Characteristics of Phenol Content in POME

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The global population has increased significantly, resulting in elevated levels of pollution in waterways. Organic pollutants are a major source of water pollution in various parts of the world, with phenolic compounds being the most common hazardous pollutant. These compounds are released from industrial effluents, such as palm oil milling effluent (POME), and cause several environmental issues. Adsorption is known to be an efficient method for mitigating water contaminants, with the ability to eliminate phenolic contaminants even at low concentrations. Carbon-based materials have been reported to be effective composite adsorbents for phenol removal due to their excellent surface features and impressive sorption capability.

adsorption graphene organic pollutants POME Phenol

1. Introduction

The world's main vegetable oils are derived from palm, soybean, coconut, olive, peanut, sunflower, cottonseed, and rapeseed [1]. Palm oil mill effluent (POME) is a liquid by-product of the crude oil palm production process that contains organic acids as well as phenolic compounds extracted from oil palm fruit and cell wall fragments. POME is an organic acid mixture that also contains hazardous organic matter, expressed in chemical oxygen demand (COD) at concentrations between 45,500 and 65,000 mg/L, which is 100 times more hazardous than residential sewage [2]. Edible oil refining processes generate a large amount of agricultural runoff with effluents that vary in quantity and characteristics between industries and mills [3]. If left untreated, agricultural wastewater would deplete water oxygen levels rapidly due to the presence of organic and nutritional elements, posing a long-term threat to aquatic life and the food chain [1][4]. Improper disposal of industrial waste, particularly palm oil mill effluent (POME), can result in significant environmental problems. According to Chantho et al. (2016), the production of one ton of crude oil generates around 2.5 tons of POME, which contains high concentrations of bio-recalcitrant phenolic compounds [5]. In recent times, the rapid expansion of the edible oil industry, increased public awareness, and tightened environmental legislation have led to the need to treat agricultural effluents before they are discharged into natural water sources [6]. Environmental policies and regulations have been helpful in preventing the accumulation of waste in agricultural systems. However, there is a growing demand to convert agricultural waste into valuable products [7]. Phenolic compounds are organic compounds that are dissociated or non-dissociated and ionize in an aqueous medium with a pH different from water [8]. The presence of phenol in water can pose a serious threat to biological systems due to its toxic and persistent nature. Al-Ghouti et al. (2022) suggest that removing phenolic waste from water and generating a secondary by-product with increased conductivity and salt content is often a difficult task due to the high levels of biomass content. The accumulation of phenol in the food chain can also be a health concern, as it can result in the formation of stable chemical species [9]. At concentrations as low as 1 μg/L in drinking water, phenolic compounds can result in taste and odor problems and be toxic to the function of the human liver and kidney when exposed to higher concentrations for a certain period of time [10].

Several techniques are available for POME treatment; however, not all are suitable as they have varying treatment efficiencies and costs [8]. POME treatment techniques can be classified into physical, chemical, and biological methods [11]. However, these methods have drawbacks such as long assembly and operation periods, high energy usage, expensive maintenance and operation costs, and the generation of sludge, which requires secondary treatment [12]. Finding a low-cost and environmentally sustainable POME waste treatment technique for industrial use is challenging. Therefore, a novel, cost-effective technique for the decontamination of POME from various contaminants, especially phenols, is necessary [13]. The wet extraction technique used in palm oil mills releases contaminants from palm fruit-derived chemicals [14], inhibiting methanogenesis due to certain simple phenolic compounds and polyphenols [2][15]. However, these treatment processes have limitations, such as the requirement of toxic chemicals and a longer decontamination time [16][17]. Adsorption has been proven to be a low-cost, accessible, profitable, and effective method for POME waste effluent treatment compared to other conventional methods. Adsorption is a critical method that emphasizes the interactions between pollutants and adsorbents at the solid-liquid interface [18]. However, limitations such as the toxicity and instability of adsorbents have led to the need for novel adsorbents for pollutant removal applications.

