Phenol

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Phenol and its derivatives are hazardous, teratogenic and mutagenic, and have gained significant attention in recent years due to their high toxicity even at low concentrations. Phenolic compounds appear in petroleum refinery wastewater from several sources, such as the neutralized spent caustic waste streams, the tank water drain, the desalter effluent and the production unit. Therefore, effective treatments of such wastewaters are crucial. Conventional techniques used to treat these wastewaters pose several drawbacks, such as incomplete or low efficient removal of phenols.

Biocatalysts Horseradish peroxidase Tyrosinase Laccase Enzyme

1. Introduction

The increment in the human population, along with the global economic development, has created a remarkable demand for petrochemical products and energy, which is expected to grow up to a further 37% over the next two decades [1]. Different processes such as thermal cracking, exploration, desalting, catalytic treatment, isomerization and distillation are involved in the petroleum refinery and petrochemical industry to produce useful products like gasoline, liquefied petroleum gas and petrochemical feedstock [2][3]. Accordingly, a large volume of water is needed in each one of these processes, making these industries among the most water-consuming establishments. The average volume of wastewater generated by these processes is almost 0.4–1.6 times higher than the volume of the produced crude oil [4]. It is anticipated that the world demand for oil will reach 107 million barrels per day in 2030 [5]. In 2018 alone, around 6500 million liters of wastewater were generated per day, as a result of an approximately 99.93 million barrels per day world oil consumption, according to the Energy Information Administration (EIA) report [6]. The increasing demand for petrochemical products, the limitation of hydric sources and the negative effects of the contaminated wastewater on the environment and health of living species are nowadays undeniable worldwide issues that have directed a lot of attention towards the safety of the ecosystem. Among them, the wastewaters discharged from petroleum refining industries and petrochemical plants are composed of various toxic organic components with significant potential threats to the environment. In general, the pollutants appearing in the petroleum refinery wastewaters can be classified into inorganic and organic matters [7]. Thus, the efficient treatment of wastewater generated by these industries should be considered as a strategic approach to sustained water resources management across the world [8]. The quality of the crude oil defines the composition of the generated wastewater by the petroleum refining industry, and it differs with the operating conditions [9]. Petrochemical wastewater is considered a major source of aquatic environmental pollution, comprising large amounts of aliphatic and aromatic hydrocarbons such as toluene, xylenes, benzene and phenolics with potential hazards to the ecosystem [10]. Among different contaminants present in petroleum refinery wastewater, ammonia nitrogen and organic compounds (such as phenols) are known as the principal chemical characteristics of environmental concern in the effluent [7]. Introducing these types of wastewaters into the aquatic ecosystem causes a significant reduction of the normal dissolved oxygen (DO) level (2 mg/L) of the water, which can increase the mortality rate of the living species in that environment [11]. In previous literature, the effect of petroleum refinery wastewater on the quality of Ubeji Creek water in the Niger Delta of Nigeria was studied, and the results suggested that the mixing of brackish waters with the discharged effluent had detrimental impacts on the aquatic life [12]. Moreover, chronic or high exposure to these toxic hydrocarbons and compounds (i.e., phenols) can be carcinogenic, and cause many severe health issues to human beings such as lung, liver, kidney and vascular system infection [10][13]. These pollutants are persistent and highly soluble in water, which can migrate into the groundwater [13]. Phenolic compounds are one of the most concerning persistent pollutants originating mainly from crude oil fractionation and catalytic/thermal cracking in petroleum refineries [14]. Furthermore, the other sources of total phenolic compounds in the petrochemical effluents are the tank water (~11.8 ppm), the desalter effluent (~1.4 ppm) and the neutralized spent caustic waste streams (~234 ppm) [15]. It has been reported that more than ten million tons of phenolic compounds are discharged into the environment every year [16]. Depending on the industrial source of wastewater, the typical concentration of phenols in the discharged waste streams can range between 100 and 1000 ppm [17]. This is while that the discharge of untreated effluents containing phenols contaminants into the environment, even at low concentrations, can lead to threatening the aquatic lives and harmony of the ecosystem as well as contaminating soil, groundwater and surface water [18]. Based on their harmful health impacts, the required standards for the discharge of phenolic wastewaters have been becoming increasingly restrictive, and these pollutants are known as priority pollutants, according to the Water Quality standards issued by USEPA [19]. Therefore, elimination of such pollutants is considered as a major importance, and there has been a growing demand for enhanced techniques of effective treatments.

