Henry, 1998). The Accidental ingestion of large quantities of these oils cause irritation of the digestive tract to human being, symptoms of nausea, vomiting and diarrhea also may occur. During prolonged exposure of mineral and base oil used in metal cutting fluids, workers may be moderately exhibit skin irritation. Repeated contact can cause defatting of the skin and give rise to signs of irritancy, i.e., redness, inflammation and cracking. These health effects may be attributed to the additive components (e.g., metals and detergents) in lubricant oils.

These water soluble fractions not only affect human health but also to the plants and animals. The composite constituents of waste lubricating or cutting oil are absorbed by living cells, go into the metabolic system and seriously affect the ecosystem. The major soil contamination was due to spent lubricating oil from engines and other machinery. The presence of oil in soil makes the soil polluted which became unfavorable for plants to grow (Udo et al. 1975). There are relatively high level amount of toxic poly aromatic hydrocarbons (PAHs) in the spent MWFs due to the repeatedly use of MWFs. Since Nigeria was reported to account for more than 87 million liters of spent oil waste annually (Anon 1985). In Nigeria the hepatotoxic effects on terrestrial organisms were also evaluated which are associated with the pollution created by spent lubricating oils. The investigation revealed the adverse effects of waste soluble fractions at three different concentrations (10%, 50%, 100%) on the function of liver of wistar albino rats in Nigeria (Kingsley et al. 2010). Therefore, the need to evaluate the risk posed by this pollutant becomes imperative.
The wide variety of organic MWFs constituents, which are biodegradable and the presence of water provide O/W emulsions a suitable environment for some microorganisms to grow increasingly (Mattsby-Baltzer et al. 1989), (Van der Gast et al. 2003). It is well known fact that the eco toxicological effects of the constituents of MWFs such as biocides, anti-wear agents, surfactants, emulsifiers, rust inhibitors, and extreme pressure additives create a major problem in the disposal and its impact on the environment. BOD, TOC, COD these pollution parameters are important for effluent monitoring but not sufficiently described the impact of waste MWFs constituents on aqueous environment (Peng et al. 2000, Liu et al. 2002, Sponza, 2002).

The United States Environmental Protection Agency (USEPA 1991) recommends that effluents must not cause acute effects in receiving waters throughout 1h of exposure at the end of the pipe as well as chronic effects throughout 4 days of exposure in the mixing zone.

Used metal working or cutting oil that is leaked, spilled or improperly discarded may enter storm water runoff and eventually enter into water bodies and adversely affect the environmental health of receiving water bodies. Studies monitoring contaminants in runoff consistently report relatively low levels (i.e., ≤ 5 milligrams per liter) of oil and grease entering into surface waters (OEHHA, 2006).

Metalworking fluids (MWFs) can cause adverse health effects through skin contact with contaminated materials, spray, or mist and through inhalation from breathing MWF mist or aerosol. Changes in chemistry during use increase the potential for skin irritation, especially if the metal removal fluids (MRF) became contaminated with fines, tramp oil or alkaline cleaners. MRF is designed for a specific dilution range, which when exceeded can increase skin irritation potential. High MRF concentration can increase mist levels and operator contact. Bacteria may also expose workers to pathogens and contribute to respiratory irritation and skin irritation, like dermatitis. Bacteria and fungi are not common causes for skin irritation. Microbiological material in MRFs can infect open cuts and prove harmful to persons with compromised immune systems. Microbiological activity can affect
fluid performance and stability. Improper use of antimicrobials and biocides increases skin irritation potential as suggested by Independent Lubricant Manufacturers Association (ILMA), Dermal Assessment Guide. Dermal exposures to MWF over a period of time may deplete the epidermis of natural lipids. Although the epidermis is normally a very effective barrier against the intrusion of external substances, the defatting process can cause localized irritation and cracking of the skin which may lead to irritant dermatitis and subsequent infections. In cases of immunological susceptibility, some workers may experience allergic dermatitis which is characterized by delayed sensitivity reactions upon contact with fluids. About 67% workers exposed to MWFs are at risk for developing dermatitis (NIOSH 1998). People working with water based, synthetic, and semi synthetic MWFs are most at risk for developing contact dermatitis. Straight oils are often associated with acne-like disorders characterized by pimples in areas of contact with the MWFs. Red bumps with yellow pustules may develop on the face, forearms, thighs, legs, and other body parts contacting oil-soaked clothing.

**Table 1.1 Overview of the number of occupational diseases (Germany, 2009-2011). (DGUV Statistics 2011)**

<table>
<thead>
<tr>
<th>Occupational disease caused by</th>
<th>2009</th>
<th>2010</th>
<th>2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>16</td>
<td>13</td>
<td>23</td>
</tr>
<tr>
<td>Cadmium</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Beryllium</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Cobalt/Heavy metal</td>
<td>1</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Nickel</td>
<td>5</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>

The mist produced during the use of MWFs may produce the respiratory disease to the workers on the site and inhalation of MWF aerosol may cause irritation of the lungs, throat, and nose. In general, respiratory irritation produces due to chemical interaction between the MWF and the human respiratory system. Irritation may affect strongly to nose, throat (pharynx, larynx), the conducting airways of the lungs
cause bronchitis, and lung air sacks (the air passage from lungs to the body). After repeated use of MWFs, the composition has been constantly changed due to some biological and chemical reactions. Respiratory system is affected by inhalation and deposition of MWFs components present in mist of MWFs e.g. amines, volatile components, or from the aerosol phase, e.g. oils, biomass and emulsifiers solid components. The problems are to be generated only if the inhaled vapors or substances are starting to irritate the respiratory organs. If the deposition of inhaled substances became overloaded on the lung surfaces then the possibilities of respiratory diseases raised. Cancer of the respiratory organs can also occur rarely due to presence of carcinogenic PAHs in MWFs as mentioned in Table 1.1. Aerosols produced during the processing with MWFs contaminated with microorganisms, so the workers may affected by serious allergic disease named as Hypersensitivity pneumonitis (HP) who are working in that area (Suuronen 2009). Swallowing problem may also occur only if, for instance, MWFs (in concentrate form) carrying pipelines or pumps or supply lines accidently burst under high pressure or any leakage occurs.