In recent times, nanotechnology has been widely employed in several applications, including wastewater treatment, as nanomaterials have been proven to be highly effective in eliminating inorganic and organic pollutants from wastewater effluents compared to conventional adsorbents due to their low toxicity and small size [19][20][21]. Among nanoparticles, nanosized graphene possesses unique mechanical, physical, and chemical properties that have gained significant attention worldwide for environmental applications [22]. Graphene is used as an adsorbent in wastewater treatment due to its large surface area, improved active sites, large-delocalized electron systems, and superior chemical stability [23]. Recently, nanosized graphene, graphene oxide (GO), and their composite materials have emerged as novel materials beneficial for wastewater treatment applications. GO has been shown to have great adsorptive efficiency due to the abundance of functional groups compared to graphene [24]. GO in its nanoscale form is a two-dimensional material composed of carbon atoms that feature various oxygen-containing functional groups, such as hydroxyl, carboxylic acids, epoxides, or alcohol, which enhance its stability in water (Gallegos-Pérez et al., 2020). The addition of oxygen-containing functional groups, such as hydroxyl, carbonyl, epoxide, phenol, and carboxyl groups, to the graphene oxide structure results in a hydrophilic nature and a modifiable functional group structure (Obayomi et al., 2022). Various composites are synthesized by modifying GO with polymers, metal and metal oxides, or hydroxide nanomaterials, as well as small molecules, to produce GO-composites, which can be utilized as membranes, adsorbents, and catalysts for decontaminating pollutants.

The utilization of nanosized GO as an adsorbent can affect the extent of oxidation via interactions and the presence of hydrogen bonds due to its complex structure [9]. Researchers have shown interest in utilizing GO-based nanocomposites for phenol removal due to their large specific surface areas and various oxygenated functional groups, such as carboxyl and hydroxyl groups, that have a high affinity for the pollutant [25]. Although graphene-based materials are utilized in adsorption studies, the adsorptive capability of GO can be enhanced through surface modification [26]. Hence, graphene-based composites are a great choice for phenolic chemical adsorption. Graphene oxide (GO), a highly oxidative form of graphene with several polar functional groups, has a theoretical surface area that is retained, which allows for its modification and hybridization with other materials [27]. Therefore, graphene-based nanocomposites are identified as an excellent choice for phenolic compound uptake compared to standalone GO.

2. Characteristics of Phenol Content in POME

The discharge of toxins from anthropogenic activities into the environment has resulted in one of the major challenges of this century, which is the scarcity of clean water. Phenol is frequently found in industrial wastewater generated by sectors such as oil, gas, medicine, and pesticide production. As it can be harmful, numerous environmental protection agencies have instituted stringent concentration limits for phenol in wastewater to safeguard human health and preserve ecological equilibrium [28]. In ASEAN countries, where palm oil is a significant economic crop, the rapid expansion of the palm oil industry has led to environmental issues caused by the release of large volumes of palm oil mill effluent (POME) into water sources. POME contains high levels of phenolic chemicals, making it a highly contaminated effluent with a colloidal suspension content of 95–96%, total solids of 4–5%, and palm oil of 0.6–7%. The dark brown color of POME is attributed to the oxidation of phenolic components, such as lignin and anaerobically reduced products [29].

