PETROLEUM REFINING TECHNOLOGY

Removal of Inorganic and Organic Hydrocarbons from Petroleum Refinery Wastewater: A Mini Review

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ABSTRACT

Degradation of inorganic as well as organic compounds consisting of benzene, toluene, xylene, phenol, polyaromatic hydrocarbons (PAH), sulfide components and persistent organic pollutants from petroleum refinery wastewater is reviewed in the following paper. Multiple methods involving biological processes, UV process, chemical processes like electrocoagulation, adsorption are used to remove the pollutants, making the refinery wastewater from petroleum safe to dispose. These methods are first broadly classified into primary and secondary treatment. There are conventional and advanced methods under each category serving the requirement of removal of pollutants. Advanced methods are more particular towards particular component specifically. Out of all types of methods for each component the most apt method was found based on multiple parameters like operating conditions, efficiency, catalyst. All these components posed threat not only to environment but to human life as well. The toxicity is reduced before disposing to ensure the nature and aquatic life is not harmed.

CHAPTER 1. INTRODUCTION

The discharge effluents from petroleum refineries constitutes of multiple toxic compounds that has harsh negative impacts on the environment. The effluents consist of hydrocarbons like BTEX, polyaromatic hydrocarbons (PAHs) which are non-biodegradable in nature, hence resulting in increase of waste and environmental impact. These components are harmful for the human body as they accumulate in different body parts and tissues. The phenolic component of the discharged wastewater has high solubility in water, hence giving rise to concentrations upto 7000mg/l depending on the geographical and climatic surroundings of the place.

1.1 Environmental problems caused by the wastewater from petroleum refinery

The pollutants mentioned above may remain in water, and under certain conditions, they can go through various reactions, such as chlorination and methylation, to produce even more harmful or more toxic materials like chlorophenols and cresols. These organic compounds are among the most common forms of contaminants in petroleum wastewater, and many of them show carcinogenic, teratogenic or mutagenic properties and were considered by the US Environmental Protection Agency EPA (USA) as priority pollutants. Thus, a great concern is raised worldwide to remove these contaminants from industrial wastewater and its effluents before discharge into water bodies posing a serious threat to aquatic life as well, which makes it mandatory for industries to treat it before letting it out in the environment.

Crude oil is a major source of energy and it accounts for approximately 32% of the world's energy supply. The industrial process of making and refining crude requires a lot of water and this huge consumption leads to generation of huge wastewater as well, contributing to the presence of contaminants in the organic wastewater. It was estimated that approximately 0.4–1.6 times the volume of the crude oil processed is generated as refinery wastewater. With increase in demand for the same and growing needs due to growing population the crude industry will continue to discharge toxic waste into the water bodies.

Because of a rising social and political concern on the environment as well as stricter norms being developed for the industry to work smoothly, this water has to be treated in compliance with the disposal limits decided by regulatory institutions. [1] [2]

1.2 Point of origin of petroleum refinery wastewater

To develop the maximum profits, the crude oil has to be refined and broken down into various products. The multiple products that are obtained by refining crude oil are kerosene, LPG, bitumen, diesel, petrol, lubricants etc, that are of vital importance for energy and world survival. These are for the petroleum industry, on looking at petrochemical industries the products are refined into platics or synthetic materials. To convert crude into the above mentioned products multiple processes are deployed which includes large consumption of water like cooling, deslating, hydrotreating and refining. For obtaining the final blending stock, multiple treatments are applied including cracking- thermal and catalytic, reformation of steam, alkylation, desulfurization, stripping columns. These processes generate a lot of wastewater,which needs to be disposed off by the refineries. The constituents of the same is dependent on the final product made and the procedures involved. Refineries are classified broadly into two types- 1. Simple hydro skimming, 2. Complex refineries. A hydro skimming refinery comprises three sub units-
1.2.1   Distillation unit that acts like a fractionation column
1.2.2   A reforming, preferably steam reforming unit
1.2.3   A desulfurization unit [3]

1.3   Propoerties of petroleum refinery wastewater

Refinery waste water (RWW) is characterized by a high chemical oxygen demand (COD) and

biological oxygen demand (BOD) which results from the overall contribution of several aliphatic and aromatic hydrocarbons, emulsified oil and grease and inorganic substances, including ammonia, sulphides and cyanides. Typical levels are 300–600 mg/l for COD, 20–200 mg/l for phenol, up to 3000 mg/l for oil and suspended solids of more than 100 mg/l. However, the quantity and characteristics of wastewater depend on the process configuration and complexity. [4]

Table 1 - Summarizes the main pollutants in different petroleum refining units. [5]

Refinery process unit	Type of waste component generated
Crude desalting	Ammonia, sulfides and solid waste
Crude oil distillation	Sulfides, ammonia, phenols, chloride, mercaptans
Thermal cracking	H2S, ammonia, phenols
Catalytic cracking	Oil, sulfides, phenol, cyanide, ammonia
Hydrocracking	sulfides
Polymerization	Mercaptan radicals
Alkylation	Spent caustic, oil, sulfides
Isomerization	Low molecular weight hydrocarbons
Reforming	Sulfide
Hydrotreating	Ammonia, sulfides, phenol

Table 2 – Petroleum refinery wastewater constituent value ranges [5]

Properties (unit)	Range
pH	8.3–8.9
Conductivity (ms/cm)	5.2–6.8
Total suspended solid (mg/l)	30–40
Total dissolved solid (mg/l)	3800–6200
SO4 (mg/l)	14.5–16
COD (mg/l)	3600–5300
Total phenol (mg/l)	160–185
Phenol (mg/l)	11–14
o-cresol (mg/l)	14–16.5
m, *p*-cresol (mg/l)	72–75

CHAPTER 2. LITERATURE REVIEW AND RESEARCH METHODOLOGY

With the purpose to treat petroleum refinery wastewater with various methods and concentrating on removal techniques of specific compounds in wastewater due their toxicity along with their impact on environment was studied through various research papers and a few review papers as well. The same were obtained through google scholar platform, which connects all published articles and papers by searching through specific keywords, in this case few of them were petroleum wastewater treatment, BTEX(benzene, toluene, ethylene, xylene) removal, phenol removal, characterization of waste water, poly aromatic hydrocarbons (PAH) removal, primary treatment, secondary treatment, dissolved air flotation (DAF), Fenton process, etc. , in the internet. The results on the platform consisted of various sites link, official journals, like science direct, PubMed, Elsevier, few patents uacademia and many more, though not all of them were accessible for free, hence had to categorize even the ones which were available easily on internet. The quality of the papers found was categories by the content, writing, citations of the publications and to the point availability in accordance with the topic. As we know crude oil/petroleum refineries is one of the oldest industries and the demand for them keeps on increasing with increase in population and lifestyle, it also is an essential worldwide and not limited to any geographic area though the quality and constituents of it do depend on the surrounding geographical region, hence searched for the various different treatments adopted in various parts of the world depending on the product of the refinery as per the requirements of the specific country. As this industry is been running since ages the papers covered from 1990's to recent 2018 too to get an idea of how the methods evolved, the difference between the conventional and the newer developed and developing methods hence considering all aspects and help in analyzing the fact that how technology is upgrading. Few papers also focused on the same process but conducted by different researchers and their personal small modifications hence helping to give a clear idea of what modifications does the best for a process.

Crude oil is a mixture of hydrocarbons, nitrate compounds, sulphur compounds, oxygen and solid chemical and metallic constituents. Water pollution through the disposal of petroleum refinery waste water is now a global issue. It has proved to cause short as well as long term effects on human bodies and environment ecosystem. [42]

Sulphur presence bifurcates the crude into two types, namely a. Sour crude oil; containing excess of sulphur b. Sweet crude oil; containing less sulphur. Sour crude oil is not preferred as it causes unpleasant odour, corrosion, inactivates the catalyst. Sulphur content arises from catalytic hydrocracking unit and causes corrosion of the sewer pipes through which it is transmitted as well, the toxicity and the odour poses a threat to sewer workers as well. The most common methods to remove them include air stripping, oxidation, chemical precipitation. [43]

Persistent organic pollutants (POPs) are now wide spreading which makes it very critical to know about them in depth. These were researched upon in Stockholm Convention 21 where the high toxicity organic pollutants are reported and their removal treatment is studied and researched on. The fact that they accumulate on the surface of the water body as a micropollutant makes it difficult to identify as well as quantify them. On a global scale they are being monitored to reduce their effect on aquatic life and environment as well as human bodies as they are not degradable. They rather accumulate in the human tissue posing life taking threat. The conventional methods were not that effective due to the hydrophilic nature of the persistent organic pollutants. It causes kidney injury, insomnia, nervous disorders. They have different effect depending on the climate find, soil, population.[42]

Treatment processes include oil desulphurization, sour water strippers and catalyst regeneration units. It is characterized by a high COD and BOD which results from several aliphatic and aromatic hydrocarbons, emulsifications of oil , inorganic components which includes mercaptan radicals and ammonia, sulfides and cyanides components. The technologies available can generate high quality water from wastewater but

majority of these techniques are not concentrated on the removal of POPs. Most of them are more harmful than the regulated compounds due to the presence of acidic functional groups. Nano technologies are the most reliable for products like these which accumulate and do not degrade.