1.3 Degradation and Disposal of MWFs

MWFs (here we are talking about industrial oil) are complex o/w emulsion mixtures of various chemicals and their cooling and lubricating properties have been deteriorated after repeated usage and generated toxic chemicals. This used oil known as spent cutting fluid (SCF) if not disposed properly creates hazardous environmental and health problems. However through cutting fluid management and recycling programs we can prolong the use of the industrial oil or coolants but due to the increasing recycling cost with time, it is necessary to take steps at initial stages for achieving significant and economic gains with safe disposal of SCF. The annual production of MWFs in UK industries alone has been estimated approximately 400,000 tons with disposal cost about £8 - 16 million in year 2000 only (Bio-wise 2001).
These figures are almost same in France, Germany and Italy whereas European industries are being under pressure for regulation of their wastes. By keeping the view of hazardous impacts of used and unused MWFs on environment, the attention should be directed to substances with occupational exposure limit values (OELs) and particularly to the treatment of the waste effluent.

1.3.1 Disposed into sewer

Some industries have disposed their industrial oil waste into the sewer which creates serious problems for municipal wastewater treatment plant. The typical problems are reported in Sutton et al. (1994) in the mechanical part of the municipal treatment plant due to the presence of oil, nature of waste o/w emulsion which may create clogging in screening process and skimming operations. The increased amount of surfactant may diminish the efficiency of treatment plant. Therefore, according to the state and federal laws, these used industrial fluids which are contaminated with bacteria, oil, fine metal chips etc. must be treated before to dispose in sewerage system of Municipal Corporation of local area because of the municipal treatment plant also have their restrictions described earlier. Sewer discharge standards restrict pH, oil, grease, solids, metals and other components. These standards vary from place to place, however some typical effluent criteria are as follows according to treatment and disposal of used metalworking fluids, (Marketing Co. Technical Report No. J/N 00/52)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sewer Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (Chemical Oxygen Demand)</td>
<td>500 ppm</td>
</tr>
<tr>
<td>TSS (Total Suspended Solids),</td>
<td>250 ppm (max.)</td>
</tr>
<tr>
<td>pH</td>
<td>6.0 - 9.0</td>
</tr>
<tr>
<td>Oil and Grease</td>
<td>10 - 100 ppm (max.)</td>
</tr>
<tr>
<td>Metals</td>
<td>Varies</td>
</tr>
<tr>
<td>Other Inorganics</td>
<td>Varies</td>
</tr>
</tbody>
</table>

For small scale industries, where less quantity of oily wastewater generates, typical evaporation or contract hauling may be the economical and effective disposal method. As the volume of oily wastewater increases, the treatment and sewerage cost
also proportionally raised up. Unless specific agreement has been granted by the local water authority, and this is strictly controlled, cutting oil disposal to drain (either foul or rainwater) is not an option. Used and degraded cutting oil fluids should be stored or collected and safely disposed through an authorized waste treatment contractor. The used and waste cutting oil fluids are normally disposed of by splitting where possible to separate the aqueous component, which is then further treated, whilst the oil component is normally incinerated. The quantity of waste cutting oil fluid, together with the associated disposal costs, can be minimized by the use of a high quality long life fluid coupled with good cutting oil fluid management.

1.3.2 Effluent discharge after treatment

Discharge Limits for Trade Effluent discharges to surface waters and of point source sewage effluent to ground/groundwater are subject to the Environmental Permitting Regulations and form part of the Environmental Permitting (EP) Charging Scheme 2010/11. Permission limits depends on volume, COD, BOD and TSS of the waste or spent MWFs or discharged effluent.

Volume will obviously depend on the size of your plant and the volume of waste MWF generated. This can be greatly influenced by careful fluid management.

COD is a measure of contamination of water by MWFs, tramp oils and many other chemical compounds such as detergents, surfactants, biocides and anti-corrosion agents found in MWFs.

BOD is a measure of how quickly micro-organisms use up the oxygen in water. It is another standard test for assaying the contamination level of water.

TSS is a measure of suspended solids in water which include a wide variety of particles from the work pieces found in waste MWFs. There may also be solids from other stray objects which sometimes find their way into machine sumps.

If you are going to make a discharge to surface water (for example a river, stream, estuary or the sea), or to groundwater (including via an infiltration system) then you may need to apply for an environmental permit to make that discharge. Discharges to surface waters and ground waters can be very harmful to the environment if they are
not carefully managed. To avoid this happening, the Environment Agency regulates such discharges through a system of permits (EP, 2011). The wide varieties of organic constituent present in spent MWFs are susceptible to biodegradation. In the presence of water, they form oil in water emulsion and provide suitable environment for the growth of various microorganisms (Mattsby- baltzer et al. 1989, Vander Gast et al. 2003) and thus deteriorate the quality of emulsion (Rossmoore et al. 1995, 2001). Spent metal cutting fluids (SMCFs) are one of the largest volumes of oily waste waters in metal working industries. They must be treated before disposal, as they have detrimental effects on the aquatic life and interfere to conventional waste water treatment process. It seems that there are many treatment technologies for the removal of spent MWFs from machining waste water but these conventional techniques have their own limitations such as less efficiency, sensitive operating conditions, production of secondary sludge and further the disposal is a costly affair. The methods that are commonly used to remove oil involve oil booms, dispersants, skimmers and sorbents but they have limitations such as their high cost and insufficient trace level sorption (Smith, 1983). Most of the dispersants are often inflammable and can also cause health hazards to the operators and potential damage to fowl, fish, marine mammals they can also lead to fowling of shoreline and contamination of drinking water resources (NRC 1989). Various treatment technologies relating to the removal of MWFs from industrial and machining waste water are classified and described as follows:

