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# RECENT ADVANCES IN THE PREPARATION OF OIL PALM WASTE-BASED ADSORBENTS FOR REMOVAL OF ENVIRONMENTAL POLLUTANTS - A REVIEW

(Kemajuan Terkini dalam Penyediaan Penjerap Berasaskan Sisa Kelapa Sawit untuk Penyingkiran Bahan Pencemar Alam Sekitar - Sebuah Ulasan)

Faridah M. Marsin[1, 2], Wan Aini Wan Ibrahim[1, 3], Hamid Rashidi Nodeh[4], Zetty Azalea Sutirman[1], Ng Nyuk Ting[1], Mohd Marsin Sanagi[1,3]*

*[1]Department of Chemistry, Faculty of Science,*
*Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia*
*[2]Malaysia Department of Chemistry (Southern Branch), 80100 Johor Bahru, Johor, Malaysia*
*[3]Centre for Sustainable Nanomaterials, Ibnu Sina Institute for Scientific and Industrial Research,*
*Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia*
*[4]Department of Chemistry, Faculty of Science,*
*University of Tehran, Tehran, Iran*

**Corresponding author: marsin@kimia.fs.utm.my*

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**Abstract**

The palm oil industry is an excellent source for huge quantities of highly useful biomass. Utilization of oil palm biomass-based materials for the removal of environmental pollutants appears to be a viable solution in the lights of promoting sustainable development. This article aims to review recent advances in the preparation of adsorbent from different parts of oil palm biomass for the removal of heavy metal and organic environmental pollutants from water. Physical and chemical factors that enhance the applicability of oil palm waste as adsorbents are also discussed. It is clear that each part of the oil palm biomass is potentially applicable as biosorbents for most environmental pollutants and the capability could be further enhanced through modifications in accordance with its intended pollutants. Modifications by chemical treatments such as acidic, basic or drying agent treatments under optimum dosages have been found to have significant effects on the selectivity of the analyte absorption. In general, basic treatment is more suitable for common pollutants such as metals, pesticide and basic dyes. Meanwhile, the acidic treatment is more suitable for non-polar organic pollutants such as phenols. Recent trends in the application of oil palm biomass as biosorbents are also discussed that together open new doors to sustainable development.

**Keywords**: oil palm biomass, adsorbent, activated carbon, environmental pollutants

**Abstrak**

Industri minyak kelapa sawit merupakan sumber yang baik untuk mendapatkan biojisim bermanfaat dalam kuantiti yang besar. Penggunaan bahan berasaskan biojisim minyak kelapa sawit bagi penyingkiran pencemar alam sekitar merupakan salah satu penyelesaian berdaya maju dalam mempromosi pembangunan mampan. Artikel ini bertujuan untuk mengulas kemajuan dalam penyediaan penjerap daripada pelbagai bahagian biojisim kelapa sawit bagi penyingkiran ion logam berat dan pencemar organik alam sekitar daripada air. Faktor fizikal dan kimia bagi meningkatkan kebolehgunaan sisa kelapa sawit sebagai penjerap juga dibincangkan. Ianya jelas bahawa setiap bahagian biojisim kelapa sawit berpotensi untuk digunakan sebagai bio-pengerap bagi kebanyakan bahan pencemar, dan keupayaannya dapat dipertingkatkan melalui pengubahsuaian sesuai dengan bahan pencemar yang digunakan. Pengubahsuaian dengan rawatan kimia misalnya rawatan asid, alkali dan ejen pengeringan dengan dos yang optimum didapati memberi kesan terhadap pemilihan penjerapan analit. Secara keseluruhan, rawatan alkali lebih sesuai bagi bahan pencemar lazim misalnya logam, racun mahluk perosak, dan pewarna alkali. Sementara itu, rawatan asid lebih sesuai untuk bahan pencemar organik yang tidak berkutub misalnya fenol. Aliran terkini dalam aplikasi biojisim kelapa sawit sebagai bio-pengerap juga dibincangkan bagi membuka laluan baharu untuk pembangunan mampan.