To come up with promising methods to remove organic and inorganic pollutants, I went through few research papers to understand what are the recent and conventional practices. It made me understand the gap between them and also the scope of improvement in the recent methods. After reading the papers, I could conclude the best possible method for their removal in my opinion.

CHAPTER 3. CONVENTIONAL & NON-CONVENTIONAL METHODS

For the treatment of waste water from petroleum refineries there are conventional and non-conventional methods. Conventional methods are the ones which are being used since the old times and is applicable to remove only few components that too until a particular concentration. These methods are not that effective and also not environment friendly hence non- conventional methods and its modifications were developed.

3.1 Conventional methods to treat petroleum refinery waste water

In petroleum refineries the wastewater generated is an oily sludge consisting of water, sediments, petroleum hydrocarbons, calcite, quartz etc. Which makes it toxic hence classified under class I of waste. It creates a very negative impact on the environment hence based on the composition of raw material, sludge and availability of equipment there are various methods to treat it. Few of them are- 1. landfilling, in which the cell is created by layering clay and then polyethene hence preventing percolation in the soil. 2. Incineration, in which thermal oxidation takes place, the new addition to make it effective is adding a steam generator before the combustion gases are released in the atmosphere but it turns out to be expensive along with the risk of formation of new toxic gases due to thermal cracking. 3. Clinkerization, in which co-processing takes place in a rotating furnace at high temperatures upto 1450'C. 4. Microwave liquefaction, in which the water is separated using an emulsifier. It has an advantage that the energy can be reused for other processes. The other conventional known processes are bioreactors, distillation, biopiles etc. The aim of the processes is - Reduction of the waste generated which can be done by improving the quality of raw material, type of process used, efficient energy utilization. Reusing, by extracting the still usable compounds from the waste before discarding, energy reuse by efficient modern techniques. Recycling, the compounds like emulsifier, coagulant and other agents aiding in the treatment process.[6]

3.2 Innovative methods by combining conventional methods together

With the increase in degrading environment the conventional methods of treating wastewater from petroleum refineries have several disadvantages such as in flocculation the device manufacturing and repairing is highly energy consuming, in coagulation the precipitate is tough to discard, in membrane separation the scaling up of the process is not efficient enough. Hence, the combination of these can lead to more effective and efficient way of treatment. Few of the combinations are

1) Pump floatation device---double filter line---electric field---water disinfection. This is innovative because the electric field generates flocculants and leads to the breaking of the molecules through the voltage generated.
2) Raw water---ultrasonic flocculation electro-cell---continuous backwash---sand filter--- ultrasonic ozone generator---water discarded. This method generates almost no waste.
3) Supercritical water oxidation, in this organic solutes are oxidized in an aqueous medium at a temperature and pressure above the critical point of water. It gives 99% clean water and is environment friendly as the only emissions from it is nitrogen, hydrogen and water droplets. [7] [8]

Many of the conventional methods have been recognized as efficient techniques for the treatment of RWW. Multiple conventional methods have proven to treat petroleum refinery waste water efficiently as they have certain advantages, few advantages include efficient energy usage and utilization, environmentally safe as well as safe to carry out the procedure by workers. However, most of these physio chemical methods have disadvantages as well, such as being costly because they require not only large amounts of capital to start off but also need a lot of money for its operation Depsite of being so costly, majority of them fail to actually destroy the component. All that is done is that the impurities and toxicity are transformed into another phase. This in turn leads to production of by products which can at times be turned into more toxic compounds hence nullifying the sole purpose of treatment. The processes which are electro chemical, tend to form chlorinated organic compounds. These were found to be removed by using activated carbon adsorption process. The processes that were involving ozonation of phenol and hydrocarbon compounds

produce by products and intermdiates like hydroquinone which increase the toxicity. Most of the above mentioned methods are not capable of treating dirty wastewater water with COD levels greater than 4000 mg/l. [9] [2]

3.3   Non-conventional methods

Non-conventional methods were developed to overcome the drawbacks of the conventional methods. They are more effective and efficient. These methods not only tend to be environment friendly but also cost effective.

3.3.1   Fenton process

The need of developing an effective treatment method other than the conventional ones for treating petroleum refinery generated wastewater few researchers tried developing a process known as the Fenton Process which uses a RSM with a cubic IV optimal design, in which ferrous ions and hydroxyl ions/radicals are used to break down the toxic compounds like benzene, ethylene, xylene etc.

The materials used to generate the ions are scrap iron from rust, an acidic medium like sulfuric acid, hydrogen peroxide and sodium hydroxide which is used for cleaning purposes. The experiment was conducted in a jar test apparatus with agitation of 200rpm for 90min.

The reaction is stopped by adjusting the pH to 8.5.
The optimum process conditions are 2-3 pH, room temperature (25'C). [10]

3.3.2   Electrocoagulation

Electrocoagulation was experimented to treat the waste water from the petroleum refineries considering it has various advantages like simple equipment, automation and does not require any additional coagulants which eases the process of flocculation. An electro coagulator reactor with a magnetic stirrer was used in which different electrodes like Aluminum, Iron and Stainless Steel were used in various combinations to understand which one would give the best results. The parameters under consideration were current density, pH, electrode type, distance between the electrodes and the electrolysis time. It was observed that Al electrode gave the best results with a pH of around 8, current density of 2-13A in 60 min with a 1-4cm distance between the electrodes. The metal hydroxide formation is the main reason that coagulation occur and hence removing the sulphate and the COD. The reaction taking place at cathode is helpful to remove COD whereas the anode reaction is useful for the sulphate removal. This method is quite effective and convenient even in large scale. [11]

3.3.3   UV-TiO2 treatment

The experiment suggests that if the untreated water to which an ultraviolet radiation generating lamp is attached is sparged with ozone in a specific range of pH and then sent to an oxidiser containing TiO2 removes the BOD and COD to a considerate level in just 10minutes. After that the three tests performed namely lumistox, poecilia vivipara and ecotoxicity it was seen that the sequence of ozone---UV---TiO2 is not sufficient to remove the metal compounds which is highly toxic, hence the semi treated water is sent to wastewater microalage depuration system where the process tends to remove the remaining toxic materials. This process is quite effective in terms of energy and cost both because the main energy required is just to sparge the ozone and provide UV and the cost of it is comparatively low than other modern methods, hence if this process is effectively and efficiently incorporated it will be a good measure to treat the waste water from petroleum refineries. [12]

CHAPTER 4. METHODS OF PRIMARY TREATMENT

Primary treatment is the basic treatment given to the waste water from petroleum refineries. It is the level one treatment used to mainly filter out the major and bigger size particles. It does not affect BOD and COD to a large extent. It helps to reduce the interference of it in further process.

4.1 Sour water stripping

Hydrogen sulphide and ammonia appear in the wastewater from petroleum Refineries due to the steps like nitrogen treatment, desulphurization and hydrotreating. This stream is referred to as the sour stream. The common practice is to treat them through steam stripping which is carried out in a reflux column. The parameters affecting it is temperature and pH. At low pH hydrogen sulphide removal is aided and the ammonia converts to its ionic form. As hydrogen sulphide can be removed at 40℃ but ammonia requires around 100° C, sometimes two stage reflux column is required. [13]

4.2 API Separator

In this separator, which is a liquid- liquid separator, the oil- water mixture is attempted to separate. In quiescent conditions the oil droplets are forced to coalesce, bubble upto the surface, form a layer, which is then skimmed through the residual water. This skimmed oil is recycled to the upstream phase of the refineries. The minor disadvantage of this is that the sludge formed underneath has to be removed and discarded in an apt manner. The formation of the floating oil layer is dependent on the size of the oil droplets, which is dependent on the three forces acting on it which are buoyant force, gravitational force, and drag force. The buoyant force takes care of the volume whereas the drag force considers the surface area. With increase in the ratio of volume to surface area of the droplets, the larger droplets rise to surface, smaller ones remain in suspension. API Separator is meant for droplets more than 150 microns in diameter. [13]