- Primary Treatment
- Secondary treatment
- Tertiary Treatment

Primary Treatment (Disposal of two waste streams categorized by hazard level): The purpose of primary treatment is to separate your waste MWFs into two waste streams, categorized by hazard level. Removal of tramp oil and suspended solids will result in a waste stream which is less hazardous and therefore cheaper to dispose of or easier to treat downstream. The tramp oil and removed solids will make up a more
hazardous waste stream but at a greatly reduced volume. Below are listed some familiar methods for the removal of oil and other contaminants from MWFs. Some of these methods are also commonly used to keep your MWFs in top condition and may also be used as preliminary treatment techniques. All of these treatment options are suitable for macro-emulsion, semi-synthetic and fully synthetic fluids. Some of the primary treatment processes are:

*Chemical Coalescence Agents*

*Skimmers*

*Magnetic Separators*

*Floatation*

*Centrifuges*

Secondary Treatment (Disposal of water and oil separately): Secondary treatment methods involve separation of the emulsified oil from the spent MWFs. This has the effect of significantly reducing the COD and may reduce the BOD of the water component. If the TSS, COD and BOD are within acceptable levels it may be possible to dispose of the water component as waste water with correspondingly low charges. The oil component will be typically only 5% of the original waste volume (depending on the initial concentration of the MWF) and so will leave a much smaller volume to be disposed of as hazardous waste. Details of the currently available techniques for the treatment of MWF are given below. Biological treatment has been included here; though it is not a technique for splitting the emulsion, it can be used to reduce the COD and BOD of spent MWFs. The processes under these treatment methods are as outlined:

*Chemical Treatment*

*Evaporation*

*Ultrafiltration*

*Biological treatment*

Tertiary Treatment (Further improvements to the quality of the waste water stream): This treatment option involves techniques for further “polishing” the end stream (or water phase) from the secondary treatment process to reduce the COD to a very low
level so that the recovered water could be re-used on-site for low grade use, such as floor washing. These techniques included in this section are:

Reverse Osmosis
Nano-filtration
Carbon Adsorption
Ion-exchange Resin

1.3.3 Technologies for Treatment of Spent Metalworking Fluids

Many new technologies are being investigated for the treatment of spent MWFs and other wastes. Most of these methods are based on combinations of filtration technologies coupled with a process of “oxidation” where the larger molecules of oil and solvents are broken down into smaller, water soluble compounds. As the molecules are broken down into smaller fragments they become less toxic, eventually only releasing carbon dioxide as the main end by-product. It should be noted that these processes have a long way to go in development but are worth watching as they show promise of high effectiveness in the treatment of spent MWFs. Some examples of these emerging technologies are given below:

• *Ultrafiltration coupled with chemical oxidation*: by chemical agents including chlorine, ozone and hydrogen peroxide, and special catalysts.

• *Ultrafiltration coupled with electrochemical oxidation*: brought about by passing an electric current through the water phase to break oil and solvent molecules into smaller fragments.

• *Mechanical vapor recompression (MVR)*: is a development of evaporation in which a mechanical blower compresses the exhaust vapour, causing a temperature rise. A heat exchanger is used to recover heat energy which is fed back into the evaporator raising overall efficiency of the process.

These three types of MWFs treatment methods may be categorized on the basis of processing as physical, chemical, biological and physico-chemical treatment methods.

1.3.3.1 Physical Treatment
Various physical treatment methods are used effectively to treat metalworking fluids for disposal. The most suitable treatment process for low to moderate discharged volume is Evaporation, the limits of discharged volume is 25 to 3,000 gallons per day. In this method the fluid have to concentrate up to the oil by using evaporation of water from the stored used fluid instead of Sewer discharge but permits for air discharge are required. Another common physical treatment method is membrane separation. There are two types of membrane separation treatments, Ultrafiltration (UF) and Reverse Osmosis (RO). The discharged volume limits for UF are 50 to 15000 gallons per day. This process works with such type of membrane which is capable in separating oil and large molecular weight material from the used fluid and provides an effluent within the sewer discharge limits. For better quality effluent plants need some improvements, which may be given by Reverse Osmosis as "secondary treatment". Besides UF and RO treatment the effluents cannot be reused due to oily concentrations and toxic wastes, therefore, Incineration must be used for final treatment of industrial fluids.

**Incineration**

Incineration is that process which converts the liquid or solid waste into gases or ash by using combustion or chemical oxidation catalytically. Direct flame incineration involves the spray of waste fluid direct into the methane, hydrogen, or liquid fuel flame. The organic materials present in the fluid converted into CO₂, H₂O and other gaseous state by oxidation and water evaporates, while the fuel used in this process is costly and may be substantially reduced. Flame incineration must be within the air discharge limits and the drawback of this process is its high operating cost. Incineration procedure also needs a membrane separation of filtration process as the final treatment.

Catalytic incineration or catalytic oxidation process used for reduce the air pollution problems which is produced by chemical and industrial processes. Catalytic incineration involves combustion at lower temperatures, catalyst used in the process take part in the reaction and is constantly changed throughout the reaction and finally
reverts back to its original state. Catalytic Incineration is widely applied in the chemical and industrial waste disposal treatment and sewage treatment field as well.

*Evaporation-distillation*

Evaporation is one of the direct methods of waste water treatment. Evaporation is an efficient and economic method for most of the industries where it must be accelerated by heating (Burke 1991). The cost of evaporation of the total effluent stream is prohibitive. Evaporation of water from concentrated sludge’s is more usual as volumes are considerably reduced. Practically again because it is not economically advantageous recovery and in-plant requirements for distilled process water may provide sufficient incentive to evaporate from compact high energy devices to large shallow ponds for natural solar evaporation. Where unless waste heat is readily available from some in-plant source, Recovery of solids for recycle is rarely oil Space requirements vary greatly.