A combination of different techniques, including chemical, biological and physical treatments, have been studied to eliminate such toxic pollutants from petrochemical industrial wastewaters [20]. In this regard, various types of oxidation (chemical and catalytic oxidation e.g., photocatalysis and Fenton and Photo-Fenton oxidation), biological processes (i.e., activated sludge process and anaerobic membrane bioreactors) and coagulation have been utilized for the treatment of such wastewaters [8][21]. However, most conventional wastewater treatment methods cannot efficiently eliminate the persistent aromatic organic and hydrocarbon compounds, i.e., phenols, due to their several inherent drawbacks such as technical complexity, incomplete removal of the pollutants, formation of hazardous by-products with more toxicity comparing with the original phenolic compounds and high capital and maintenance/operation costs [22][23]. These constraints adversely affect the economic viability and technical feasibility of the treatment processes. Among the aforementioned treatment techniques, biological treatment is considered one of the most effective methods for the elimination of persistent pollutants. In such a technique, a limited number of microbial species can degrade the recalcitrant pollutants. For phenols, it is done by opening the aromatic rings, while microbes derive carbon and energy from the contaminants [23]. In most cases, however, a long retention time is needed for biological degradations, while the variation of the operating conditions, such as pH and temperature, can easily influence the process performance [14]. Furthermore, biological wastewater treatment methods suffer from other serious disadvantages as well. Firstly, the control of the optimum level of microbial growth conditions is always challenging. Thus, specific conditions might have a significant impact on the survival rate of microbes within the system leading to inefficient wastewater treatment [24]. Secondly, some of the bioproducts of biological treatment processes (i.e., the generated sludge) can be toxic [25]. Thirdly, microbes are mostly ineffective when the pollutants exist at very low concentrations. To overcome this issue, surfactants and organic co-solvents are usually added to improve the bioavailability of the pollutants. This process might have negative economic and technical effects on microbial wastewater treatment efficiency. Therefore, cost-effective, eco-friendly, easy-to-operate and novel wastewater treatment technologies are required to efficiently remove various phenolic compounds from different effluents without producing harmful metabolites and sludge.

Accordingly, a relative novel trend has been introduced in recent years on employing extracellular enzymes, rather than whole microbial cells for eliminating phenols and some other organic pollutants from industrial wastewaters. Enzymes selectively catalyze reactions under moderate conditions [26], and their corresponding process can be considered as a feasible alternative to the other traditional treatment methods [14]. The use of enzymes for wastewater treatment purposes was first suggested in the 1930s [17]. Nonetheless, the concept of utilizing enzymes to eliminate individual contaminants in wastewater streams was not fully developed until the 1970s [17]. Over the past decades, the application of enzymatic wastewater treatment processes has been investigated based on oxidoreductive enzymes, especially polyphenol oxidases and peroxidases. In this process, the enzyme catalyzes the oxidation of phenols and catechols, and generates reactive radicals [27]. Enzymatic processes offer more valuable advantages over microbial treatment. Enzymes can retain their activities and effectiveness over a wide range of environmental conditions [28]. Moreover, they are capable of converting the substrate with reasonably high selectivity over a wide range of pollutant concentrations [26]. It has been reported that the phenolic compounds with concentrations higher than 100–200 mg/L can be toxic to some of the species utilized in biological wastewater treatment, modifying the microbial structure and negatively affecting microbial growth [17][29]. Compared to the other conventional catalytic techniques, enzymatic systems produce less waste and consume less water. On this account, enzymatic wastewater treatment processes are progressively becoming an attractive sustainable alternative and environmentally friendly approach. Moreover, the possibility of the production of enzymes on a higher scale with improved activity and stability at a lower cost using the recombinant-DNA technique further encourages the usage of enzymes in wastewater treatment processes [30]. However, more cost-effective approaches for even the enzymatic wastewater treatments are yet to be discussed.

Since the removal of phenolic contaminants from industrial wastewaters using peroxidase and polyphenol oxidase enzymes has been scarcely discussed in the previous literature reviews, the main purpose of this study is to demonstrate a general picture of the obtained results in this research field, as well as those parts which are still uncovered. In this regard, the ability of the aforementioned enzymes in catalyzing the reactions for removing phenols from the wastewater is thoroughly investigated. This can be helpful to determine the feasibility and applicability of biocatalytic processes for the elimination of phenolic compounds from the petroleum refinery wastewaters. After proving the feasibility of this technique, it would be possible to conduct further research and development studies in this field in order to considerably lower the cost of the application. Justifying the replacement of current wastewater treatment technologies with enzymatic treatment techniques is not the scope of this current study. Rather, the intention is to provide a clear insight into the future potential feasibility of enzymatic treatment methods for treating real wastewater samples under certain conditions.

