Chapter 1 General Introduction

1.1 Overview and problem statement

Coal and crude petroleum are the most important fossil fuel resources that play an imperative role in the modern world economy. Though global efforts are being made to develop renewable energy resources to act as possible fossil fuel replacement, however; the crude oil is currently accounting for 32.9% of the current global energy demand which is likely to grow continuously in the coming future due to changing lifestyle and industrial development [1]. In order to get useable products like gasoline, diesel, kerosene, etc. the crude petroleum is subjected to a sequence of physical and chemical separation as well as conversion techniques collectively known as petroleum refining. The crude petroleum refining operation comprises cracking, fractionation, blending/combination processes, hydro-treating, transport, and manufacturing. The petroleum products supplied by refineries mainly include gasoline, jet fuel, diesel fuel, kerosene, asphalt, tar, paraffin wax, lubricating, and various other heavy oils [2]. The production of all these useful products in refineries also causes the generation of gaseous, liquid, and solid wastes that pollute the air, water, and soil. There are mainly two types of solid wastes that are generated during the recovery of crude oil from petroleum wells and the manufacture of various products from it. These include drilling waste and process waste. The drilling waste is a kind of waste produced during exploratory drilling and it is less problematic and hazardous. The process wastes are produced in varying amounts from crude receiving and conditioning sections and various refining and blending units. It is a thick mixture of oil and water (sludge) as well as a dilute oil-water mixture [3]. As a result, two types of wastes come to the waste treatment plant of petroleum refineries which affect air, water, and soil. The first type is generally called petroleum refinery effluent (PRE) and the other one is known as oily petroleum sludge (OPS). All these are of major environmental concern because several constituents of waste are hazardous and are generated in a substantial amount in petroleum refineries globally. The reusing of waste in an environmentally friendly way is one of the most suitable solutions for waste management. OPS is categorized as hazardous waste and in utmost cases, it is categorized as a liquid phase, which indicates that it cannot be disposed of directly to landfills. It also contains a complex mixture of contaminated soil or sediments, hydrocarbons, and metals which constitute different chemical species with different physicochemical properties depending upon the source of generation [4, 5].

The refineries and petrochemical industries consume maximum water and are the major source of PRE generation [2, 6]. It is reported that 80-90% of the total input water to these industries is discharged as wastewater or PRE [7]**.** Coelho et al. [8] reported that approximately 0.4-1.6 times wastewater is produced per unit volume of crude oil refined [9, 10]. The OPS is accumulated in crude oil tanks, desalters, refinery product tanks, and throughout the production and processing [11-13]. It is reported that approximately one ton of OPS is produced for every 500 tons of crude oil processed. It is estimated that more than 60 million tons of OPS are produced annually globally [14, 15]. Indian refineries produce more than 28,220 tons of sludge every year [16].

The petroleum crude is a mixture of a very large number of hydrocarbons which are mainly grouped as saturated hydrocarbon, aromatic hydrocarbons, resins, asphaltenes (higher molecular weight polycyclic compounds containing nitrogen, sulfur, and oxygen (NSO)), and, organometallic compounds [2, 6]. These organic compounds are highly toxic, hazardous, and show unfavorably carcinogenic, teratogenic, or mutagenic properties, and are considered as the priority pollutants [17]. Exposure or injection of these compounds even at low concentrations can cause severe health problems and environmental impacts [18, 19]. The capability of hydrocarbons to cause various health effects mainly depends on three factors- the exposure route (ingestion inhalation, and dermal absorption), chemical properties (viscosity, volatility, and surface tension), and the level of exposure.

According to the Indian "The Environment (Protection) Act", 1986, the hazardous substance means "*any substance or preparation which, by of its chemical or physicochemical properties or handling, is liable to cause harm to human beings, other living creatures, plants, micro-organism, property or the environment*" [20]. The PRE and OPS are hazardous and concern has been raised worldwide to remove/reduced these contaminants from petroleum refinery waste [21, 22]. Their direct discharge on the surface and groundwater sources will have an undesirable impact. For the disposal of PRE and OPS, the government of India established the law under the Environment (Protection) Act, 1989, and Rule 1986 in Schedule 1 for the oil refinery industry limiting the contamination levels for PRE and OPS [20].