*Electro-floatation (EF)*

Electro-floatation is differing from direct air flotation (DAF), EF involves flotation using bubbles of hydrogen and oxygen which are generated electrolytically to separate suspended materials from aqueous phases. This process was first proposed by Elmore in 1905 for flotation of valuable minerals from ores. EF has high flotation efficiency, compact units, easy operation, and less maintenance and more effective in treating oily wastewater or oil-water emulsion, mining wastewater, groundwater, foods processing wastewater, restaurant wastewater, industrial sewage, heavy metals containing effluent in compare to direct air floatation.

*Electrocoagulation*

Electrocoagulation process is used for destabilizing suspended or emulsified or dissolved contaminants from an aqueous medium by passing an electrical current through the medium. The electrical current generates electromotive force and the chemical reactions are forced to occur and compounds get the stable state. Compounds in this state are generally less colloidal, less emulsifiable, or less soluble than the earlier and form hydrophobic entities such as precipitates which can easily be removed by a number of secondary separation techniques. Electrocoagulation is a
physical process for treatment of waste MWFs and limited literature has been available only for the treatment of synthetic metal cutting fluids by EC (Carmona et al. 2006), (Khemis et al. 2004), (Bergmann et al. 2003). The results in this study were evaluated by using Al and Fe electrodes with different pH, current density and operating time. It was reported that COD was reduced from 17313 to 1385 mg/L and 1212 mg/L while using Fe electrode and Al electrode respectively. Al electrode appeared to be more efficient than Fe electrode at the optimum current density 60 A/m² and operating time 25 min. (Koby et al. 2008).

Membrane filtration
Membranes are engineered barriers that exclude or separate colloids, emulsified molecules or salt (Baker, 2000). This major property exploited in membrane technology is the ability of the membrane to control the permeation of a chemical species through the system. In fact, a membrane is nothing more than a thin discrete interface that moderates permeation of chemical species in contact with it. It is different from a general filter which is limited to separate particles larger than 10μm and only because of their size. Membranes separate colloidal particles, emulsified molecules and chemical species because of their size, shape and their chemical and physical properties. Membranes are able to control the rate of chemical permeation. This effect is widely used in medicine to relieve chemicals in the human body. Membrane filtration technologies are also playing a prominent role in accomplishing emulsified oil separation.

This review pays particular attention to four filtration processes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Fig. 2.10). All of them are well-established technologies developed at small and large industrial scales. They are pressure driven filtration processes that use membrane technology to allow the passage of water and the passage or retention of particles, molecules or salts.

Microfiltration
A synthetic membrane, most often polymeric, is used as a selective barrier in Microfiltration processes. Certain feed stream components are permitted passage by
the membrane pores into a permeate stream, while other, usually larger feed components, are retained by the membrane. These retained species accumulate in the retentate stream. Pressure-driven membrane processes use the pressure difference between the feed and permeate side as the driving force to transport the water through the membrane (Van der Bruggen et al., 2003). Particles and dissolved components are partially retained based on properties such as size, shape, and charge. Nazzal et al., 1996 had examined the effect of trans-membrane pressure on the rejection of emulsified oil drops by ceramic membranes and also determined the limiting operating pressure for a specified membrane-emulsion combination.

**Ultrafiltration**

Ultrafiltration (UF) is a pressure driven membrane technique that uses porous membranes for the separation of material in the 1nm to 10µm size range or compounds with molecular weights in excess of 5000. Colloidal material, macromolecules and micelles can be fractionated through it. Clean water is forced through the porous membrane (permeation) while the waste that is retained by the membrane becomes more concentrated. Many research workers have reported on effectiveness of ultrafiltration (UF) technique for treating waste water. Results showed the reduction in volume of waste-cutting oil emulsion by 98% and concentrated oil and solids up to 60% (Pinto et al. 1978). Reed et al. (1997) have studied the UF technique in the waste water treatment from metal industry using two types of membranes having different molecular weight cutoff (MWC) and surface charge. Oil concentration for both membranes were < 50 mg/L and TSS levels < 25 mg/L. Some research workers (Hilal 2004) have used two-system filtration technique, in which first system consisted ultrafiltration membrane of 200 kD and 100 kD MWC and a nanofiltration membrane were used. The second system consisted of direct filtration of MWFs by a nanofiltration membrane. The performance and characterization of each filtration system such as foaming and emulsion stability were discussed and compared for the same metal working emulsions.

**Nanofiltration**
Nanofiltration is works on the basis of same principal as ultrafiltration, a less open structure material is used as the active layer and charges may be added to the surface in order to control the passage of solute salts. Nanofiltration is used for the removal of dissolved material in the molecular range of 100 to 500 kDa. A nanofiltration membrane has a pore size around 0.001μm and 0.01 μm described as solution diffusion membranes (Baker, 1992) and (Noble et al. 1995). Nanofiltration removes most organic molecules, nearly all viruses, most of the natural organic matter and a range of divalent ions which make water hard, so nanofiltration is often used to soften hard water. Salts and charge species are transmitted through the membrane preferentially. The operating pressure applied on the membrane is in the range of 10-40 bar that is little higher than in UF. Orecki et al. (2007) has been investigated the possibility of treatment of oily wastewater by using the nanofiltration (NF) process. The permeate flux obtained from ultrafiltration (UF), process used in nanofiltration contaminated with oil and some inorganic metal ions. Influence of trans-membrane pressure on a permeate flux, the degree of the rejection of oil and inorganic compounds was investigated. The retention coefficient of the inorganic compounds was found higher than 75% for all the monovalent and bivalent cations examined and higher than 95% for sulphates. Therefore, it was concluded that the permeate obtained in the NF process can be reused for fresh emulsion preparation.

