GTL in Wastewater Treatment

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Gas-to-liquid (GTL) technology involves the conversion of natural gas into several liquid hydrocarbon products. The Fischer–Tropsch (F–T) process is the most widely applied approach for GTL, and it is the main source of wastewater in the GTL process. The wastewater is generally characterized by high chemical oxygen demand (COD) and total organic carbon (TOC) content due to the presence of alcohol, ketones and organic acids. The discharge of this highly contaminated wastewater without prior treatment can cause adverse effects on human life and aquatic systems.

Here, we provide an overview of recent literature related to the application of biotechnology for the treatment of GTL process water. It examines aerobic and anaerobic biological treatment methods that have been shown to reduce the concentration of COD and organic compounds in wastewater. Advanced biological treatment methods, such as cell immobilization and application of nanotechnology are also evaluated. The removal of alcohol and volatile fatty acids (VFA) from GTL wastewater can be achieved successfully under anaerobic conditions. However, the combination of anaerobic systems with aerobic biodegradation processes or chemical treatment processes can be a viable technology for the treatment of highly contaminated GTL wastewater with high COD concentration. The ultimate goal is to have treated wastewater that has good enough quality to be reused in the GTL process, which could lead to cost reduction and environmental benefits.

Keywords: nanoparticles ; Fischer–Tropsch (F–T) process ; biological treatment ; biomass immobilization

1. Introduction

Considerable amounts of was tewater are often released to the environment worldwide from industrial activities including oil refining, coal conversion, pharmaceutical and petrochemical industries, as well as coke and oil mill industries [1][2][3]. This wastewater usually contains different organic and inorganic pollutants including dissolved and suspended solids. The discharge of such wastewater into water bodies can cause serious problems to human health and the environment. Therefore, wastewater must be sufficiently treated to meet the discharge limit. Several physical and chemical methods were developed to reduce the concentration of phenols, COD, TOC and heavy metals in wastewater streams [4][5]. However, these methods are often costly due to the cost of chemicals, chemical sludge production and equipment. Biological methods are favorable in the area of wastewater treatment, due to their simplicity, low cost and environmental friendliness.

Biological treatments usually utilize microorganisms, such as yeast, bacteria, fungi and microalgae to reduce the concentration of organic compounds under aerobic or anaerobic conditions [6][7]. Several reactor schemes have been developed to operate in suspended growth, attached growth and hybrid systems. These systems are applied in batch reactors, membrane systems, fluidized beds and activated sludge systems [4][5][6]. The selection between the various biological processes is based on cost, land availability, operation simplicity and discharge limit of the pollutant. In industrial operation, biomass immobilization as biofilms is known as an efficient method to overcome the incorporation of free cells in wastewater treatment [8]. It offers several advantages including high removal efficiency, protecting the biomass from harsh environmental conditions and the possibility to reuse the microorganism and scale up of the process [9][10][11]. The use of nanoparticles to reinforce biomass immobilization matrices offers new bio-carriers that have increased strength and durability, and also has higher mechanical stability after long operation periods [12]. Several nanoparticles such as iron oxide (Fe_2O_3), gold (Au) and platinum (Pt), were investigated [13]. Among them, Fe_3O_4 nanoparticles were widely applied for enzymes immobilization [14].

The natural Gas-to-liquid (GTL) process has gained special attention due to several advantages [15]. In GTL processes, the Fischer–Tropsch (F–T) synthesis is the major step, which results in the production of large amounts of wastewater [16]. This wastewater is characterized by a high dissolved hydrocarbon content, COD and TOC content, thus proper treatment should be applied before discharge of this wastewater into the water body [17]. Although anaerobic biological treatment has been commonly applied for F–T wastewater treatment, incomplete mineralization of some pollutants, such as butyric acid and propionic acid, can be the major limitation of this treatment method [18]. Therefore, there is still a challenge to develop anaerobic biological methods and/or to find new advanced methods to overcome these drawbacks.

2. Biological Treatment of Industrial Wastewater

2.1. Main Industrial Wastewaters Composition

Most industries including pulp and paper, coal plants, olive mills, oil refineries, chemical plants and petrochemical operations generate significant amounts of wastewaters [3][18][19]. The characterization of industrial wastewater streams differs within and among industries [2][3]. Industrial wastewaters vary in volume, flow, strength and composition, according to the specific manufacturing process and the water usage in each industry. In addition, the environmental impact of industrial wastewater depends on several characteristics including chemical oxygen demand (COD), biochemical oxygen demand (BOD), amount of suspended and dissolved solids, and also on organic and inorganic contents [20]. Table 1 shows the concentrations of major pollutants in examples of industrial wastewater effluents.

Table 1. The concentrations of major pollutants in different types of industrial wastewater.