**Kata kunci:** biojisim kelapa sawit, penjerap, karbon teraktif, pencemar alam sekitar

## Introduction

In recent years, increasing costs and environmental considerations have led to the use of new low-cost adsorbents derived from renewable resources. Numerous researches have expanded the idea of utilizing inexpensive adsorbents from natural materials, such as agricultural waste and minerals for removal of environmental pollutants. We have dedicated time in search towards a greener and sustainable alternative adsorbents for removal of pollutants using biomaterials such as starch [1], alginate [2], agarose [3], and chitosan [4, 5]. The booming of the *Elais guineensis*, or generally known as oil palm, triggered the massive increase in oil palm plantation area of more than 5.74 million hectares in Malaysia in 2016 [6]. With the rapid growth of palm oil production, the amount of waste generated also shows a corresponding increase. An approximate 85.5% of agricultural wastes in Malaysia came from palm oil plantations [7]. The oil palm biomass waste consists of mainly empty fruit bunches (EFB), shell and kernels, fronds, leaves and trunks. The huge amount of waste generated has to be utilized efficiently to promote sustainability.

Currently, various technologies have been applied to convert palm oil waste to renewable energy, value-added products and bio-based products such as pellet for feedstock, fertilizers, fillers, bioplastics and adsorbent (Figure 1). Limited work has been made to retrieve valuable components such as carotene, tocopherols and tocotrienols in residue oil from palm pressed fibers [8]. However, there have been considerable developments where oil palm waste is turned into adsorbents via activated carbon, char, ash and combination with other suitable material to enhance its ability and selectivity for adsorption. This article reviews current trends in physical and chemical preparation treatments of different parts of palm oil waste as adsorbent to maximize its potential for selective removal of assorted environmental pollutants such as dyes, pesticides, metals and other organic pollutants.

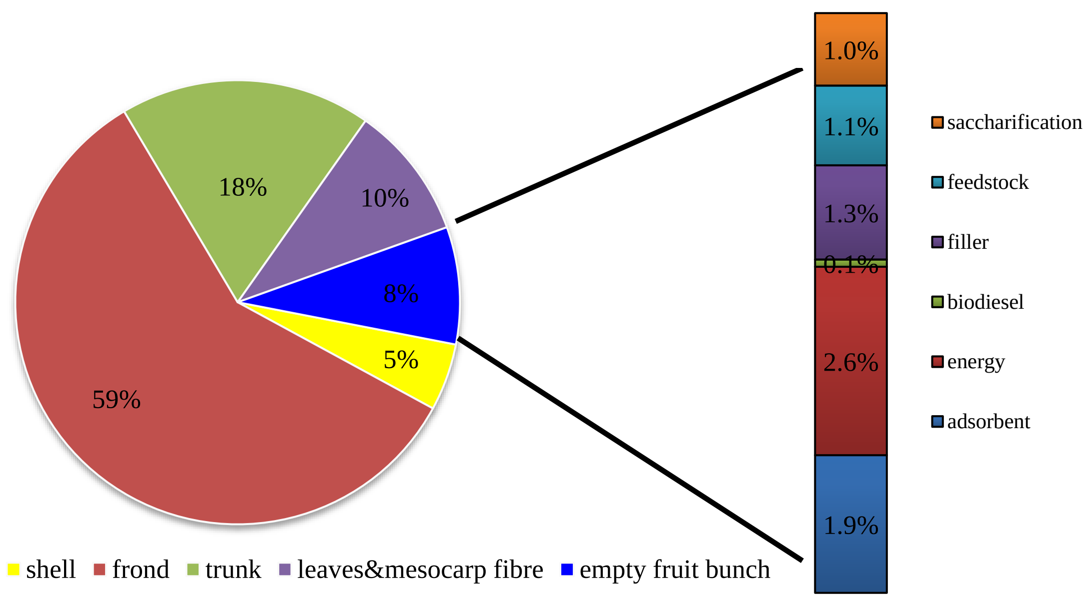


Figure 1. Oil palm biomass percentage in 2009 [9] and percentage of work towards recyclability of oil palm empty fruit bunch in recent years (2013-2016) [10]

**Oil palm waste as adsorbent**

In general, oil palm mills generate a number of biomass wastes. The amount of biomass produced by an oil palm tree, inclusive of the oil and lignocellulose materials is on the average of 231.5 kg dry weight/year [7]. EFB and mesocarp fiber is the highest contributor of oil palm waste, with approximately 15.8 and 9.6 million tonnes, respectively [11]. EFB, mesocarp fiber and shells are collected during the pressing of sterilized fruits whilst oil palm fronds are available daily throughout the year when the palms are pruned during the harvesting of fresh fruit bunch for the production of oil. Oil palm trunk is obtained during the replantation of the oil palm trees that occurred every 15-20 years. Recent research output proved that each part of oil palm waste could be converted into value added products such as oil palm activated carbon that has been used to treat air toxics such as carbon monoxide (CO) and sulphur oxides ($SO_x$) [12, 13].