4.3   Dissolved Air Floatation

Dissolved air Flotation is a gravity-based process in which the oil droplets forms an agglomerate with the air which is lighter than air, hence due to the density difference, this rises up forming a layer of oil which is continuously scraped and resent to the refinery. The air bubbles are introduced by injecting a liquid stream under pressure in the flotation system and releasing it via a pressure reducing valve. This process of DAF is similar to API separator, but the only difference is that the air bubbles surround the oil droplets which enhances the buoyant force hence making this process more efficient. This can be further improved by adding coagulant such as alum and ferric salts, which increase the droplet size, adhesion of oil air molecule due to their physiochemical effect. It is used to treat droplets above 40 microns. [13]

4.4   Desalination

For pre-treatment of wastewater discharged from petroleum refinery various treatment procedures were available. To understand the impact and result, both were deployed for comparison. The first step for these was similar involving chemical coagulation. The further procedure differentiated the both, in the sense the first process consisted of precipitation and the second process consisted of dissolved air floatation. For chemical coagulation, the coagulant used was either of ferric chloride (FeCl3·6H2O), alum (Al2(SO4)3·18H2O) or ferrous sulphate (FeSO4·6H2O) individually or in combination. For the adjustment of pH due to introduction of other chemical component, another coagulant - lime (CaO) was used. To derive a result as to which coagulant proved to the most effective it was observed on following paramters – 1. COD removal which was found to be 75.8, 77.5 and 76.7% by ferric chloride, ferrous sulphate and alum respectively, 2. BOD removal was found to be 78, 78.7 and 74.1%, for ferric chloride, ferrous sulphate and alum respectively, It was observed that alum was producing a sludge with less solid content, more of thick liquid, ferric chloride had produced a sludge which was more compact hence had good settling properties. In the second method where coagulation was followed by dissolved air flotation, alum proved to have higher COD removal as compared to other coagulants (ferric chloride and ferrous sulphate). The first process where

chemical coagulation was followed by precipitation he COD removal was in the range of 75.8, 77.5 and 76.7%, using ferric chloride, ferrous sulphate and alum respectively. The BOD removal values were found to be 78, 78.7 and 74.1 by using ferric chloride, ferrous sulphate and alum respectively Therefore, the process consisting of chemical coagulation followed by dissolved air flotation takes up 30% less space than the other process hence it is more economical for the treatment of the wastewater. [14]

CHAPTER 5. SECONDARY TREATMENT

Secondary treatment are the processes followed after primary where the major pollutants of high concentration are removed. It affects the BOD and COD a lot. It is the core treatment stage. It has various processes depending on the quality of wastewater.

5.1 Biological treatment (Activated Sludge Process)

It is done via heterotrophic bacteria. They work in two processes namely catabolism and anabolism. The combined process is known as metabolism. In this method the molecule is split into hydrogen ion, co2 ion and electrons. Under aerobic conditions the electron acceptor is oxygen. The activated sludge process involves the addition of oxygen through injection of air in the mixed reactor, the oxygen transfer takes place at the gas- liquid interface. The microbial culture called as flocks, reduce the organic waste into solid phase. This solid phase due to gravity settles down in the system which is returned back to the bio reactor via reversed activated sludge method. This is sent through a process of decay and death but it is made sure that the solid is purged from time to time to avoid accumulation and hence eventual failure of the system. The major parameter in this is the sludge age. Nitrification occurs in activated sludge process.

This process involves two steps. First is to convert ammonia into nitrite and the second one is to nitrite and nitrate, both are oxidation processes. The end product which is nitrate is less toxic as compared to the starting product, hence not causing major harm to the aquatic life.

Stripping of volatile materials, in the water there are quite a few volatile organic materials known as VOC for example benzene toluene xylene etc. Which have to be stripped out. The stripping is done via the usage of their volatility ratios.

Few of the toxic compounds can be removed by adsorbing them on the microorganisms via physical adsorption, chemisorption and ion exchange. The most effective microculture for this is the combination of 5 compounds Lindane, diazinon, malathion, pentachlorophenol, 2chlorobiphenyl. [13]

5.2 UV H2O2 photoreactor

The treatment of a petroleum refinery wastewater using UV/H2O2 photoreactor in batch mode is also an effective method. In the experiment of using this process it was noted that the initial total organic carbon present in the sample was 42mg/l .The process when ran for 45 minutes under an operating condition of pH of 5.0, and then performing statistical tests considering various parameters like carbon and hydrogen peroxide ratio, reaction time, pH, UV light concentration , it was found that if the pH is lowered to around 4.0, on acidic side, and reaction time was also reduced there was an increase in the value of TOC removal.

The UV/H2O2 process was not taken as an efficient method to consider as a secondary treatment method if the incoming wastewater is consisting of microorganisms or is based off biologically activated sludge. The reason was that the water was biodegradable which was not compatible with the involved chemicals.[15]

CHAPTER 6. PHENOL REMOVAL

Phenol found in the waste water from petroleum refineries affect its toxicity and is a pollutant which needs to be treated before discarding the waste water. Phenol exposure is one of the hazards in the industrial wastewater treatment basin of any refinery. It additively interacts with hydrogen sulphide emitted from the waste water. Hence to remove it there are a few processes.

6.1 Peroxidase-catalyzed removal of phenols

The phenol content in the wastewater from petroleum refinery is one of the major reasons to the toxicity. Hence to remove that the water is treated with horseradish peroxidase and H2O2. The treatment with this leads to the conversion of phenol-based compounds into a less biodegradable compound which can then be removed by coagulation and precipitation using alum. Batch experiments were carried out of 15ml each for 6mins and then by various measuring techniques the requirements of materials and the result of removal of toxic compounds were measured. The batch experiments aided in the minimization of amount of HRP and peroxide used. The ratio of HRP:peroxide was found to be optimum at 1:1. Efficiency of 58%.

6.2 Date pit activated removal of phenol

The batch adsorption of phenol from petroleum refinery wastewater was carried out on a locally prepared date-pit activated carbon (DP-AC). Any process involving adsorbing on activated carbon, should have great regeneration capacities, hence to understand which process, either thermal or chemical, would suit for this process, multiple tests were done. As a result it was found that ethanol is the most suitable and effective way. It regenerates 86% of the saturated activated carbon.

During the process the initial condition was set at 10grams/litre of adsorbent for 100milligram/litre of phenolic compounds. It was observed that the adsorption rate and hence the removal of toxic phenol compounds increased with the increase in concentration of adsorbent. The reason for this increase was that the phenolic component concentration was fixed as compared to the incoming adsorbent concentration, which provided more sites for adsorbing the impurities.

We know that hydrocarbon, especially phenolic compounds, adsorption onto activated carbon can occur via electrostatic and dispersion interactions in addition, electrostatic interaction only if the phenol constituents are in their ionic state (phenolate ion). This is necessary as it aids in interaction with the activated carbon charged surfaces.

At the operating condition of 25°C and pH range of 8-11, basic side, it was seen that there is effective removal of phenol compounds. On changing the pH to 3 from 8, on the acidic side, it was observed that there was a negative impact on the adsorption of phenol. The acidic environment increases the H+ adsorption on the carbonyl sites. The phenol adsorption on activated carbon turned out to be a pseudo second order reaction.

The process was repeated multiple times, and in the fourth cycle it was observed that a combination of the adsorbent for adsorption and ethanol for regeneration accompanied with alkalis to provide a basic environment gave an efficiency of 66%.

This process was found to be a cost effective method. It was cheaper than the traditional activated carbon. It also aids the palm industry, because the date pit needed here is form of a waste for the date palm industry, hence even environment friendly. [17]

6.3   Electrocoagulation specifically for phenol removal

Electrocoagulation method was experimented to observe its effect on the phenol removal from the oily wastewater generated by the petroleum refineries. The experiment was conducted in batch mode in plexiglass container with horizontal aluminum rod as cathode and horizontal aluminum screen as anode in a solution of sodium chloride. The parameters found to affect the phenol removal were pH, current density, operating time, concentration of NaCl and initial concentration of phenol.

It was observed that the optimum pH was 7. At a low pH the aluminum hydroxide ion is formed which start to form a precipitate and hence not participating in the electrocoagulation process and at a high pH there was formation of (AlOH4-) which was soluble in the solution leaving no Al ions for the process to be carried on.