**Reverse Osmosis**

Reverse Osmosis have membranes with polymer network (dense active layer) and no macroscopic pore structure, it works with high pressure up to 60 bar allowing the retention of almost all particles and ionic species. The permeation through RO membranes are described with the solution diffusion model. Reverse osmosis have membrane of pore size around 0.0001 µm. After water passes through a reverse osmosis filter, it is essentially pure water. In addition to removing all organic molecules and viruses, reverse osmosis also removes most minerals that are present in the water. Reverse osmosis removes monovalent ions, which means that it desalinates the water. To understand how reverse osmosis works, it is essential to understand osmosis. In Fig 1.1(A, B), osmosis occurs when a semi-permeable
membrane separates two salt solutions of different concentrations. The water will migrate from the low concentration solution to the strong concentration solution, until the two solutions are of the same concentration, because the semi-permeable membrane allows the water to pass through, but not the salt. In reverse osmosis, the two solutions are still separated by a semi-permeable membrane, but pressure is applied to reverse the natural flow of the water. This forces the water to move from the more concentrated solution to the weaker. Thus, the contaminants end up on one side of the semi-permeable membrane and the pure water is on the other side. In the diagram below, reverse osmosis is represented in Fig.1.1(C).

![Diagram of Osmosis and Reverse Osmosis](image)

Fig. 1.1. (A) and (B) illustrate the process of Osmosis, (C) Reverse Osmosis
Benito et al. (2002) have successfully investigated the application of reverse osmosis process in the treatment of global effluent from electroplating industry. The results revealed that the reverse osmosis recovered 75–96% treated water.
The traditional methods for the separation of oil emulsion can be classified as chemical, mechanical and thermal. These methods of oily wastewater treatment are frequently not efficient especially when the oil droplets are finely dispersed and their concentration is very low. The treatment process is additionally complicated due to different compositions of this oily wastewater from different fabrication companies/metal machining sectors. The membrane techniques such as ultra-filtration (UF) seem to be a promising method for the separation of emulsion. The advantages of membrane separation are the high efficiency in conjunction with a high quality of permeates, not achievable by other methods.

The main drawback of the UF is it requires huge expenditure for the installation of the plant, fouling and short average life of ultra-filtration membranes. Due to these drawbacks UF technique had limited industrial and commercial application. It seems that there are many treatment technologies relating to the removal of MWFs from machining waste water but these conventional techniques have their own limitations such as less efficiency, sensitive operating conditions, production of secondary sludge and further the disposal is a costly affair.

1.3.3.2 Chemical Treatment
Chemical treatment uses various inorganic chemicals (e.g. aluminum sulfate or ferric chloride) or organic chemicals (e.g. cationic or anionic polymers) to destabilize the emulsions of used oily wastewater. Chemical treatment can be used for volumes of wastewater from 50 to over one million gallons/day, however it is generally more cost-effective for larger volumes of oily wastewater. Chemical treatment is effective for treatment and removal of metals in oily wastewater. A by-product of chemical treatment is a sludge or oily waste concentrate that requires further treatment for oil recovery. Some of the chemical treatments methods in general use are:

**Acid-Alum**

The simple and best understood method of waste treatment is acid-alum treatment, in this type of treatment the wastewater is acidified with sulfuric acid to a pH of 4.0 or lower, alum or hydrated aluminum sulfate is added and mixed, and the pH is raised slowly, with slow stirring by the addition of caustic or NaOH. As the pH is raised above 4, the alum precipitates, as a solid.

Small particles of aluminum hydroxide agglomerate and form floc particles, which sweep through the partially clean water and attached to other particles. This sweeping action, combined with electrostatic charges and absorption of oil into the floc takes place, finally clarifies the wastewater. Floc is removed by sedimentation (settling) or flotation and the clarified effluent discharged to the sewer or is fed to additional (secondary) treatment. Depending on applicable federal and local regulations and on the degree of clarification, the effluent may be suitable for direct discharge to a stream or waterway.

Sulfuric acid is preferred but others including nitric, hydrochloric, or solid sulfamic acids work as well in most applications. Lime, limestone, potash, and soda ash have all been used to neutralize acidic solutions in waste water treatment, depending on their expense and availability relative to sodium hydroxide.

To insure proper waste water treatment, laboratory or bench scale tests are run before treatment to determine the approximate dosages of each chemical required. Jar testing is the standard industrial method for pretesting acid-alum and other chemical breaks because it is repeatable and easy to perform.
**Ferric Chloride, Ferric Sulphate**

Aluminum sulfate is only one of many inorganic chemicals which precipitates (forms a floc) as pH is raised. Ferric chloride, ferric sulfate, sodium aluminate, or magnesium chloride are often used instead of aluminum sulfate. Sulfuric acid is most often used when a sulfate compound such as aluminum sulfate or ferric sulfate is used because of the synergistic common ion effect. Hydrochloric acid may be used for the same reason with ferric chloride or magnesium chloride as a flocculant but is rarely employed because it is less effective than sulfuric acid.

**Polyelectrolytes**

Synthetic organic compounds have become generally accepted alternatives to inorganic chemical waste treatment. Modern polymer chemistry provides an unlimited selection of charged, high molecular weight molecules listed as emulsion breakers, flocculants, coagulants, Poly-electrolytes or polymers with the help of which treatment of waste water held under several mechanisms. Most spent cutting fluids are anionic, that is, they contain negatively charged molecules and solid particles suspended in the fluid. Particle charges help keep the particles suspended in the fluid. Neutralization of these charges by the high molecular weight cationic (positively charged molecules) coagulants and settling aids promotes agglomeration of solids into settled particles. Once floc has formed, the mechanical sweeping action and absorption found in inorganic flocculation occur, further clarifying the effluent. Emulsion breakers or de-emulsifiers have been widely used in the petroleum industry and may soon be applied to oils-carrying cutting fluid waste. They are not floc forming substances and have the advantage of producing a clear oil layer which can be skimmed off the wastewater. De-emulsifiers are most successfully applied with anionic wastes. Poly-electrolytes have several advantages over inorganic flocculants. As they are used in neutral and slightly alkaline wastes so little pH adjustment is necessary, they produce less floc and, therefore, less sludge produced and they do not add dissolved solids (like sulfates and chlorides) to the effluent, this makes the prospects for reusing the effluent as makeup water more promising because of the absence of these corrosion promoting ions.
The primary disadvantage of using poly-electrolytes is cost, several times more expensive than inorganic treatment chemicals such as acid-alum. Many liquid polymers have short shelf lives and require a continuously renewed supply. Dry polymers can be stockpiled but are difficult to mix, forming viscous, slimy solutions at concentrations below half of one percent. Weaker solutions have storage lives of only one or two weeks in many cases.