The adsorbent obtained from different parts of oil palm biomass show different morphology in accordance to its composition (Table 1) as it was turned to activated carbon for the enhancement of adsorption process. Biomass with higher cellulose composition will produce low molecular weight products comprising anhydro-sugar, aldehyde, hydroxyl, furan, acetic acid and the carbonaceous chars. On the other hand, when lignin decomposes under elevated temperature, unsaturated chain and phenolic compounds with higher molecular weight, such as eugenol, styrene, alcohols, and carbonaceous chars will be produced [14]. This occurrence will in turn have an effect on selectivity of the analytes towards the carbon produced.

Table 1: Basic composition percentage of oil palm waste

| Oil Palm Waste | Cellulose (%) | Hemicellulose (%) | Lignin (%) | Inorganic Compounds (%) | Waste Percentage Generated from Palm Oil Industry (%) | References |
|---|---|---|---|---|---|---|
| Empty fruit bunch | 25 | 28 | 27 | 16 | 22 | [15] |
| Frond | 35 | 36 | 29 | n.a. | 14 | [16] |
| Shell | 28 | 22 | 44 | n.a. | 5 | [17] |
| Trunk | 50 | 70 | 20 | n.a. | n.a. | [18] |
| Leaves/mesocarp fiber | 45 | 48 | 27 | n.a. | n.a. | [19] |

* n.a. – not available

The adsorption characteristics of activated carbons are generally governed by the surface area pores formation on the surface, and surface functional groups. It is believed that mesopores are more suitable for adsorption as compared to micropores and macropores [18]. Surface functional groups play an important role during cationic and anionic adsorbate removal. Thus the specific treatment of each part of oil palm waste is a crucial step in the advancement of oil palm waste based adsorbent.

The difference in thermal treatment gave a significant impact on the textural properties of the oil palm-based adsorbent. This was proven by Hamza et al. [20] who reported that the pore networks in oil palm shell increased with increase of up to 700 °C. Nomanbhay et al. [15] found that microwave assisted extraction followed by basic treatment of oil palm EFB significantly improved the saccarification of EFB by removing more lignin and hemicellulose, and increasing the accessibility to hydrolytic enzymes. Furthermore, a recent study also concluded that the increment of activation temperature on oil palm empty fruit bunch will noticeable decrease the pore size, increase the surface area and the amount of carbonyl groups, thus increasing the probability of phenolic analyte adsorption [21].

The use of dehydrating agent can be categorized into either acid or basic treatment, whereby both treatments are efficient methods used to produce adsorbents with high surface area and porosity. Wirasnita et al. [22] found that the evaporation of the chemicals impregnated on the surface of the precursor-EFB, formed smaller cavities during activation process, and at the same time restricts the formation of tar.

Other impregnation treatments such as chitosan coating-oil palm waste – based adsorbent was also studied to improve the structure and surface area of the adsorbent [23]. The coating was found to increase its hydroxyl groups for more adsorption of polar pollutants. Such treatment onto different parts of oil palm waste to develop suitable adsorbent was discussed in accordance to the type of pollutants generally common in water matrices.

**Removal of dyes using oil palm adsorbents**

Dyes are a major source of pollution that is generally present in effluents from textile industries. These dye effluents are considered toxic as they reduce photosynthetic activity due to the coloration of water, and in turn affects the symbiotic process in the aqueous system. Palm oil mill effluents derived from bleaching process can cause coloration of streams. Thus, adsorption studies have been carried out using oil palm biomass-based adsorbents for the removal of dyes in streams.

The procedure of turning waste into adsorbents generally requires physical treatment. This was evident from recent studies on the removal of dyes (Table 2). Hameed et al. [24] postulated that pyrolysis at an optimum temperature of 862 °C can change the characteristics of oil palm EFB-based carbon for maximum removal of targeted dye, methylene blue. They also applied the same procedure to prepare adsorbent from oil palm trunks without treatment and found high malachite green uptake of 149.35 mg/g [25]. Meanwhile, Montoya-Suarez et al. [26] studied the physical treatment of oil palm shell at 600-800°C and obtained adsorbent with high surface area of 1268 $m^2$/g.