With increasing current density, it was found that the phenol removal was increased, this was due to the fact that this process was in accordance with the Faraday's law. At a range of 20- 23mA there was optimum removal of phenol. The experiment had 97% removal of phenol by the end of 2hrs. As the initial concentration of phenol increases, the removal efficiency decreases, this could be due the fact that the Al ions available are constant from the sacrificial anode. The increase in concentration of NaCl is beneficial because the chloride ions remove the passive layer formed during the process, hence aiding in a more efficient process. It was observed that by using array of small screens of Al as anode provided more efficient results than using a single screen and the more the number of screens in one array, better the phenol removal. Hence, electrocoagulation is found to be a promising method for phenol removal. [18]

6.4   Conventional treatments

There are certain traditional methods used by petroleum industries for ages like distillation, extraction and chemical processes, they are are efficient in terms of removal of phenol with less energy consumption but high usage of chemicals and mot achieving optimum level of removal, while advanced treatments such as Fenton processes, ozonation, wet air oxidation, and photochemical treatment use less chemicals but have high energy costs. biological treatment is environment friendly and energy saving, but it is not efficient for removal of phenol from wastewater having high concentrations of phenol. Out of the available physical, chemical, biological process the enzymatic treatment under biological processes has been able to stand out as it can effectively remove phenol and phenol compounds by using multiple enzymes like peroxidases, laccases and tyrosinases. [19] [20]

A)   Fractionation

Fractionation is traditionally used for the removal of phenols as it requires low energy for the process to take place. The process involves using the relative volatility as a parameter for phenol compounds. The steam jet plasma treatment setup is introduced with the phenolic wastewater, this disintegrates the phenol due to the presence of thermal heat which produces hydroxyl radicals. This setup generates high enthalpy which initiates the activation of decomposition of phenol compounds. They are eco-friendly, which makes them as a method to approach for removal of phenol. The parameters taken into consideration while testing the solar distillation were operating conditions like temperature, sludge composition, antioxidants used, vapor pressure and the intensity of solar rays. These helped to test the drying rate of the feeded refinery wastewater, from where the decomposed phenol sludge could be discarded. It proved to be economical as well as eco – friendly. [19]

B)   Adsorbent

Activated carbon is the most used and an efficient but an expensive adsorption method.The most common adsorbent is activated carbon, although it proves to be expensive. Adsorption followed by extraction is quite effective because of the energy consumption, it also makes use of the secondary materials hence recycling them. This makes them more adaptive and approachable process. Modifications are being introduced such as chemical modification of the activated carbon, impregnation with nanoparticles, different

sources of carbon, different activation methods, as well as substitution with low cost biosorbents such as lignocellulose and chitosan. A study tested the adsorption of phenol hydrocarbons wherein the adsorbent used was pine bark. The optimal pH was 6, operating time was 2hrs with phenol removal of 143 mg/g. The other adsorbents used along with activated carbon were biosorbents, usually chitosan. The ratio in combination used was 1:1. This pair helped to achieve 95% efficiency. The carbon used was in two forms – Granular and Pelletized. Phosphoric acid was injected into these to increase the surface area, and volume of pores. Even potassium hydroxide could be used for the same.

C)   Extraction (liquid- liquid process)
Liquid – liquid extraction is also traditionally known as solvent extraction. This process is used widely for phenol removal due to the fact that it is cost effective and simple standard procedure. It has proven to work over a varied range of phenol and its compound concentrations.

Cumene is used as an extracting agent which acts as a solvent, making it liquid (refinery wastewater) – liquid (fluid cumene) extraction process.

It was observed that the reaction time did not impact the extraction whereas the temperature range played a vital role. With every 30°C rise in temperature, there was 5% increase in extraction of phenolic compounds, but at 67 °C, the cloud point of phenol, it was seen that the surfactant did not impact the efficiency.

6.5   Membrane Technologies
Membrane technologies can also be used for phenol removal. This method has been proven to be economical and a reliable process in terms of feasibility. Memberane technology consumes very less power and still gives a very clean quality of effluent. It is also easily scalable but during the process fouling due to colloid formation of memberane particles remain an issue here. Memberane technologies are of multiple types such as fibre, high pressure, photocatalytic, extractive, nano pore, reverse osmosis type etc. Pervaporation is done in extractive bio reactor and hollow memberane.

A)   Extractive and hollow fibre membrane bioreactor
Bioreactor having extractive and hollow memberane is a combination of liquid-liquid extraction with biodegradation which is highy effective in removing phenol compounds because its design is very compact taking up less space and it also provides flexibility during equipment changes or installation.. The hollow memberane consists of layers of polydimethylsiloxane and polyetherimide, subtrates of these aid in phenol removal. The process involves inducing trioctylphosphine oxide in the composite memberane which makes it immobile, hence the phenol particles collect in the layer of memberane which is extracted later.

B)   Reactor with a photocatalytic memberane
The memberane reactor consisting of photocatalytic memberane is a hybrid reactor where in photocatalysis takes place with a barrier in between. The barrier serves as a selective path for only the molecules of phenol that are to be removed can be passed.

Reverse Osmosis (RO) and Nanofiltration (NF) - RO is a membrane-based demineralization technique that is used to separate dissolved solids, ions. NF is widely used for removing organic pollutants, inorganic salts, colour, and hardness. NF is suitable to use in front of a RO unit in order to decrease the load on RO process. microfiltration/ultrafiltration membranes prior to NF or RO systems avoids the fouling of membranes. removal of phenol from wastewater can be done by using a polyamide thin film composite RO membrane. The parameters considered were feed concentration, ionic strength, transmembrane pressure, and the elimination Bisphenol A (BPA) removal from wastewater using a low-pressure RO system which consumed less energy, had a lower pressure requirement.

C) Pervaporation (PV)

Pervaporation is another method that can be deployed to treat phenol constituent wastewater. It serves as an alternate method for processes that consume very high amounts of energy. It has several advantages like it is easy to operate and it does not result in contamination after the process is over, hence avoiding secondary contamination. The process involves feeding the wastewater on the side of permeate memberane. The memberanes are made up of polymers, urethane, amide polyether. It is more efficient than zeolite removal.

D) Fractionation using memberanes

In this process via the Taguchi optimization process, in the presence of a vacuum operating condition, a polytetrafluroethylene memberane was deployed which had a pore size of 0.22micro meter. This process is non-isothermal in nature and results in fouling as well as wetting of pores, making it difficult to apply.

6.6 Oxidation by chemicals

Certain chemicals like oxidants of ozone, chlorine, mines, iron prove to be very strong agents for removal of phenols, but in the liquid or aqueous phase. The process involves converting phenols into flocs by the reduction of ferrate materials to ferric. This is done with the help of permanganate. This process is very cost effective, requires very less amount of chemical oxidants to remove a high quantity of phenol under moderately convenient operating conditions. It does not even result in formation of by products.

6.7 Chemical oxidation via electrons

Oxidation via electrochemical treatment involves an anodic direct treatment where the anode is either Platinum or oxides of lead and Tin. in this process there is adsorption of phenol constituent pollutants on the surface of anode. The observed parameters which were controlled under the operating conditions were current density, type of anode and PH. although it has no cost of the reagent but has high cost for equipment installation.

When indirect oxidation takes place it is advantages because it does not fall the electrode. this happens because there is Redox reaction between the pollutant which is phenol and the electrode which is usually Platinum. to enhance the removal of phenol pollutant chloride ions in the form of CA can be added as it forms an active chlorine component. hybrid technique of Advanced oxidation process and electrochemical oxidation with ruthenium oxide as anode was tested in the absence of chlorine for 6 hours and a current density of 20 milliamperes. when active chlorine was introduced in the above process the removal efficiency turned out to be 96% as compared to the efficiency of 71 % in the previous process. although there is no effect of active chlorine if the anode is boron-doped diamond.

6.8 Hydrogen Peroxide and UV radiation process

For the phenol removal there has been processes developed which use UV light as a photo source to degrade the phenyl constituents. Hydrogen peroxide has also been seen as a useful process to remove phenol constituents from petroleum refinery wastewater. it was observed that if both these processes are used together as in use of UV light with the presence of hydrogen peroxide it gives amazing results in the removal phenol pollutants. this is so because integrates the organic micropollutants because of the photo lenses taking place which generates hydrogen peroxide and hydroxyl radical. this hydroxyl radical is a free radical which is highly capable of mineralizing phenolic compounds. it gives an efficiency of 95% and remove 78% of total carbon content.

6.9 Advance methods

Conventional methods do not provide with the required efficiency as well as the process is cumbersome hence advanced methods were identified. Advanced methods take the above conventional methods as base and then transform it by improving catalyst or environmental conditions by altering the process.

A) Fenton and Fenton-Like Treatment

In an advanced oxidation process compare oxide iron compounds and favourite agents in an Operating condition of acidic pH is highly used to remove the phenol components from petroleum refinery wastewater. in this process the hydrogen peroxide is supposed to react with ferrous ions to form free hydroxyl radicals. these radicals intern help in the removal of phenol treatment. To regenerate free radicals, hello pH is maintained. This fenton process can take place in many variations such as photo-fenton or a fenton process involving electrons or a simple fenton process. When advanced oxidation process is combined with fenton process and efficiency of 82.5% is achieved. higher pH is not recommended as the formation of hydroxyl radicals slows down this is so because there is precipitation of ferric oxy hydroxide.