2. PRPP Wastewater Characteristics and Disposal Standards

The characteristics and total volume of the generated wastewater in an oil refinery plant heavily depend on the quality of the crude oil, the final products and the process's complexity and configuration. The general characterization of these types of effluents is presented in **Table 1**. The generated wastewater by different processes is mainly characterized by a high COD [31], which is mostly due to the overall contribution of several inorganic substances (i.e., cyanides, sulfides and ammonia), emulsified oil and aromatic and aliphatic hydrocarbons (especially up to C_{10}) such as ethylbenzene, benzene, methyl tertiary butyl ether, polycyclic aromatic hydrocarbons (PAHs), toluene and phenolic compounds [31]. In addition, high concentrations of total dissolved solids (TDS), phenol, benzene, xylene, heavy oil, total suspended solids (TSS) and toluene in different petroleum and petrochemical wastewater were observed in the previous literature [32]. Most of the pollutants present in the petrochemical effluents are persistent in nature, and considerably increase the chemical oxygen demand level and toxicity of the produced wastewater streams. Heavy oil is known as a key pollutant in the petrochemical effluents, which can contaminate the groundwaters and water bodies through oil discharge and spills. They are large hydrocarbons consisting of a higher number of carbon atoms with high chemical stability and viscosity, together with low water solubility and biodegradability [33]. Polycyclic aromatic hydrocarbons are considered as another major component of petroleum refinery wastewater, belonging to the polycyclic aromatic hydrocarbon groups with more than one benzene ring. They are almost colorless, hydrophobic, and with higher boiling and melting points along with comparatively less vapor pressure [34]. These compounds are also very toxic and can undergo bioaccumulation. A remarkable amount of phenolic compounds, along with high levels of COD, Total Organic Carbon (TOC) and BOD, can be detected in the wastewater treated by the conventional methods, which confirms the incompetence and low efficiency of these techniques [35][36]. Due to the presence of the noticeable amount of various persistent and toxic pollutants, such as phenols, in the effluent of the petroleum refinery industry and their detrimental and toxicological impacts on the ecosystem, many existing environmental agencies provide standard limits for each contaminant in the wastewaters before disposing them into the marine water and environment or in the agricultural field. For example, the World Bank Group (WBG) and USEPA set the concentration of 10 ppm as the limits for total nitrogen in the treated effluent [37]. However, some of these regulated standards are challenging to be met by conventional treatment techniques. Thus, this creates opportunities for developing novel, eco-friendly and efficient technologies.

Table 1. Characterization of petroleum refinery and petrochemical effluents.

Parameter	Typical Value Range(s)	Environmental Standards *	References
BOD (mg/L)	718 90–685 3378 8000	30	[10][37]

Parameter	Typical Value Range(s)	Environmental Standards *	References
TSS (mg/L)	28.9–950 2580	30	[31][37][38]
Conductivity (ms/cm)	5.2–6.8	-	[31]
COD (mg/L)	3600–5300 300–800 550–1600 7896	125	[10][31][37]
Total phenol (mg/L)	10–233	0.35	[10][31][39]
pH	6.5–10.8	6–9	[37][38][40]
Heavy metals (mg/L)	0.01–100	-	[10][37]
Sulfide (mg/L)	142 1222 15–30	0.5	[39][41]
Temperature	23.9 °C **	<3 °C at edge of mixing	[15][37]
Benzene (mg/L)	-	0.1	[39]
Mercury (mg/L)	-	~0.03	[37]
SO_4 (mg/L)	14.5–16	-	[31]
o-Cresol (mg/L)	14–16.5	-	[31]
Phenol (mg/L)	11–14	-	[31]
Total dissolved solid (mg/L)	3800–6200 1200–1500	1500–2000	[31][42]
n-Hexane (mg/L)	1.8–1.85	-	[31]
Grease and oil (mg/L)	12.7–3000	10	[10][39][43]
Total organic carbon (mg/L)	220–265 119 398	50–75	[42][43]
Ammonia (mg/L)	4.1–33.4 69	15	[40]
2,5 and 2,4- Dichlorophenol (mg/L)	28–32	-	[31]

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