Sajab et al. used oil palm EFB for the removal of anionic and cationic dyes [27]. They noticed changes in selectivity when using different types of treatments. The EFB-citric acid treated is more selective towards targeted cationic dye (methylene blue) with an uptake of 450.4 mg/g of adsorbent, whilst EFB-polyethylene imine has higher tendency to adsorb the targeted anionic dye (phenyl red) with 555.4 mg/g [28]. When combined in a continuous column bed, EFB-polyethylene imine was more dominant compared to EFB-citric acid, which influenced the simultaneous adsorption of methylene blue and phenyl red.

The ability of oil palm fiber-based adsorbent was investigated by Kietkwanboot [29] for the decolorization of highly alkaline palm oil mill effluent (POME). With the combination of oil palm fibers and *Trameters hirsuta* AK4 microorganism embedded onto the fiber, up to 82.4% POME decolorization was achieved. Meanwhile, Hussin et al. [30] successfully treated oil palm fronds with mixtures of acid and basic treatment to extract microcrystalline cellulose and tested the adsorption of methylene blue with a mild uptake of 51.81 mg/g.

The oil palm ash from oil palm waste was tested for its adsorption ability by Khanday et al. [25]. To compensate for the loss of lignocellulose in oil palm ash, it was added with chitosan and treated using sodium hydroxide for the removal of methylene blue and acid blue 29 dyes. They noticed that both acid blue 29 and methylene blue were able to be absorbed by the oil palm ash-chitosan adsorbent with and uptake of 270 mg/g and 199.2 mg/g, respectively. This was due to the presence of more anionic sites from the oil palm ash and cationic sites from amino and hydroxyl groups from chitosan.

Wong et al. took it one step further by using oil palm shell activated carbon with the addition of magnetic nanoparticles for easier separation of adsorbents from water samples [31]. They tested and found that it has the ability to adsorb methylene blue with a good uptake of 163.3 mg/g due to hydrophobic interactions between oil palm shell and analytes, and the presence of magnetite that contributes via ionic interaction between metal and analytes.

Table 2. Literature studies on preparation of oil palm waste-based adsorbent for removal of dyes

| Oil Palm Waste Part | Activation Temperature | Treatment | Dyes | Removal Percentage / Uptake | Ref. |
|---|---|---|---|---|---|
| Oil palm EFB | 862 °C | Potassium hydroxide | Methylene blue | 400 mg/g | [24] |
| | 120 °C | Citric acid and polyethylene imine | Methylene blue and phenyl red | 130 mg/g and 170 mg/g | [28] |
| Oil palm fibers | Nil | *Trameters hirsuta* fungus | Decolorization POME* | 82.4% | [29] |
| Oil palm fronds | Room temperature | Acetic acid and sodium hypochlorite, followed by sodium hydroxide | Methylene blue | 51.81 mg/g | [30] |
| Oil palm fronds and leaves | 80-100 °C | Nil | Methylene blue | 88.72% | [32] |
| Oil palm trunks | Nil | Nil. | Malachite green | 149.35 mg/g | [25] |
| Oil palm shell | Microwave | Zinc chloride | Methylene blue | 0.73 mg/g | [33] |
| | 600-800 °C | Nil | Methylene blue | 110 mg/g | [26] |
| | | Magnetic nanoparticle | Methylene blue | 163.3 mg/g | [31] |
| Oil palm ash | Nil | Nil | Bleaching palm oil | 97.3% | [34] |
| | Nil | Sodium hydroxide and chitosan addition | Methylene blue and acid blue 29 | 192.2 mg/g and 270.3 mg/g | [35] |

POME – palm oil mill effluent, Nil – no treatment reported.

**Removal of pesticides using oil palm adsorbents**

Pesticides are one of the sought-after environmental pollutants for their carcinogenic effects and accumulation into aquatic life that will cause dire effects to human health. The chosen oil palm waste-biosorbents need to have the chemical affinity towards these polar pesticides for successful adsorption.

Oil palm EFB-based adsorbent was chemically treated with basic solution of ammonia solution for the removal of 2,4,6-trichlorophenol with an impressive uptake of 168.89 mg/g [36]. Salman et al. [37] used similar KOH treatment on oil palm fronds for successful removal of bentazon. Oil palm shell treated with NaOH reported by Hamad et al. [38] gave a maximum uptake of 454.5 mg/g of 4-chloroguiacol. Hamad et al. [39] also found that with the use of $K_2CO_3$ as activating agent, the oil palm shell based adsorbent is able to successfully remove 2,4-dichlorophenol with an uptake of 323.62 mg/g. The use of alkaline treatment was found to effectively remove the hemicellulose part of oil palm EFB [40], leaving the lignin and cellulose part as an active adsorption sites.