Temperature has no major impact on this process and this reaction has to be turned into a heterogeneous process. if the process is photo-fenton then the wavelength of the ultraviolet rays used plays an important role. It gives an efficiency of 82.5%.The photo- fenton reaction is less pH- dependent than the fenton process and the phenol removal rate was 60% at pH 2 and 70% at pH 5. UV wavelength plays an important role in photo fenton process. [19]

B) Wet Air Oxidation (WAO) and Catalytic Wet Air Oxidation (CWAO)

In the process of oxidation in the presence of air it can be either wet air oxidation or catalytic wet air oxidation. the high pressure and temperature process with a temperature range of 150 to 400 degrees celsius and a pressure from 2 to 40 MPA.

Normal wet oxidation process could convert only maximum 40% of the phenolic pollutants into disposable grade. to improve its efficiency a catalyst of a man MnO- Ceo- Al2O3 was used which gave an efficiency of around 74%. [19]

C) Ozone

The ozonation process can be of two types of the direct or with the help of transformation of ozone in to free radicals such as PH or hydroperoxyl radicals. this process uses the intermediate switch are formed like or gallic acid malic acid hydroquinone to remove the phenol components.

At a pH of 2 in an acidic environment the process is faster as compared to an environment with PH 7 there was decomposition of p nitrophenol. ozonation can also be accompanied with photo process in the presence of UV rays and in this process the phenol components are decomposed by the radiation of UV light as well as irradiating of the ozone.

Most efficient combination is ozone with UV light with titanium oxide. to achieve this combination of quads class outer surface is coated with titanium oxide and Ozone is fed into it with the presence of UV rays. [19]

6.10 Biological Treatment

The most abundantly used treatment method to remove phenol components from petroleum refinery wastewater is by the use of biological treatment.

This process is very cheap and it does not require complicated designs. the optimum operating conditions are found to be a pH of 7 at 30 degrees celsius.

If the waste water contains synthetic phenol components than a hybrid membrane reactor is used. the hybrid membrane reactors are then combined with carriers involve fouling of the membrane which reduces the span life and the efficiency of membrane which is a major disadvantage of the process.

6.11   Photodegradation using nanoparticles of TiO2

This process involves the setup gas chromatography and a flame ionization detector. it is mostly used for preliminary removal because it avoids the formation of colloids and flocs. multiple parameters like pH temperature type and quantity of catalyst were measured and observed during the experiment. it is favourable to use this process because it is both in expensive and gives a removal efficiency of 90%.

The process first involves circulating the petroleum refinery wastewater consisting of phenol pollutants into a circulating reactor which is continuously aerated the catalyst is added to the reactor. to start the process the UV light is showered with a protective aluminium Shield deployed inside the surface of the reactor. was found that at a pH of 3 and a temperature of 318 Kelvin with hundred gram per litre of catalyst proved to give a very high efficiency by degrading the phenol constituents. [21]

6.12   Anaerobic Stabilization

In the anaerobic stabilization process the reactor is of rectangle shape which is called the anaerobic stabilization pond. consists of a tank in which the petroleum refinery wastewater is fed. with the help of response surface methodology it was seen that the optimum temperature was 24 degrees celsius and with increase in temperature there was decrease in the phenol constituent amounts. This process gave an efficiency of 82%. The advantage of this process is that the anaerobic digestion of organic compounds such as phenol, produced the rich in nutrient sludge which can be used as a fertilizer in agricultural soils. The first step involves carboxylation of phenol in para position to 4-hydroxybenzonate. The enzyme used for the same is 4-hydrobenzonate carboxylase. The pond is very flexible, simple and inexpensive as compared to activated sludge process [22].

Table 3 – Phenol removal techniques

Phenol Removal Technique	Catalyst / electrolyte (if) required	Catalyst Ratio	Removal Result	Reference
Peroxidase Catalysed Removal Of Phenols	Chitosan, HRP	1:1	58%COD 78%BOD	16
Date Pit Activated Removal Of phenol	Activated Carbon	1:4	66% efficiency	17
Electrocoagulation	NaCl	1:2	97% efficiency	18
Distillation	Steam	-	56% efficient	19
Adsorption	Activated Carbon	1:1	95%efficient	19
Liquid-Liquid Extraction	Cumene	1:1	87% efficient	19
Extractive Membrane Bio Reactors (EMBR)	Trioctylphosphine oxide (TOPO)	-	56% efficient	20
Photo chemical membrane reactors	Polyamide Thin Film	-	62% efficient	20
Pervaporation	Urethane	-	57% efficient	20
Membrane Distillation	polytetrafluroethylene	-	67% efficient	20
Oxidation by chemicals	Permanganate	1:2	87%efficient	19
Chemical oxidation via electrons	PbO_2	1:1	96% efficient	19
UV Treatment	H_2O_2	1:1	95% efficient	19
Fenton Treatment	Ferrous ion	1:1	82.5% efficient	19
Wet Air Oxidation	MnO-CeO-Al2O3	1:1	74% efficient	19

	catalyst			
Ozone Treatment	O3–UV–TiO2	1:1	95% efficient	19
Biological Treatment	Hybrid Memberanes	-	86% Efficient	19
Enzymatic Treatment	Oxidoreductases like laccases, tyrosinases, and peroxidases	1:2	74% efficient	19
TiO$_2$ Treatment	UV	1:1	90% efficient	21
Anaerobic Stabilization	Organic Matter	1:1	82%	22

CHAPTER 7. BENZENE (BTEX) REMOVAL

Benzene is a carcinogen. Long-term exposure to this compound may provoke leukemia . Due to the toxic behaviour of these compounds, it is essential to minimize their release into the environment and, particularly, into the atmosphere and water bodies, hence to remove it there are a few processes developed

7.1 Solvent Extraction

To improve the efficiency of benzene removal from petroleum refinery wastewater the brine solution was treated by a combination of the aluminium chlorohydrate and a polymer which was water soluble followed by solvent extraction. the polymer was cationic in nature. the optimum temperature was found to be 250 degree fahrenheit. The preffered ppolymer was polydiallydimethyl ammonium chloride in the ratio of 6:1 of salt to polymer. [23]

7.2 Multi-stage Biological System

To overcome the drawbacks like rate of energy and expensive conventional process a biological process was devised.

The filter used was packed with the Peeth packing material that was used in the bio filter. this process was seen to be very helpful because a to remove the benzene components way beyond the required limit without additional nutrients for catalyst added. the optimum combination was single stage biotrickling filter edulyse mitulis shells. The system consisted of bio scrubber, tow bio- trickling filters and one biofilter, which obtained removal efficiency of around 70% giving good results with fluctuating concentrations. [24]

7.3 2-Stage Desalter System

It was found that crude oil desalting (removal of impurities) can be done in a two-stage desalter system with reduced benzene levels in the effluent wash water. The method involves- the first stage of a desalter system at low or ambient temperatures which reduces mixing of the wash water and raw crude which will be fed to the first stage desalter unit. Huge amounts of demulsifier are added in order to compensate for the lower temperature. The crude oil drawn off from the top of the first stage desalter is mixed with fresh water and heated before feeding to the second stage desalter unit. Mixing prior to the second stage is vigorous in order to compensate for the light mixing in the first stage and it also ensures that adequate salt removal is achieved. The second stage de salter unit is operated at high temperatures in the range of 90 to 150° C. The results was an effluent brine which has a significantly lower benzene concentration. [25]

Figure 1. A schematic showing a two-stage desalter system in accordance with the present invention [25]
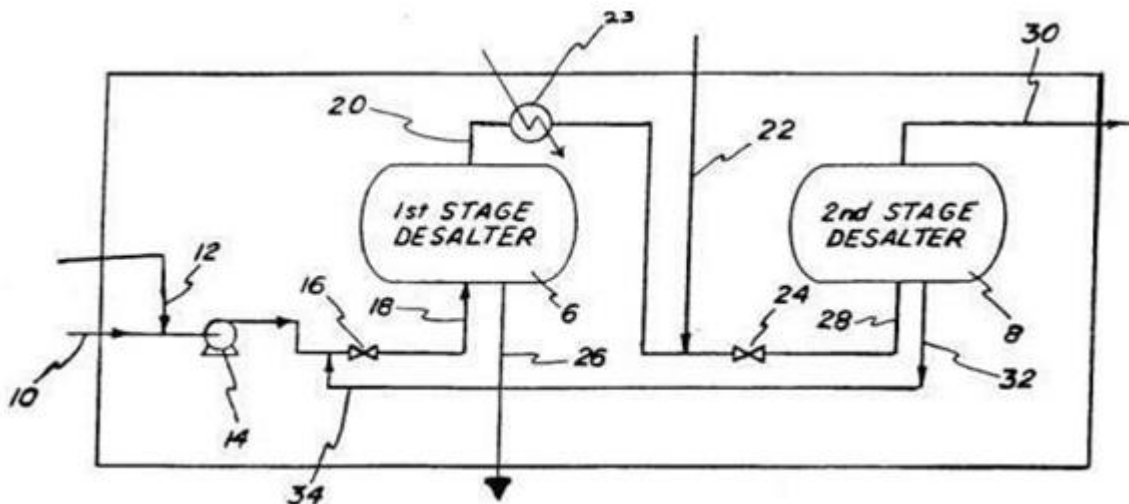
7.4 Removal of hydrocarbons by UV/TiO2

For this process a reactor was used for simple in construction and it used the UV light as in radiation in the presence of titanium oxide nanoparticles. It proved in a very efficient manner in a very short span of time because the degradation system was very Apt for aromatic compounds.