Wastewater	pH	TDS (mg/L)	TSS (mg/L)	Phenols (mg/L)	COD (mg/L)	BOD (mg/L)	Nitrates (mg/L)	OC (mg/L)	Ref.
Gas to liquid (GTL)	3	-	-	-	28,910.6–31,230.8	118,533–13,116.9	-	9540.5	[17]
Refinery	8.3–8.7	3800–6200	30–40	-	3970–4745	-	28	-	[21]
Coal gasification	7.6 ± 0.3	-	-	545 ± 61	2723 ± 280	805 ± 96	109	-	[22]
Coke oven	-	-	200	150–2000	1500–6000	1000–2000	-	-	[2]
Pharmaceutical	3.98	-	407	-	3420	-	160	775	[3]
Textile	9.44	-	-	-	850–1065	200–300		240–410	[23]
Olive oil mill	5.2			12,800	124,000	-	-	-	[24]
Palm oil mill	3.5 ± 0.1				55,775	25,545	711	-	[25]

2.2. Biological Treatment

Biological treatment has been widely applied in the area of water and wastewater treatment, presenting a highly efficient alternative in reducing the concentration of phenols, COD, TOC, heavy metals and oil traces from wastewater [16][17][18]. Biological treatment systems are generally classified into three different categories: suspended growth systems, supportive or attached growth and hybrid systems. In suspended growth systems, microorganisms are maintained in suspension mode within the liquid in batch reactors under aerobic or anaerobic conditions [26]. In contrast, the attached growth process is formed by granulation of activated sludge or attachment of the biomass as biofilms [26][27]. This technique has a greater concentration of biomass within the biological system and is applied in fluidized bed bioreactor

(FBB), granular sludge reactors, packed bed reactor (PBR), spouted bed bioreactor (SBBR), rotating biological contactor (RBC) and biological activated filters [20][21][24][26]. The application of an attached growth system introduces a surface that is necessary for biofilm structure development. This biofilm, however, can achieve higher biomass concentration, and the microorganisms can stay in the reactor for unlimited time, resulting in better environmental conditions [9]. Hybrid systems are based on the combination of suspended and attached growth systems in the same reactor, such as the combination of activated sludge with fixed bed biofilters and submerged membrane bioreactors [21][22].

In biological wastewater treatment, several microorganisms are widely applied, such as bacteria, yeast, fungi and algae [28][29]. These microorganisms may degrade organic compounds to form carbon dioxide under aerobic conditions, or to produce biogas which is a mixture of CO_2 and CH_4, under anaerobic conditions [30]. Biological techniques shown high efficiency in wastewater treatment, particularly in the reduction of organics including phenols, COD and oil and grace [25][31]. However, cost, energy required, odor and sludge production vary according to the application of aerobic or anaerobic treatment. Generally, an aerobic condition can be applied as a stand-up wastewater treatment unit, while anaerobic conditions are mostly applied in a pretreatment unit. Aerobic degradation has several advantages over anaerobic treatment, including high removal efficiency, low start up time, low odors production and excellent effluent quality. In contrast the anaerobic treatment is favorable in certain types of wastewater treatment, since it produces bioenergy in addition to low nutrients requirements and low sludge production [32].

2.3. Advanced Biological Techniques

The application of granulation activated sludge or the immobilization of biomass is good alternative for the conventional biological treatment systems. Immobilized biomass including activated sludge can be applied to improve the reduction of COD from wastewater, especially for high strength wastewater such as GTL-processed water.

The use of nanoparticles in cell immobilization can be considered as a high performance and cost-effective method for heavy metal removal from wastewater, and for the removal of other pollutants from several types of wastewaters including GTL wastewater. Additionally, the presence of these additives in the immobilized carrier will enhance the stability and offer the possibility of the use of biomass over long period of time.

3. GTL Wastewater

3.1. GTL Process and Wastewater Generation

Nowadays, natural gas is taking a more important share in the global energy market compare to other fossil fuel sources. Natural gas conversion to liquids, through the (GTL) process, is achieved using several chemical reaction paths ending with the formation of a range of hydrocarbon products. The Fischer–Tropsch (F–T) process is the most widely applied, this process basically involves the conversion of CO and H_2 into several hydrocarbon derivatives [33]. The products of this process can be used directly as fuel such as gasoline, kerosene and diesel, in addition to other special products including lubricants [34]. The produced gas using F–T process usually has low sulfur and aromatic compound contents [35]. In addition, the low CO_2 emission, nitrogen oxides, hydrocarbons, and other particulates make GTL process an environmental friendly alternative and one of the cleanest burning fuels [36]. The GTL process mainly contains three main stages; synthetic gas production where the natural gas steam reforms to produce syngas (CO and H_2), followed by the Fischer–Tropsch (F–T) reaction to form hydrocarbons, and syncrude. Finally, upgrading the liquids in which liquid hydrocarbons are formed by cracking and hydro-processing. Then, the produced hydrocarbons products meet market specifications [34].