Yavari et al. [41] worked on oil palm EFB using low temperature pyrolysis at 300-700 °C for the synthesis of biosorbents for the removal of imazapyr and imazapic herbicides and concluded that the reduction of pyrolysis temperature increased the adsorption of polar analytes. Similar results were reported by Salman et al. [42] who prepared oil palm fronds-based adsorbents using pyrolysis and used it for the removal of glyphosate with an uptake of 104.2 mg/g. Beforehand, most of the studies used a temperature of above 800°C for the preparation of the adsorbent [43, 44]. Tan et al. [45] described an ineffective adsorption using oil palm shell-based adsorbent that was treated with a solution of $HNO_3$ for atrazine removal with uptake of a mere 0.046 mg/g. This showed that basic treatment is preferred for the adsorption of pesticides, as it provided basic sites for the adsorption of pesticides to occur. The maximum uptake levels of various pesticides using oil palm biomass-based adsorbents are listed in Table 3.

Table 3. Literature studies on preparation of oil palm waste-based adsorbents for removal of pesticides

| Oil Palm Waste Part | Activation Temperature | Treatment | Pesticides | Removal Percentage / Uptake | Ref. |
|---|---|---|---|---|---|
| Oil palm EFB | 814 °C | Potassium hydroxide | 2,4,6-tricholorophenol | 168.89 mg/g | [43] |
| | 814 °C | Ammonia | 2,4-dichlorophenol | 285.71 mg/g | [36] |
| | 300-700 °C | Nil | Imazapyr, imazapic | 24 mg/kg | [41] |
| Oil palm fronds | 850 °C | Potassium hydroxide | Bentazon | 99.85% | [37] |
| | 700 °C | Potassium hydroxide | Dichlorophenoxy acetic acid | 353 mg/g | [44] |
| | 700 °C | Potassium hydroxide | Glyphosate | 104.2 mg/g | [42] |
| Oil palm shell | 800 °C | Sodium hydroxide | 4-chloroguiacal | 454.5 mg/g | [38] |
| | | Nitric acid | Atrazine | 0.046 mg/g | [45] |

**Removal of metal using oil palm adsorbents**

Metal pollution is one of the most important environmental concerns due to their toxicity and accumulation in the food chain. Wastewaters from various industries such as mining, metallurgical and electronics may contain one or more toxic metals. Oil palm biomass waste has been investigated for the removal of diverse metals from water. Salamantinia et al. [46] investigated copper and zinc uptake using oil palm fronds-based adsorbents. Oil palm EFB-based biosorbents were thoroughly investigated by Wahi et al. [47]. They used chemical treatment with NaOH at activation temperature of 400-700 °C to prepare the adsorbent. The removal uptake for copper, lead and mercury were at a high of 52.5 mg/g. Meanwhile, Montoya-Suarez et al. [26] found that adsorbent obtained from pyrolysis of oil palm shell at 600-800 °C was able to remove only 0.37 mg/g of chromium ions. Similar findings were reported by Rehman et al. [48] who studied oil palm clinker sand as adsorbents and obtained an arsenic uptake of 9 mg/g. However, a recent work by Daneshfozoun et al. [49] who used grinded oil palm EFB without any treatment for removal of lead in water and found that the lead uptake is at par with alkaline-treated based adsorbent with an uptake of 47.49 mg/g. It was observed that the metal ion adsorption occurs onto the lignocellulose sites in the adsorbent. With pyrolysis, the disappearances of cellulose sites decrease the uptake of metals onto the adsorbent.