The reactor was conical shaped , circulating, upward mixing reactor without deadzone. The paramters considered were suspended catalyst concentration, fluid pH and temperature. [26]

7.5 Removal of hydrocarbon from desalting

In the desalting process the toxicity is reduced into stages stage the toxicity is removed in the terms of bod and COD. second stage the toxicity removal is with respect to microtox society which occurs during biological treatments. this toxicity is removed by using the biodegradability properties of benzene pollutants.

This gave an efficiency of 93% in terms of b o d and 77 in terms of COD as well as the output stream consisted of only 25% of the benzene pollutants. [27]

7.6 DAF used for removal of hydrocarbons

The dissolved air flotation method was used along with the chemical flocculation process. the output was measured in terms of odor removal COD removal and hydrocarbons and btx removal. deficiency values different types off flocculant agent used. be either alum or cat ionic polymer.

The output stream emulsified the incoming petroleum refinery wastewater and 70 to 80% of the benzene components were stable be removed in the form of suspended solid.

The flow of the process basically involves the pollutants aggregating and binding into flocks because of the fact that they are hydrophobic in nature. the pollutants of first chemically flocculated and then those dogs are removed with the help of dissolved air flotation. The results indicated that the chemical flocculation followed by DAF efficienty removed the emulsified phase, which could then be aggregated and separated to the surface. It was found that the process could also remove substantial amounts of dissolved organic matter, which was the only slight disadvantage of the process. Soluble organic matter which contained compounds of low solubility achieved better removal when flocculation was performed by cationic polyelectrolyte.[28]

7.7 Chemical Coagulation

Chemical coagulation basically involves chromatography using gas liquid chromatography and this process turns out to be a very efficient process as it removed not only benzene but other hydrocarbons as well and converted the output stream to a very low concentrated pollutant stream. [29]

7.8 Vertical Flow Wetlands

It was observed that wetlands remove benzene very efficiently. to employ this method thereof or 12:00 vertical flow wetlands which were used among which six were placed inside and 6 were placed outside.

The rig that were placed outside were not that efficient as they were able to remove only 58 % of the total benzene components whereas the Rig that were placed inside showed efficiency as high as 92- 95%.

The flow lands work basically on the concept of volatilization.

This process can be enhanced if used at 20 degree celsius in the presence of oxygen which act as a fertilizer by providing a nitrate Ion as an electron acceptor if there is absence of air.

If the wetlands are surrounded by biodegradable mass it showed higher benzene removal efficiency. time the benzene was accumulated in the flow lands which in turn reduced the efficiency of the vertical flow

lands. [30]

7.9   Surfactants
As we know that benzene and other hydrocarbon are very volatile in nature and aromatic which cause a lot of harmful effect on human body. hence to avoid this a process was employed where in zeolite was used but in its modified forms. it was modified by using hexa decyl tri methyl ammonium chloride and N cetyl pyridinium Bromide.

Because of the structural form of these two above-mentioned surfactants it was seen that they are selective towards the hydrocarbons which are aromatic. even activated carbon can serve the purpose although it offers an efficiency less than the above mentioned surfactants.

The surfactants have a benzene efficiency removal of 97% toluene efficiency removal of 94% and xylene efficiency removal of 92% along with ethylene benzene efficiency removal of 91%. [31]

7.10   Ionizing Radiation Method
The removal of benzene can be done if it is exposed to a radiation by merging and trapping the ionized radiation into sea water. It has proven to be efficient because this process generate no solvent wastage because the sea water having Gamma radiation in it also helps although it is very complex to yield purified water. [32]

7.11   Anaerobic sequencing group biofilm reactor (ASBBR)
In an anaerobic biofilm reactor a gas chromatography along with fire ionization with sufficient head is installed. It is highly adaptable in terms of operational activities and it is very practical cost-effective and very innovative method for benzene removal under the optimum conditions of 20 litre or its service and efficiency of around 80%. [33]

CHAPTER 8. POLY AROMATIC HYDROCARBON (PAH) REMOVAL

The structure of polycyclic aromatic Hydrocarbons consists of more than two aromatic ring which are formed because of the incomplete combustion of organic components. because of its semi volatile nature it is proven to be a very dangerous hydrocarbon which causes carcinogenic effects on human being and poses a threat to environment as well in the form of air pollutant. [34]

8.1 Adsorption

Removal of polycyclic aromatic hydrocarbons (PAHs) for e.g. pyrene, anthracene, acenaphthene, naphthalene from petrochemical wastewater can be done using various low-cost natural adsorbents such as sugar cane bagasse, green coconut shells, chitin, and chitosan. Adsorption of mixtures of PAHs are carried out at ambient temperature of 27°C and a pH of 7.5. The adsorption isotherms of PAHs were in agreement with a Freundlich model. The capacity of adsorbents in terms of PAH removal followed the order- green coconut shells > sugar cane bagasse > chitin > chitosan. [35]

8.2 Pre-filtration & Ultra-filtration

During ultrafiltration processes the quantity of PAH has to be determined, which is done by using gas chromatography and mass spectrometry. The filtration process is done under various the first one being using a sand bed to filter very large particles. After the sand bed filtration the resultant wastewater is sent for ultrafiltration. When ultrafiltration takes place the concentration of PH reduces considerably. the output stream from ultrafiltration is then sent to a membrane for separation processes. The sand bed used earlier does not let the membrane be polluted. [36]

8.3 Nano-hybrid Adsorption

It was found that NAP had the maximum capacity to dissolve being 1.92 milligram per gram and phn had the least capacity to absorb beings 0.76 milligram per gram. The experiment had followed a pseudo second order reaction world mass transfer via pores. this process is highly temperature sensitive as well as endothermic. [37]

8.4 Biologically active process

For treating wastewater polluted with petroleum products a biologically active process was conducted. In each experiment 17 alkylated and 19 non-alkylated polycyclic aromatic hydrocarbons (PAHs) were removed using semipermeable membrane devices from wastewater before and after treatment. The treatment system removed dissolved PAHs with a removal efficiency of 96.9-99.7%. The major contributor to their removal was sorption rather than biodegradation. Combinations of long process contact time of 24 hours with temperature of 24°C and moderate oxygen concentration of around 6-7mg O2 L-1 resulted in good removal of PAHs. In addition small amount of PAHs were volatilized and released during the wastewater treatment. [38]

8.5 Chromatography

There are multiple PAHs of them being fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene. These can be removed by using chromatography involved is an ultra performance liquid along with spectrometry.

The column used for chromatography had dimensions of micrometre bi 2.1 millimetre and the height of 50 milli metres. was also lined with a pre column filter which helped the column to sustain the process.

It also required a grit chamber which was very aerated as well as biologically treated in nature.

It also required a grit chamber which was very aerated as well as biologically treated in nature. It proved to be almost 100% efficient wherein in the first stage around 75% of the PAH was removed, and

25% of the hydrocarbon was removed in the grit stage it was the second stage. The last step involved station which help to get rid of the hydrocarbons and then later disinfecting the columns for the next batch. [39]

8.6   Hydrophobic Adsorption

By making use of the hydrophobic nature of these hydrocarbons adsorption is majorly used. By using a disorder band like activated carbon or modified clay and Minerals or bio ka it was seen that due to the sorptive ability the hydrocarbons were slowly immobilized.

The efficiency was a factor of multiple parameters like type and size of the adsorbent the pH and operating conditions. [40]

8.7   Microbial Transformation

To remove PAH from waste water, the analysis of microbial transformation of polycyclic aromatic hydrocarbons is observed. For this the sample is incubated. Evolved CO_2 is trapped in KOH, unaltered PAH and polar metabolic intermediate fractions are quantitated after extraction and column chromatography. PAH compound in petroleum contaminated sediment increased from 7.1 h for naphthalene to 400 h for anthracene, 10,000 h for benz(a)anthracene, and more than 30,000 h for benz(a) (micrograms of PAH per gram of sediment per hour).The result showed that four- and five-ring PAH compounds, several of which were carcinogenic, may persist and support microbial populations capable of transforming two- and three-ring PAH compounds.[41]

8.8   Activated Carbon

Activated carbon is the most abundantly found and most easily operated method for what is option of components.