Phenol, a white, crystalline, and volatile aromatic chemical compound, is widely found in wastewater from several industries, including oil, gas, medicines, and pesticides, and even at low concentrations, it can affect the taste and odor of water [30]. Phenol is prone to vaporization, resulting in its widespread distribution in the atmosphere, where it can interact with hydroxyl and nitrate radicals and participate in photochemical reactions, generating dihydroxybenzenes and nitrophenol. This process represents the principal mechanism for the removal of phenol from the atmosphere [31]. Factors such as temperature and season, as noted by Møller et al. (2014), can impact the half-life of phenol, which ranges between 2.28 and 22.8 h for reactions with hydroxyl radicals [32]. Phenol is not fully degraded in water due to its short half-life, resulting in its concentration in urban and industrial areas. Moreover, phenols have low sorption due to low partition coefficients between phenol and octanol and minimal water or organic carbon content in soils and sediments, causing them to seep into groundwater close to industrial plants and waste sites [33]. Phenols have rapid biodegradability as they are used as substrates by both aerobic and anaerobic bacteria, with half-life values ranging from 2.7 to 552 h in soils and sediments, depending on their inherent properties [32]. Additionally, phenols can undergo adsorption, volatilization, and oxidation in addition to biodegradation [33]. While phenol is more persistent in water than in air, soil, or sediment, it still degrades in low concentrations. Phenols undergo volatilization, photodegradation, and biodegradation in aquatic environments, with the latter being the most common elimination method. Phenol reacts with hydroxyl and peroxyl radicals in surface waters, with mean half-lives of 100 and 19 h, respectively [33]. However, volatilization often takes more than three months.

Numerous studies have shown that phenol is becoming a concern due to its persistence in the environment [33]. An unintentional spill that occurred in Wisconsin (USA, 1974) is an example of the risk associated with phenol. A concentrated phenol-containing solution contaminated an aquifer for nineteen months, which negatively impacted the health of the people in the affected area. In addition, the high phenol content hindered the biodegradation process of the water [34]. Even though phenol has a short half-life, its continuous release into the environment can have significant impacts on humans and other living organisms. Therefore, it is classified as a priority pollutant by both the US Environmental Protection Agency (USEPA) and the Canadian National Pollutant Release Inventory (NPRI) because it can result in both immediate and lasting effects, even at reduced levels [35]. Human exposure to phenol can occur via inhalation, cutaneous contact, or ingestion of products that are contaminated and can spread rapidly throughout the body once ingested. Phenol can penetrate the membranes of cells and be metabolized into intermediates (e.g., quinone groups) that can interact with protein functions and cause cell death [28]. Symptoms of acute phenol exposure include skin, eye, and mucous membrane irritation, but they can progress to more severe conditions, such as breathing difficulties, weakness in the muscles, lowered body temperature, convulsions, and death, depending on the level of exposure [36]. Abnormal development and behavior in offspring, fertility decline, and fetal body weight reduction have been recorded in animals exposed to phenol [37]. Kulkarni and Kaware (2013) indicate that the concentrations of phenol that can cause negative effects in humans and aquatic species are 10–24 and 9–25 mg/L, respectively [38]. Various conventional strategies, including distillation, chlorination, and absorptive extraction approaches, have been used to eliminate phenol from aqueous media. However, these techniques have certain disadvantages, such as limited efficiency, the ability to generate sludge and harmful byproducts, a high cost, and high energy requirements [39].

Adsorption and advanced oxidative processes (AOPs) have been demonstrated as viable, practical, and environmentally friendly alternatives for removing phenol from water among the advanced remediation technologies. In recent years, tertiary treatments have been successfully used to increase phenol absorption and meet stringent water quality requirements. Advanced oxidation technologies and adsorption are reported as highly viable approaches among these tertiary methods. Adsorption is an advantageous technique for phenol removal due to its simplicity in construction and use, cost-effectiveness, and ability to handle low-concentration fluids [40]. In addition, AOPs have become increasingly popular due to their low environmental impact, fast reaction times, ability to mineralize organic molecules, and complete elimination of pollutants [41]. Combining these approaches is considered a promising option for phenol removal [42]. To date, several chemical-based materials have been utilized as conventional adsorbents for phenol removal applications, including metal oxides [22], activated carbon [43], silica-based aerogels [44], and natural materials such as activated carbon from lignocellulosic agricultural wastes [45], zeolites [46], and rice husk [47]. However, these macro-materials cannot completely remove phenols from environmental conditions with high efficiency due to their larger size. Thus, novel structures or nanosized materials are required to improve phenol removal efficiency. Among these novel structures, graphene oxides (GOs) have recently been reported to possess enhanced ability to remove phenols from contaminated sites due to their unique two-dimensional (2D) morphology [48].

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