**Polymer- Inorganic Chemical Combinations**

Many polymers that work poorly or not at all by themselves, can work successfully in combination with alum, ferric chloride, or one of the other inorganic flocculants. The inorganic is the primary flocculants, while the polymer serves to accelerate coagulation and agglomeration of small floc particles.

In chemical treatment by-products require disposal, consumables and payback is unacceptable for small volume users and also not suitable for synthetic fluids.

1.3.3.3 Biological treatment

Biological treatment method is suitable for macro-emulsions and semi-synthetic fluids. Micro-organisms are added to a bioreactor containing spent MWFs to reduce organic and inorganic materials. The treated water may be acceptable for discharge as trade effluent and the sludge by-product is re-used in the process. Excess sludge must be disposed of periodically. This treatment is only suitable for large users because it requires continuous feed, disposal of biomass, susceptible to toxic and non-biodegradable substances and having slow treatment rate (Muszynski et al. 2007).

The high organic content of most metalworking fluids makes them good candidates for degradation by bacteria for waste treatment. However, the high oil content of these fluids typically eliminates using biological treatment as the secondary treatment method. A chemical or physical treatment process precedes the use of biological treatment for metalworking fluids.

Though, a number of studies have been carried out for removal of the waste MWFs from aqueous system by using microorganisms. Sutton et al. (1985) have investigated the fluidized bed reactor that dealt with high volumes of influent and
provided large surface area for microbial growth, while in another study Kim et al. (1992) have used two types of carriers, namely, sand and granular-activated carbon (GAC) for waste MWF treatment as they both provided large surface area for biological growth and adsorption capacity. Adenipekun et al. (2013) have investigated white rot fungus *Pleurotus pulmonarius* for bioremediation of contaminants such as heavy metals and total petroleum hydrocarbons potentially in their pilot study at 10, 20 and 30% contamination levels from spent and fresh cutting fluids. The results indicated the efficiency of *P. pulmonarius* as a bioremediating agent of heavy metals and TPH in contaminated soil.

1.3.3.4 Physico-chemical Treatment

**Hydrothermal Oxidation**

In addition to waste water treatment, there is another treatment called hydrothermal oxidation process which has proved effective to treat a wide variety of industrial wastes. Portela et al. (2001) have examined the use of free radical promoters to enhance the efficiency of wet air oxidation and supercritical oxidation at mild conditions. Normal and promoted hydrothermal oxidation have been tested to treat cutting oil wastes in a continuous flow system between 300 and 600 °C. As a source of oxygen and free radicals, H₂O₂ was used. More than 90% TOC reduction was obtained within 10 s at 500 °C.

**Ion Exchange Resins**

Dissolved metal salts, acids and bases found in spent MWFs are removed by contact with functional chemicals attached to beads of resin. Ion exchange technology is used to purify the end stream from secondary treatments. Organic material, oil or grease can foul the resin and therefore the technique is only suitable for water phases where the COD is less than 150 mg/l.

**Microwave irradiation**

The concept of microwave irradiation for demulsifying the o/w emulsion in waste MWFs was first introduced by Wolf et al. (1986) while Fang et al. (1995) carried out a field test on 188 barrels of crude oil in water emulsion tanks and found that more
than 80% of water could be separated from emulsion. Rios et al. (1998) destabilized a cutting oil emulsion by adding an inorganic salt and over 90% separation efficiency was obtained. Fortuny et al. (2007) investigated the effect of pH, salt (NaCl) and water content on a crude oil emulsion (w/o) by a microwave demulsification process. According to this study, the addition of dissolved salts significantly increases the heating efficiency and destabilizes the emulsions.

**Adsorption**

Out of these methods adsorption process is recognized of major interest due to its surface phenomenon in which a multi component fluid mixture attracted to the surface of a solid adsorbent and form attachments via physical or chemical bond. Adsorption is therefore, recognized as the most efficient, promising and widely used fundamental approach in wastewater treatment process. Adsorption is favored universally due to its simplicity, economically viable, technically feasible and socially acceptable (Foo et al. 2010). A large number of different adsorbents containing a variety of attached active chemical groups have been reported for this purpose. Adsorption through peat bed reactors has been used as the first sorbent for the removal of MWFs from industrial waste water by Viraraghavan et.al. (1990). Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It may be termed as the adhesion in an extremely thin layer of molecules (as of gases, solutes, or liquids) to the surfaces of solid bodies or liquids with which they are in contact. The use of solids for removing substances from either gaseous or liquid solutions has been widely used since ancient times. This process, known as adsorption, involves nothing more than the preferential partitioning of substances from the gaseous or liquid phase onto the surface of a solid substrate. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate. Adsorption is thus different from absorption, a process in which material transferred from one phase to another (e.g. liquid) interpenetrates the second phase to form a "solution". The term sorption is a general expression encompassing both processes.
Adsorbents are usually porous solids, and adsorption occurs mainly on the pore walls "inside" particles. Examples of adsorbents include:

- Activated carbon (adsorbs organics)
- Silica gel (adsorbs moisture)
- Activated alumina (adsorbs moisture)
- Zeolites and molecular sieves
- Synthetic resins

Activated carbon is most widely used adsorbent material for adsorption due to its efficiency and economic feasibility. It is used in the form of powder, granular and fiber or cloth. Activated carbon cloth having high surface area, controllable pore structure, thermo-stability, low acid base reactivity, high adsorption capacity and mechanical strength has gained increasing attention in recent years. If the adsorption system is designed correctly, it would produce a high quality of water. Activated charcoal is charcoal that has been treated with oxygen to open up millions of tiny pores between the carbon atoms. The use of special manufacturing techniques results in highly porous charcoals that have surface areas of 300-2,000 m²/g. These so-called active, or activated, charcoals are widely used to adsorb odorous or coloured substances from gases or liquids (Moreno et al. 1995).