There are multiple adsorbing surfaces available like rice bran and saw dust.

But when all these three were compared together understable operating conditions found that the activated carbon had an efficiency of 92%, in comparison to sawdust giving 88%. [42]

Table 4 – Polycyclic Aromatic Hydrocarbon Removal

PAH removal technique	Catalyst used	Ratio used (if any)	Efficiency	Reference
Adsorption	Sugar cane bagasse, green coconut shells,	1:1	84%	35
Pre & Ultra Filtration	Sand bed	-	85%	36
Nano Hybrid adsorption	NH2-SBA-15 organic inorganic nanohybrid material	2:1	76%	37
Biologically active process	semipermeable membrane	-	96.9-99.7%	38
Chromatography	UPLC-MS/MS	-	73-83%	39
Hydrophobic Adsorption	activated carbon, biochar, modified clay minerals	1:1	86%	40
Microbial Transformation	CO2 trapped in KOH	-	92%	41
Activated Carbon	Rice bran, sawdust and activated carbon	1:1	92.5%	42

CHAPTER 9. SULFIDE AND ITS REMOVAL TECHNIQUES

Sulphur content and petroleum refinery wastewater is classified into two types. One being sweet which has a very low sulphur composition and the other is called sour crude oil when the sulphur composition is very high.

Petroleum refinery waste water with Sulphur content cannot be discharged as it is in the environment because it imports and order which is very unpleasant. Because of 8 Shroff properties it causes a lot of corrosion in the pipe equipment that it is sent through. It also causes the catalyst to be inactive.

It was observed that sulphur content is generated when the crude oil is send through the process of hydrocracking and catalytic refining. It is produced in many forms like elemental Sulphur, mercaptans, hydrogen Sulphide gas, naphthenic acid, cresylic acid. This when reacted with NaOH forms caustic soda mixture which produces maximum Sulphur content, This content is quite hazardous and toxic because it is highly reactive and it increases the pH to greater than 12 which is not an ideal scenario to dispose of the petroleum refinery waste water.[43]
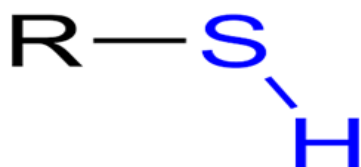

Figure 2. 2D structure of mercaptan; R being a radical

9.1 Chemical Precipitation
To remove sulphur from petroleum refinery waste water chemical precipitation which is considered to be a physical chemical process was combined with a coagulant which contain ions of ferric and ferrate.

These ions reacted with the sulphide In petroleum refinery wastewater. it was seen that f e 2 + ions were more effective in removing the sulfide content as compared to fe3 + ions. the former gave a COD removal of around 96 to 99% with Sulphur removal of around 50 to 80%. whereas the latter was able to remove only 62% of COD and sulphur of around only 50%.

It was seen that if the pH is increased into the basic side there was more efficient removal of sulphur because precipitation to place efficiently and the flocks formed were removed very effectively.

When both the ions are compared It is seen that if Fe 2 + ions are cheaper and more cost-effective wherease fe 3 + ion is better if the pH of wastewater is high..[44]

Operating conditions were found out to be consisting of Standard pressure and temperature, pH of 7, the catalyst used was $Fe^{2+}/3+$ with $Ca(OH)_2$. It resulted in an efficiency of the range 96- 99%.

9.2 Oxidation by using hydrogen peroxide
To remove sulfide contents from the petroleum refinery waste water oxidation was employed using hydrogen peroxide. To achieve almost 99.9% removal the hydrogen peroxide is combined with spent caustic.

The resultant removal is around 98% for COD and the pH turns out to be 8.5 in the outlet stream. This process is very cost effective as well as very operationally effective. it is an environment friendly process. it is easier to this process over other biological methods. Operating conditions were found out to be of room temperature, with a pH of the range 5.5-9, using the catalyst H_2O_2. It resulted in an efficiency of the range

98-99.9% [43]

9.3 Adsorption on modified activated carbon (MAC)

As the amount of adsorbent used is increased the sulfide content removal increases from the petroleum refinery wastewater. This was valid because as the amount of absorbent increases, more sites for adsorption is available to the sulphur components. it was observed that 4 gram per litre of MAC, is enough to remove almost all of the sulphide components from varied petroleum refinery wastewater constituents.

When modified activated carbon is used the efficiency of removing sulphur components increases by 2.5 times as compared to normal activated carbon.[45] Operating conditions used were a temperature of 27-34°C. This process doesn't require any specific pH. The catalyst used was $AC-HNO_3$. It gave an efficiency of the range 96-99%

9.4 Catalytic Oxidation

The refinery wastewater was treated with air, NaOCl, H_2O_2 as oxidants with Fe^{3+} and Mn 2+ as catalysts. To assess the effective combination of catalyst–oxidant for Sulphide removal after oil separation in parallel plate interceptors the water was sent through the combination.

The oxidant used in this process is 22% air, which is oxygen and then the catalysts used are Fe^{3+} and Mn^{2+}, the efficiencies of which are then observed and compared.

It was seen that ferric ions were more effective in comparison to the managanese II ions. Oxygen was tried to be replaced with sodiumhypochlorite ions and hydrogen peroxide. When these were combined separately with the two catalyst it was seen that ferric ion with sodiumhypochlorite gave the best sulfide removal efficiency.[46] Operating conditions were of room temperature. pH has no specific requirements for this process. Catalyst used was NaOCl with Fe^{3+}. It gave efficiency of around 92%

9.5 Modified bentonite clay

The bentonite clay was modified with Fe and H to improve the sorbent surface performance. The H particles used were of the size 1.763micro meter to 159 micro meters. The Fe particle used was of the size 0.036 micrometer to 127micro meters. This addition of Fe enhanced the surface area, pore size decreasing particle size took care of the acid treatment hence high desulphurization took place in the presence of Fe particles. The modified bentonite clay was used with the wastewater in several ratios and the ratio of wastewater to adsorbent of 10:1.2 was found to be the most optimal at 5hour reaction time. The Fe particles were preferred over H particles because of the decreasing particle size, pore size, more absorption area and it provided higher efficiency of 81% in comparison to 34% of H particles.[47]

Operating conditions were a temperature of 40°C. No specific pH is required, the catalyst used was modified bentonite clay. It gave efficiency of around 82%.

9.6 Advanced oxidation process

Zeolite catalyst bed was used in the process of desulphurization by the process of advanced oxidation as the catalyst is easily to regenerate and has high adsorption properties. Zeolite is the most commonly and widely used catalyst because of its porosity. The mixture of the wastewater was sent through the zeolite rotating bed at the speed of 90 rpm for 45 min with zeolite catalyst dosage of 1.5g/l. [48] The operating conditions were standard temperature and pressure. No specific pH requirement is there. The catalyst used was zeolite bed. It gives efficiency of around 92%.

9.7 Wet air oxidation

In wet air oxidation, air is used as a medium of oxidation, specifically the oxygen component along with steam hence the name wet air oxidation. It is one of the best processes to use for removal techniques

because it is:
a. Safest
b. More resistant
c. Works not only in pilot or laboratory scale but has proven itself on industrial scale as well [8]

The operating conditions used were a temperature of 175°C with a catalyst as air specifically oxygen. Efficiency of 99.95 % was achieved.

Table 5 – Sulphur Removal Techniques

Process	Temperature	pH	Catalyst	Process
Precipitation	STP	7	$Fe^{2+}/^{3+}$ with $Ca(OH)_2$	Precipitation
Hydrogen Peroxide	RT	5.5 – 9	H_2O_2	Hydrogen Peroxide
Modified Activated Carbon	27°C-34°C	-	Modified Activated Carbon (AC-HNO_3)	Modified Activated Carbon
Catalytic Oxidation	RT	-	NaOCl with Fe^{3+} and Mn^{2+}	Catalytic Oxidation
Modified Bentonite Clay	40°C	-	Modified with Fe^{2+} bentonite clay	81.44
Advanced Oxidation Process	STP	-	Zeolite	92
Chemotrophic bacterial sulfide removal	$1*10^5$Pa	-	Chlorobium thiosulfatophilum	99.2
Wet Air Oxidation	175°C	-	Air/Oxygen	99.9

CHAPTER 10.PERSISTENT ORGANIC POLLUTANTS AND ITS REMOVAL

Persistent organic pollutants (POPs) constitute a class of man-made chemicals with pronounced persistence against chemical/biological degradation and environmental mobility.