1.2 Treatment of petroleum refining effluent

The PRE mainly consists of a large amount of colloidal, organic, and inorganic compounds with metals that fluctuate the pH and increases the level of chemical oxygen demand (COD), turbidity, total dissolved solids (TDS), and color of water above the permissible limits [23]. The highly acidic or alkaline nature of wastewater unswervingly affects the properties of water [23, 24]. Consequently, adequate treatment of PRE is necessary before its reuse and discharge [17].

Conventionally, the treatment of typical wastewater involves two general stages. The first stage is a pre-treatment process which includes a sequence of mechanical and physicochemical techniques; and the second stage is an advanced treatment process that involves the biological treatment in addition to other advanced methods such as advanced oxidation process (AOP), adsorption, membrane separation, etc. The pre-treatment stages reduce the pollution load and increase the efficacy of the advanced treatment processes. Pre-treatment processes primarily focus on the reduction of suspended solids, oil, and grease mechanically, and then use a set of physicochemical processes to reduce the soluble or emulsified organic contaminants. The advanced treatment processes focus on decreasing the amount of contaminates present to meet the specified discharge limits [9, 25]. The various treatment processes that have been used for treating PRE with favourable results include coagulation-flocculation, adsorption, chemical precipitation, electrocoagulation, Fenton oxidation, wet oxidation, photocatalytic oxidation, catalytic vacuum distillation, photo-degradation, microbial degradation, ultrasonic degradation, and membrane bioreactor [25-27].

The conventional processes like adsorption, chemical precipitation, and coagulation, and flocculation depend upon the selection of adsorbents, catalysts, and coagulants, respectively. These processes work on the principle of charge neutralization and adsorption [28-30]. Adsorption with activated carbon is frequently used method; and it is preferred when the spent carbon can be re-generated [28]. The membrane separation processes (e. g. micro-filtration reverse osmosis) are used for the removal of inorganic salt, organic matter, and heavy metal in the wastewater. However, the method is not appropriate for PRE treatment due to membrane fouling and the high cost of membrane replacement [31]. The electrochemical method uses metal electrodes like boron diamond doped anode, ruthenium mixed metal oxide, and iron electrode, which are quite expensive. Corrosion of the electrode further increases the cost of electrode replacement [32]. The catalytic processes of degradation (photo-catalytic and non-photo-catalytic, microbial) degradation processes degrade pollutants dissolved in water by the action of catalyst and ultra-violet (UV) light, visible light and ultrasonic waves, and microorganisms (bacteria). In terms of scale-up, photo-catalytic oxidation and catalytic wet air oxidation are challenging as these processes require UV light and high-pressure reactors which are expensive and limit the application of these processes at the industrial level [33, 34]. In the advance/chemical oxidation process, a large amount of oxidants such as ozone (O_3), chlorine dioxide (ClO_2), Cl_2, and hydrogen peroxide (H_2O_2) is required, which are expensive and limit their application for PRE treatment [35]. The advance oxidation processes (AOP) work on phenomena of oxidization of organic pollutants to harmless pollutants but the incomplete oxidation (partial oxidation) may create products that may be more toxic than the initial pollutants. The AOPs are more beneficial when implemented as post-biological processes [8]. In biological treatment, organic pollutants are oxidized by microorganisms in suspended growth or an attached growth reactor where pollutants are used as a carbon source (or nutrients). The degradation process can take place either in the presence of oxygen (aerobic treatment) or in the absence of oxygen (anaerobic treatment) [36]. The membrane reactor includes a biological aerated filter (BAF), cross-flow membrane bioreactor (CF-MBR), membrane sequencing batch reactor (MSBR), and hollow fiber ultra-filtration membrane bioreactor (HF-UF MBR) which has been tested efficiently to treat PRE [37-40].

Each type of treatment has its advantages and disadvantages for the complete removal of pollutants (Diyaudden et al. [41] and Yu et. al. [9]). The catalytic thermochemical treatment and coagulation and flocculation are cost-effective pre-treatment processes for the PRE treatment.

1.2.1 Catalytic thermolysis

The thermal treatment (catalytic or non-catalytic) can be an effective technology to remove the organic contaminants present in PRE. The thermal treatment alters the physical and chemical properties of the wastewater [42, 43]**.** Thermolysis is a thermal process in which a dissolved organic and inorganic substances present in wastewater are decomposed by the application of heat to produce soluble and insoluble liquids and solids as well as gaseous products [43], where the temperature is less than the boiling point of the effluent at the ambient pressure [44-47]. The catalyst provides an alternative route of reaction by lowering the activation energy and better control of selectivity which makes a substantial impact on process viability. Thermolysis is a cost-effective process due to its low operating pressure and temperature [48].