Table 4. Literature studies on preparation of oil palm waste-based adsorbent for removal of heavy metal

| Oil Palm Waste Parts | Activation Temperature | Treatment | Metal Ions | Removal Percentage / Uptake | Ref. |
|---|---|---|---|---|---|
| Oil palm EFB | 400-700 °C | Sodium hydroxide | Cu, Pb, Hg | 52.5 mg/g | [47] |
| | Nil | Grinded | Pb | 47.49 mg/g | [49] |
| | Nil | Magnetic nanoparticle | Pb | 93.7% | [50] |
| Oil palm fronds | 70 °C | Sodium hydroxide | Zn, Cu | 90% | [46] |
| Oil palm shell | 600-800 °C | Nil | Cr | 0.37 mg/g | [26] |
| Oil palm ash | Nil | Nil | As | 9 mg/g | [48] |

**Removal of phenolic compounds using oil palm adsorbents**

Oil palm waste-based adsorbents have also been applied in the removal of other phenolic compounds (Table 5). Lua and Jia [51] used oil palm shell treated at steam activation temperature of 675 °C to produce the adsorbents for phenol removal. They reported a successful removal of phenol with an uptake of 166 mg/g. Alam et al. [52] also used steam activation for the preparation of oil palm EFB-based adsorbent obtained at a temperature of 800 °C with an uptake of 300 mg/L water. This indicates that the uptake of phenolic compounds increases with higher activation temperature. Al-Aoh et al. [53] examined oil palm ash that has been treated with acid and found that the uptake of 4-nitrophenol was high (1000 mg/g). Hamad et al. [38, 39] reported the removal of chlorinated phenolic compounds using oil palm shell activated at a high temperature of 800 °C with potassium carbonate treatment to attract the anion site of the analyte. Thus, it is apparent that high activation temperature serves as the main factor in increasing the phenolic compound adsorption capacity. Elevated activation temperatures and further acidic treatment tend to decrease the amount of oxygen groups from cellulose, thus helping in the formation of more non-polar sites on the adsorbent that in turn increases the adsorption ability of the adsorbent towards organic pollutants.

Table 5. Literature studies on preparation of oil palm waste-based adsorbent for removal of phenol

| **Oil Palm Waste Parts** | **Activation Temperature** | **Treatment** | **Analyte** | **Removal Percentage / Uptake** | **Ref.** |
|---|---|---|---|---|---|
| Oil palm EFB | 800 °C | Nil | Phenol | 200-300 mg/L | [52] |
| Oil palm shell | Steam 675 °C | Nil | Phenol | 166 mg/g | [51] |
| | 800 °C | Potassium carbonate | 4-Cl-2-methyoxyphenol | 323.62 mg/g | [39] |
| Oil palm ash | Nil | Sulfuric acid | 4-nitrophenol | 1000 mg/g | [53] |

* nil – no further treatment

## Conclusion

To uphold sustainability in the expanding palm oil industry, oil palm waste was proven a viable alternative source of adsorbent for various types of pollutants. Surface modification by physicochemical methods directs an alternative approach for the improvement of each oil palm waste-based adsorbents towards the pollutant uptake from aqueous solution. Therefore, the technique of choice could be attuned in accordance to the analytes of interest. It was also observed that for different part of oil palm waste, different activation treatment is needed for optimum removal of targeted pollutants. In general, physical activation at high temperatures was needed for all parts of oil palm bio-waste for the adsorption of organic pollutants as more covalent and hydrophobic interactions may occur on the surface of the activated carbon. Chemical treatment of the adsorbent is to improve the selectivity of the adsorbent towards the analyte. Basic treatment is more suitable for anionic dyes such as acid blue 29 and phenyl red compared to cationic dyes. The addition of dehydrating agents such as zinc chloride affects the physical type of pore produced on the adsorbent.

Most of the studies reported on the removal of pesticides utilized basic treatment (ammonia, potassium hydroxide and sodium hydroxide) for enhanced chemisorption of the pesticides onto the oil palm waste-based adsorbents. The use of acid treatment reduces the uptake of pesticides, as they are repelled from the active sites of the adsorbent. It is noteworthy that adsorbents obtained from oil palm waste via basic treatment are favorable for the removal of metal ions. This preparation technique generates more hydroxyl active sites on the surface of the oil palm waste-based adsorbents for more efficient removal of metal ions. The trends also show that most organic pollutants studied favor adsorbent prepared using acid treatment and higher temperature. This is because less oxygenated active sites are produced, thus more non-polar interactions occur, increasing the uptake of organic pollutants such as phenols and glyphosate. Despite numerous works on oil palm waste-based adsorbents, there seem to be the lacking of studies on the addition and combination of other compounds with oil palm waste-based adsorbents in pursue of improved adsorbents. Thus, there is ample opportunity for future investigations such as combining palm oil waste-based adsorbents with compounds such as molecular orbital framework compounds or polymers. Such innovations might increase the chances of these low-cost adsorbents to be used as greener and more sustainable alternatives to more conventional adsorbents.

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