It has a tendency for bioaccumulation in human and animal tissues. The chemical properties of POPs are:
- low water and high fat solubility
- stability to all degradation processes
- low vapour pressure [42]

There are various types of POPs like –
a. HCB- Hexa chlorobenzene
b. PCDD – Polychlorinated dibenzo p-dioxins
c. PCDF- Polychlorinated dibenzofurans
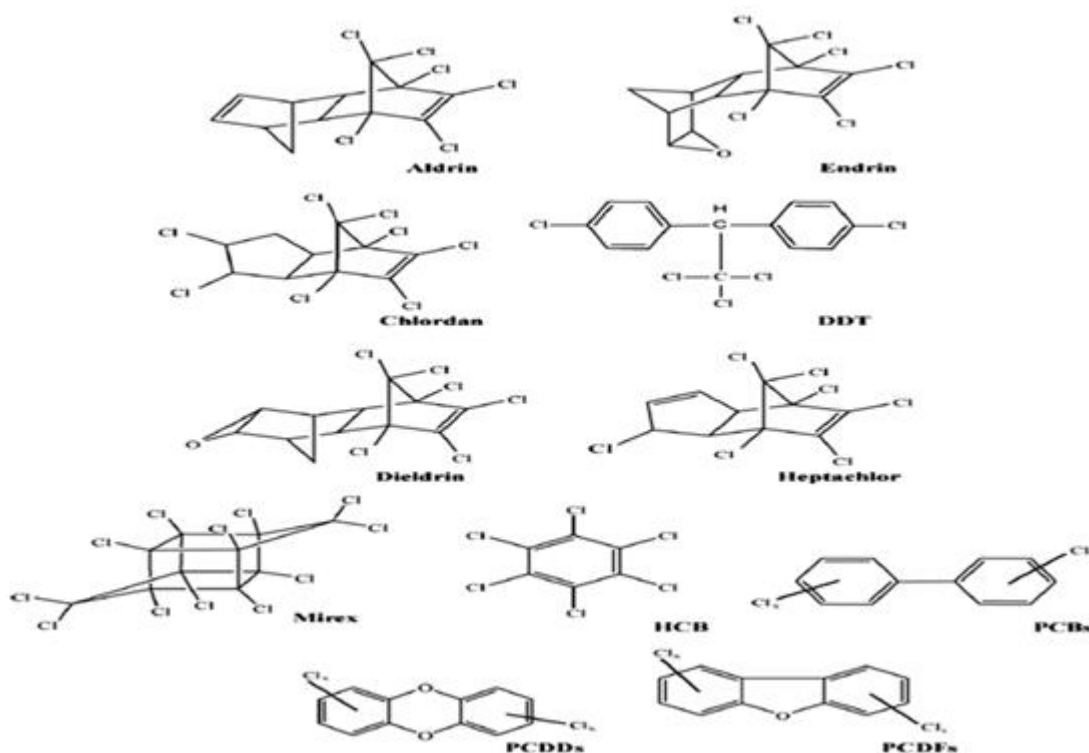d. PBD – Polybrominated diphenyl
e. PCB – Polychlorinated biphenyls

Figure 3. 2D structure of different type of POPs

10.1Adsorption

Persistent organic pollutants (POPs) are hydrophobic in nature which makes them really sorptive. Using this characteristic, it is absorbed on sludge particles in an octanol solution. This makes this process a solid liquid separation process. In this process majorly used to remove polychlorinated biphenyls. Operating conditions were room temperature. Efficiency of around 65-91 depending on the wastewater constituents.[50]

10.2 Nano Particles

Reactor description- conical in shape, the mixing took place in an upward circulating manner with the absence of a dead empty area at the bottom.

Process- The first step involves trying to homogenize the nano sized particle by sonicating them. After sonication the mass is sent to the reactor where it is mixed in a circular fashion with continuous inflow of air. The operating conditions in the reactor are maintained as required and then the UV rays are projected into it.

A very low catalyst concentration is introduced at the observed correct temperature, pH and UV light concentration.[51]

Operating conditions used were a temperature of 45°C, pH of 3. The catalyst used is TiO2. Efficiency achieved was around 78%. It was majorly used to remove polychlorinated dibenzo-p-dioxins.

10.3 Ammonia stripping

Ammonia stripping was done to remove Sulphur by using the base acid catalysed reaction. The mixture was stripped in a stripping column by running ammonia or basic solution through the and the remaining spent was half recycled and half thrown away consisting of impurities. [52] The operating conditions were a temperature of 25-40°C, pH<=4. Catalyst used was ammonia. It gave. An efficiency of the range 89-94. It was used to remove polychlorinated furans.

10.4 Electrocoagulation:

Electrocoagulation was done by using the coagulant consisting of $FeCl_3$. This process is majorly helpful to remove Hexa chloro benzene.

The electrolyte is passed through the wastewater which accumulates the POPs by creating a coagulated mass which is removed easily by filtration.

The operating conditions used were a temperature of 28°C, pH of 7. The efficiency was around 78-96%.[53]

10.5 Mesoporous catalyst

In this process polychlorinated dibenzofurans are removed by the use of bentonite clay.

Bentonite clay is mixed with silica gel and they are absorbed on sol gel. The mixture is then used as a catalyst at around 28°C with a basic pH. Acidic pH has a reaction with the clay, which disintegrates it, hence it should be avoided.

Based on the constituents of the wastewater it gives efficiency between 84%. The bentonite clay serves as a mesoporous surface helping to seep in the pores and hence separating the POPs.[54]

10.6 Nano structured particles

This process specifically uses tio2 particles of size 15nm to remove polybrominated diphenyl ethers. This size is smaller than the normally used tio2, this increase the surface area and hence enhancing performance. It does not require UV light but requires high temperatures of around 50°C at a low pH of 3. It always ends up giving 99% efficiency.[55]

10.7 Bioremediation

This is a biological process to remove polychlorinated biphenyls which uses the bacteria streptavidin. It is exposed to UV light which activates it, leading to eating up the pops. It gives 96% efficiency on an

average.

It is a biological process which makes it not that available for industrial scale yet as the bio bacteria leaves a pungent smell and is not used widely. [56]

Table 6- Persistent Organic Pollutant Removal Technique

Process	Type of POP removed	Temperature	pH	Catalyst	Efficiency (%)
Adsorption	PCB	STP	-	Octanol Solution	65-91
Nano Particles	PCDD	45 °C	3	UV/TiO_2	78
Ammonia Stripping	PCB/PCF	25 °C-40 °C	<=4	NH_3	89-94
Electrocoagulation	HCB	28 °C	7	$FeCl_3$	78-96
Mesoporous	PCDF	STP	5-6	Bentonite clay+ silica gel	84
Nano Structured Particles	PBDE	49-54 °C	3	(15nm)TiO_2	99
Bioremediation	PCB	UV	-	Strepavidin	96

CHAPTER 11. CONCLUSION

The conventional methods for the treatment of waste water of petroleum refineries were not that effective even after combining a few of them together as with increasing concentration of pollutants and strict policies, hence there was development of various advance processes. The processes are broadly classified as primary, secondary and tertiary treatment. Each treatment has various processes included in it as mentioned above. The waste water consists a lot of pollutants especially in terms of hydrocarbons like phenol, BTEX, PAH etc. which are necessary to be removed for the safe environment and better disposal of the same. Each component is treated in a different way and hence the parameters for it also differ. Phenol is treated by fenton process, UV/TiO2 photo radiation process etc., benzene is treated via wetlands, ozone, DAF, pervaporation etc., the polyaromatic hydrocarbons are removed by ionizing radiation treatment, sludge process, catalysis process etc.

For phenol Fenton process was found to be the most used and apt way as it not only reduced the concentration of phenol but also is an economically feasible process. For benzene all methods somewhat give the same results just that the wetland process is tedious and sometimes time consuming as well depending on the concentration of the initial incoming waste water. For PAH the catalysis process gives quite an impressive result but as there is catalyst present not only does the cost rise but also the fact that the catalyst forms a sludge as the end product makes it difficult to remove and dispose, sometimes it also affects the process in terms of quality and operating time. Nevertheless, there is still development going on in each phase and modifications are being done to help to selectively remove/reduce the concentration of various components.

Sour petroleum refinery wastewater is not the way to dispose it. It creates a lot of havoc to humans as well as environment. POPs accumulate into body tissues causing life risk. They do not disintegrate and are not degradable as well. There are multiple POPs and for every type there are multiple specifications.

The best way to remove Sulphides from the waste water is – Modified Activated carbon process. The reason is that Temperature requirement is approx. room temperature. There is no specific pH required. Absorption is the most effective and clean process. It gives up to 99% efficiency.

The best method to get rid of POPs is – Nano structured particles.

The reason is that it used a basic catalyst in presence of UV light. It is a clean process. Gives efficiency above 98% always. Easily removes multiple POP types.

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