1.2.2 Coagulation and flocculation

Coagulation is a very effective process for the reduction of organic matter, suspended and colloidal materials, which are mainly responsible for higher COD, biochemical oxygen demand (BOD), TDS, turbidity, color, and pH of the wastewater. The colloidal particles (0.01- 1μm size) present in wastewater are mostly negatively charged and the force of attraction among the particles is less than the electrical charge thus particles are repelled; Brownian motion holds the particles in a static suspension; so that the colloidal particles cannot be detached by simple sedimentation process in a shorter period. The chemical coagulants and flocculants are used in this process for the reduction of colloidal and suspended particles existing in wastewater by neutralizing the repelling forces to help in increasing the size of and density (to some extent) of particles to enable them to settle.

Coagulation in water treatment occurs predominantly by two mechanisms:

1. Adsorption of soluble hydrolysis species on colloid subsequent and destabilization; and
2. Sweep coagulation, where, the colloid is entrapped within the precipitation product.

The flocculation works after the coagulation, the destabilized particles collide successfully and are driven towards each other by the hydraulic shear force in rapid mixing and flocculation basin. Subsequently, the particles agglomerate and speedily bridge with each other, and adsorbed over the suspended particles to form micro-flocs that develop together to form big floc [48, 49]. The specific mechanism occurring depends on both the turbidity and alkalinity of the water being treated [50].

1.3 Treatment of oily petroleum sludge

The traditional methods used for solid waste disposal and treatment are not suitable for OPS. Since OPS cannot be incinerated because it comprises too much oil with water, makes it practically impossible to incinerate. It cannot be filtered because of the high solids content and clogging of the filtration systems. However, appropriate treatment and disposal of this kind of waste are compulsory to prevent surface and groundwater contamination and reduce the possibility of fires, explosions, and damage to the soil. Consequently, refineries are looking for the technology, which is intended to remove the hydrocarbons from the sludge to the maximum extent and therefore reduce the sludge quantity to be treated and disposed of in a cost-effective and environmentally friendly manner.

Various methods have been employed for the recycling, oil recovery, removal of toxic metals and for the remediation of OPS such as solvent extraction [51], sludge dewatering [52], thermo-chemical treatment [53], oxidation [54], stabilization/ solidification [55], and phytoremediation method [56], bioremediation [57], land treatment [58], bio-slurry treatment [59], and compositing/bio-piles [60]. Using an appropriate solvent to dissolve oily components of soluble in it and separate to get some value-added product for some gainful use offer a viable and practical solution to manage OPS.

A solvent extraction process is used to extract the oil present in OPS by using a solvent that will dissolve the required oily substance, leaving others. At the laboratory scale, a Soxhlet extraction apparatus can be used for the solvent extraction of OPS by transferring the partly solvable constituents of OPS into the liquid phase. The solvent extraction process provides the more segregated OPS after extraction of oil/water present in OPS. Among the various explored processes for the treatment of segregated OPS, thermochemical treatment of it has received significant attraction in recent years for efficient utilization. The thermochemical treatment processes can be characterized as combustion, gasification, pyrolysis, torrefaction, etc. [61, 62]. Moreover, the complex physicochemical characteristics of OPS have an impact on the selection of the thermochemical treatment process for appropriate use and discarding. The physicochemical characteristics of feedstock, such as moisture content, volatile matter, chemical composition, kinetic parameters, and surface characteristics, play a crucial role in the selection of appropriate thermochemical conversion techniques [63].

1.4 Broad objective of present work

From the above, it is clear that pre-treatment of PRE by catalytic thermolysis and coagulation and flocculation can modify the chemical nature of the constituents of PRE and reduce their amount to make it amenable to further treatment through biological and/or advanced oxidation processes. For OPS, through solvent extraction, some more volatile components can be removed to obtain more useful value-added products, and remaining OPS after solvent extraction may be used for the thermochemical techniques as a feedstock. In view of these following broad objectives were set for the present work:

1. Treatment of a typical petroleum refinery effluent (PRE) through catalytic thermolysis and coagulation and flocculation to evaluate the efficacy of this pre-treatment in reducing COD, turbidity, etc.
2. Evaluation of the possibility of recovery of value-added fractions from oily petroleum sludge (OPS) and evaluate the thermal degradation behavior of the residue thus obtained for possible use as feed-stock for pyrolysis and gasification.