Adsorption phenomena are operative in most natural physical, biological, and chemical systems, and adsorption operations employing solids such as activated carbon and synthetic resins are used widely in industrial applications and for purification of waters and wastewaters. From the early days of using bone char for decolorization of sugar solutions and other foods, to the later implementation of activated carbon for removing nerve gases from the battlefield, to today's thousands of applications, the adsorption phenomenon has become a useful tool for purification and separation (Siejko 1985).

1.3.4 Types and Mechanism of Adsorption

The process of adsorption involves a solid phase (sorbent) and a liquid phase (solvent) containing a dissolved species to be sorbed. Adsorption process (Fig. 1.3) is generally classified as *Physisorption* [physical adsorption is a type of adsorption in...]

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which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behavior of real gases, it has low enthalpy of adsorption of about 20-40kJ/mole, adsorption occurs in multilayer form mostly, this type of adsorption does not require any activation energy, this is a reversible process and observed under the condition of low temperature] and **Chemisorption** [Chemical adsorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, it has high enthalpy of adsorption, adsorption occurs in monolayer form generally, this process is temperature based and requires activation energy to occur, this is an irreversible process]. It may also occur due to electrostatic attraction (Ferrari et al. 2010).

Physical adsorption is caused mainly by van der Waals forces and electrostatic forces between adsorbate molecules and the atoms which compose the adsorbent surface. Thus adsorbents are characterized first by surface properties such as surface area and polarity. A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces. The size of the micropores determines the accessibility of adsorbate molecules to the internal adsorption surface, so the pore size distribution of micropores is another important property for characterizing adsorptivity of adsorbents. Especially materials such as zeolite and carbon molecular sieves can be specifically engineered with precise pore size distributions and hence tuned for a particular separation.
Fig. 1.3 Distinction between physical and chemical adsorption process

Surface polarity corresponds to affinity with polar substances such as water or alcohols. Polar adsorbents are thus called "hydrophilic" and aluminosilicates such as zeolites, porous alumina, silica gel or silica-alumina are examples of adsorbents of this type. On the other hand, nonpolar adsorbents are generally "hydrophobic". Carbonaceous adsorbents, polymer adsorbents and silicalite are typical nonpolar adsorbents. These adsorbents have more affinity with oil or hydrocarbons than water (Suzuki, 1990).

The mechanism behind adsorption as proposed by Shimizu et al. (1992), that the organic compound of MWFs (soluble oil) surrounded by an envelope of structural water, are apolar and, therefore, only able to link the adsorbent through weak Vander-Walls forces, whereas according to the study done by Kumagai et al. (2007) during fluid adsorption on agricultural fiber, there are several mechanisms that may be followed:

☐ Interaction with oleophilic compounds and functional group on the fiber surface;
Physical trapping on the fiber surface related to fiber density, fineness and irregularity;
Capillary action via oil diffusion into pore on the fiber surface.

1.3.5 Theories of Adsorption

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH (Limousin et al., 2007). Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration (Ghiaci et al., 2004). Typically, the mathematical correlation, which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration (Ncibi, 2008). Its physicochemical parameters together with the underlying thermodynamic assumptions provide an insight into the adsorption mechanism, surface properties as well as the degree of affinity of the adsorbents (Bulut et al., 2008). There are three fundamental approaches on the basis of which, various equilibrium isotherm models have been formulated. The first approach is referred as Kinetic consideration. By this means, adsorption equilibrium is defined being a state of dynamic equilibrium, with both adsorption and desorption rates are equal (Langmuir, 1916). Whereas, thermodynamics, being a base of the second approach, can provide a framework of deriving numerous forms of adsorption isotherm models (Boer et al., 1968, Myers et al., 1965) and potential theory, as the third approach, usually conveys the main idea in the generation of characteristic curve (Dubinin, 1960). Out of those isotherm models, three are described here which may be applied to our adsorbent-adsorbate system. These isotherm models are:

1.3.5.1 Langmuir Isotherm Model
In 1916, Irving Langmuir published a new model isotherm for gases adsorbed to solids, which retained his name. It is a semi-empirical isotherm derived from a proposed kinetic mechanism. This isotherm was based on different assumptions one of which is that dynamic equilibrium exists between adsorbed gaseous molecules and the free gaseous molecules. It is based on four assumptions:

The surface of the adsorbent is uniform, that is, all the adsorption sites are equivalent.

Adsorbed molecules do not interact.

All adsorption occurs through the same mechanism.

At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

At equilibrium saturation point, once a molecule occupies a site, no further adsorption can take place (Demirbas et al., 2008). Moreover, Langmuir theory has related rapid decrease of the intermolecular attractive forces to the rise of distance.