3.2. The Nature of Gas to Liquid (GTL) Process Wastewater

Wastewater from typical GTL plant generally contains a high concentration of dissolved solids, since the produced cooling water from the blowdown system contains inorganic salts. The total organic compounds are generally measured collectively as COD; besides, GTL wastewater contains number of inorganic compounds including metals, chloride, sulphate, acetate, bicarbonate and dissolved gases such as H_2S and CO_2 [37]. The contaminants that are present in GTL wastewater vary according to the GTL process unit. The F–T unit results in wastewater contaminated with inorganic compounds and oxygenated hydrocarbons. However, cooling tower and blow down water has significant concentration of dissolved solids, suspended solids and heavy metals. The steam generation unit generates water with high concentration of dissolved solids and minerals. Additionally, wastewater with emulsified oil and other hydrocarbons is often generated in the process area, equipment wash and maintenance activities [38].

3.3. Methods for GTL Wastewater Treatment

Various technologies have been applied in the treatment of GTL produced water depending on the characterization of the stream. These techniques such as membrane filtration, advanced oxidation process, thermal evaporation and bioreactors vary in their removal efficiency of the toxic compounds from GTL wastewater [39]. A typical GTL wastewater treatment plant consists of combination of two or more treatment technologies; however due to the negligible amounts of sulfur and nitrogen in GTL wastewater, that are highly distributed in other wastewater streams, GTL wastewater is mainly treated by the anaerobic biological digester. The conventional GTL wastewater treatment plant is composed of coarse screening to remove large materials, followed by biological treatment process to remove the soluble materials by adding coagulant. Then, a separation step using coagulation to collect the produced waste in colloidal form. After coagulation, wastewater is treated by adding oxidizing and disinfecting agents to reduce (BOD) level [15].

3.4. Biological Treatment of GTL Wastewater

Most of the COD content in the integral GTL wastewater stream is due to alcohols, and this water can be successfully treated biologically under anaerobic conditions. The combination of anaerobic and aerobic processes can be suitable for the treatment as well. Beside the removal of organic pollutants from GTL wastewater, the anaerobic process can also produce energy by achieving methane production as byproduct, this make anaerobic biological treatment more preferable [40].

Biological systems can be combined with chemical agents, such as Zero valent iron (ZVI) that is generally utilized as a reductive agent for pollutants control. Recently, scrap Zero valent iron ZVI was applied and combined with the biological systems for F–T wastewater treatment in order to reduce the process cost and improve the anaerobic biological treatment [41]. SZVI was used in up-flow anaerobic fixed bed (UAFB) reactor to study the F–T wastewater purification and compared with controlled UAFB reactor. The role of SZVI was to buffer the acidity of the raw wastewater, and at the same time introduce more reductive microenvironment for methanogens. The obtained results indicated enhancement in the COD reduction and methanol production of 11.2% and 0.42 L/L.d, respectively [41]. Although the use of ZVI in the anaerobic biological system could be suitable for generating iron oxides (IO) and enhancing the removal efficiency, it may not be used for pilot scale applications. Direct addition of ZVI shavings or powder may cause a rise in iron precipitation, hence, it was suggested for use in plate electrodes [42].

4. Conclution

Several researchers have focused their efforts, in recent years, on the aerobic and anaerobic biological treatment of industrial wastewater, in which several reactors were developed to reduce the concentration of organic compounds to the acceptable limit. Most of the studies available in the open literature concentrated on the reduction of, COD and TOC from industrial wastewater using pure culture or mixed culture consisted of yeast, bacteria fungus and microalgae. Among them, the removal of alcohol and VFA that are considered as major contaminants in GTL wastewater are rarely studied under aerobic conditions; however, the removal of the alcohols and VFA is well documented using several anaerobic reactors. Although advanced biological treatments, such as cells immobilization and application of bio-nanotechnology for industrial wastewater treatment have been thoroughly reviewed in the literature, the number of studies that have highlighted the biological treatment of GTL wastewater, which is mainly generated from F–T process, are rather limited. Anaerobic biological treatment showed good performance in the F–T wastewater treatment, but it still suffers from some drawbacks, including the accumulation of butyric acid and propionic acid, as well as the generation of considerable amounts of sludge. To overcome this drawback, it is often suggested to optimize the anaerobic biological treatment process or to combine anaerobic biological treatment with an aerobic treatment processor to modify the anaerobic reactor by adding a chemical treatment step. This combination, however, may possess some disadvantages, such as high cost and long start up time.

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