The model can be written as:

\[ q_e = q_m b C_e / (1 + b C_e) \]  \hspace{1cm} (1)

Linearized form of above eq. is:

\[ C_e / q_e = 1 / (q_m b) + C_e / q_m \]  \hspace{1cm} (2)

\( q_e \) = value of adsorbate adsorbed per unit weight of adsorbent at equilibrium (g/g)

\( q_m \) = maximum adsorption capacity corresponding to monomolecular layer coverage (g/g)

\( C_e \) = adsorbate concentration at equilibrium (g/L)

\( b \) = Langmuir Constant

On plotting the graph between \( C_e / q_e \) and \( C_e \), a linear graph is obtained which has an intercept and slope corresponding to \( b \) and \( q_m \) respectively. The essential feature of the isotherm is expressed in terms of separation factor or equation parameter \( R_L \) calculated as:

\[ R_L = 1 / (1 + b C_o) \]  \hspace{1cm} (3)

\( C_o \) = initial concentration of adsorbate (metal cutting oil in water emulsion)
Value of $R_L$ shows the favorability of isotherm (Webber et al., 1974). $R_L=0$ indicates irreversible isotherm, $R_L>1$ shows unfavorable and $0<R_L<1$ indicates favorable isotherm.

1.3.5.2 BET Isotherm Model

Brunauer–Emmett–Teller (Bruanuer et al., 1938) isotherm is a theoretical equation, most widely applied in the gas–solid equilibrium systems. It was developed to derive multilayer adsorption systems with relative pressure ranges from 0.05 to 0.30 bar corresponding to a monolayer coverage lying between 0.50 and 1.50 bar. Its extinction model related to liquid–solid interface is exhibited as:

$$Q_e = \frac{(q_s C_{BET} C_e)}{[C_s - C_e] (1 + (C_{BET} - 1)(C_e/C_s))}$$  \hspace{1cm} (4)

where, $C_{BET}$ = BET adsorption isotherm (L/mg),

$C_s$ = adsorbate monolayer saturation concentration (mg/L),

$q_s$ = theoretical isotherm saturation capacity (mg/g),

$q_e$ = equilibrium adsorption capacity (mg/g)

As $C_{BET}$ and $C_{BET} (C_e/C_s)$ are much greater than 1, the equation is simplified as:

$$Q_e = \frac{q_s}{[1-(C_e/C_s)]}$$  \hspace{1cm} (5)

1.3.5.3 Freundlich Isotherm Model

Freundlich (Freundlich et al. 1906) expressed an empirical equation for representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation or simply Freundlich Isotherm. Though Freundlich Isotherm correctly established the relationship of adsorption with pressure at lower values, it failed to predict value of adsorption at higher pressure. The Freundlich isotherm does not have much limitation, i.e., it can deal with both homogeneous and heterogeneous surfaces, and both physical and chemical adsorption. Especially, this model frequently succeeds in depicting the adsorption behavior of organic compounds and reactive matters. The Freundlich isotherm is expressed as:
\[ q_e = K_F C_e \frac{1}{n} \] (6)

- \( q_e \): amount of removed oil per unit weight of adsorbent in g/g
- \( C_e \): adsorbate concentration in solution at equilibrium g/L
- \( K_F \): adsorption capacity
- \( n \): sorption intensity

The above eq. can be written in its linearized form:

\[ \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \] (7)

\( K_F \) and \( n \) values are calculated from the graph (plotted between \( \ln q_e \) and \( \ln C_e \) from the equilibrium data). The isotherm would be favorable if \( n > 1 \) and also indicated the heterogeneity of adsorption process, becoming more heterogeneous as its value gets closer to zero. Whereas, a value below unity implies chemisorption process where \( 1/n \) above one is an indicative of cooperative adsorption (Haghseresht et al., 1998).

### 1.3.5.4 Thomas Isotherm Model

The Thomas model is another one frequently applied to estimate the adsorptive capacity of adsorbent and predict breakthrough curves, assuming the second-order reversiblereaction kinetics and the Langmuir isotherm (Han et al., 2008, Ghasemi et al., 2011). Theoretically, it is suitable to estimate the adsorption process where external and internal diffusion resistances are extremely small (Aksu et al., 2004).

The Thomas model is given by:

\[ \ln [(C_0/C) - 1] = \frac{K_{Th} Q_0 m}{D} - (K_{Th} C_0 t) \] (8)

- \( Q_0 \): max. adsorbate concentration per unit mass of adsorbent
- \( M \): amount of adsorbent
- \( K_{Th} \): Thomas rate constant
- \( D \): flow rate

By plotting \( \ln [(C_0/C) - 1] \) against \( t \) the values of \( K_{Th} \) and \( Q_0 \) were calculated.

Most commercial systems currently use activated carbon as adsorbent to remove heavy metals, dyes, organic / inorganic oil from wastewater (Demirbas et al. 2009, Gupta et al. 2000, Rajeshwarisivaraj et al. 2001). Use of activated carbon adsorption
has been recommended by the US Environmental Protection Agency (EPA) as one of the best available technology (Derbyshire et al. 2001). However, activated carbon is associated with several disadvantages such as it is expensive (higher quality, greater in cost), non-selective and inefficient against dispersed and vat dyes (Babel et al. 2003). The regeneration of the saturated activated carbon is also expensive, not straightforward and result in loss of adsorbent. Use of activated carbon can’t be justified and therefore, it is necessary to explore some inexpensive alternate adsorbents which replace the expensive activated carbon are derived from agro-waste materials. These agricultural byproducts are readily available, cheap, ecofriendly as they solve waste disposal problem. In this way they are superior to the conventional adsorbents like activated carbon.

1.4 Objective of the study

Keeping all these views, the objective of the present research work involves the use of previously untried adsorbents (derived from agro-waste materials) for the removal of metal cutting fluids (MCFs) by adsorption.

The aim of this study is also to identify the natural agro-industrial based by product as adsorbents having high specific area with better adsorption capacity, high mechanical strength, thermally stable, low cost/economical feasible, ecofriendly behavior and be easily/abundantly available in India.

This study can be easily adopted by the industries (commercially) to make the aquatic environment safe and unpolluted from toxic Metal Cutting Fluids by removal of metals cutting oil from industrial effluents by adoption of fixed bed continuous adsorption process.

This study may also be helpful to expand the potential commercial application of agro-based industrial waste materials in waste water treatment and to solve the scarcity of water to an extent by reuse of treated industrial waste water for the agricultural purposes.