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Modified Activated Carbon Synthesized from Oil Palm Leaves Waste as a Novel Green Adsorbent for Chemical Oxygen Demand in Produced Water

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Abstract: Palm tree waste is one of the most widespread forms of agricultural waste, particularly in areas where oil palms are cultivated, and its management is one of the industry’s key concerns. To deal with this palm waste, researchers are working hard to work out the ways to convert this plentiful waste into useful material for future beneficial applications. The objective of this study was to employ chemical activation techniques to prepare a new activated carbon (AC) using discarded oil palm leaves (OPL) in Malaysia. Three chemical agents (H₃PO₄, NaOH and ZnCl₂), as well as three pyrolysis temperatures (400 °C, 600 °C and 800 °C) and various impregnation ratios (1:0.5–1:3) were used to optimize the preparation process. As a result, the oil palm leaves activated carbon (OPLAC), with prominent surface properties, was obtained by ZnCl₂ activations with a 1:1 impregnation ratio and carbonized at a pyrolysis temperature of 800 °C. The OPLAC-ZC had a surface area of 331.153 m²/g, pore size of 2.494 nm and carbon content of 81.2%. Results showed that the OPLAC-ZC was able to quickly (90 min) remove the chemical oxygen demand (COD) from produced water (PW), through chemical adsorption and an intraparticle diffusion mechanism. The material followed pseudo-second order kinetic and Freundlich isotherm models. The maximum adsorption capacity of organic pollutants forming COD in PW was found to be 4.62 mg/g (59.6 ± 5%). When compared to previous studies, the OPLAC-ZC showed equivalent or better COD removal capability. It is the first detailed study reporting the preparation of AC from OPL and applying it for organic pollutants adsorption forming COD in PW.

Keywords: wastewater; oil palm leaves activated carbon; chemical activation; COD; adsorption; green technology

1. Introduction

Activated carbons (ACs) have been widely used in adsorption studies due to their chemistry, textual qualities, high surface area and, most notably, surface adsorption properties, for a range of organic and inorganic compounds [1–6]. They have been proven to be extremely useful materials for the adsorption of different contaminants, such as pesticides [7], heavy metals [8,9], dyes [10,11] and hydrocarbons [12]. ACs are produced by combining activation processes (chemical and/or physical) with the thermal decomposition of carbonaceous raw materials [13]. There is growing interest to develop synthetic routes for ACs with stable structures and better adsorption properties, using sustainable and less expensive agricultural by-products. Various materials have been used in this regard, such as tea leaves waste [14], rice husk [15], apricot stones [16], avocado peels [17], pecan nutshell [5], banana peels [18], palm shells [19] and date palm stones [20].
Palm tree waste is one of the most common types of agricultural waste, especially in regions where oil palms are grown. The waste is found in deserts, tropical and semi-tropical regions all across the world [21]. A huge amount of palm waste, including palm seeds, leaves, leaflets, fibers, fronds, trunks, shells and fruit bunches is produced every year in these regions. In the worldwide market, Malaysia is a leading exporter of palm oil and generates huge amounts of waste each year [22]. The management of this waste is one of the major issues in the industry. Open burning is the traditional method of disposing of this waste. It creates smoke, lowers soil fertility and has long-term accumulative impacts on the ecosystem of neighboring countries [23–25]. This method has been banned due to its environmentally hazardous impacts. Palm waste is often littered in milling sites, resulting in contamination of the underground water by leaching [26]. It also releases harmful chemicals into the soil, creates insect colonies and pollutes the atmosphere. Researchers have been determined to investigate ways to turn the plentiful oil palm waste into useful material for future beneficial uses, in an attempt to handle the environmentally daunting palm waste.

Over the years, oil palm waste has been investigated to be used as a precursor material for AC because of its high carbon content. It has been used for the adsorption of various organic and inorganic pollutants in wastewater, such as oil palm shell AC being used for the adsorption of methylene blue (MB) [27] and phenol [28]. Oil palm frond AC was used for adsorption of 2, 4-dichlorophenoxyacetic acid [7] and Janus green dye [29]. Palm empty fruit bunch AC was used for the adsorption of dyes [30] and oil palm kernel shell AC was used for the adsorption of chemical oxygen demand (COD) and color [4]. Oil palm fiber has been reported to have been used for the adsorption of chromium (VI) [31]. However, only a few studies have reported the preparation of AC using the abundantly available oil palm leaves (OPL) waste [32]; no study has been found in Malaysia. Hence, this study focused on the preparation of a novel AC using the OPL waste in Malaysia. The characteristics of AC are dependent on the nature of the precursor material and the activating agent's performance [13]. Chemical activation uses chemical agents for activation, such as alkalis, acids and oxidizing agents, whereas physical activation includes gases, such as steam or CO₂. Usually, chemically activated carbons need a lower temperature and time during thermal decomposition, and also have higher porosity obtained in the final products, when compared to physically activated carbons [33].

The objective of this study was to prepare an oil palm leaves AC (OPLAC) with a comparatively higher surface area and carbon content, to be used as an adsorbent for organic pollutants forming COD in produced water (PW). The PW is a large effluent, generated as a result of oil extraction, accounting for around three times the amount of extracted oil [34]. Three chemical agents, viz., H₃PO₄, NaOH and ZnCl₂ were used for the activation of OPLs. The OPLACs were prepared initially at 800 °C with a 1:1 impregnation ratio. The OPLAC with the highest surface area was further evaluated for carbon content at three pyrolysis temperatures (400 °C, 600 °C and 800 °C) and chemical agent to material ratios (1:0.5–1:3). The OPLAC with the highest surface area and carbon content was applied for the adsorption of organic pollutants forming COD in PW. The effects of adsorption factors, such as adsorbent dosage, initial pH and contact time on the COD removal percentage were studied. The equilibrium isotherm and kinetic studies were also performed. A comparative analysis with other studies was made to evaluate the performance of the prepared OPLAC. It is the first detailed study reporting the preparation of AC from OPL and applying it for COD removal in PW. The study will help to extend the application of abundantly available OPL waste, to achieve the goals of sustainable development through waste management.

2. Materials and Methods

2.1. Materials

The OPL waste was collected from FELCRA Berhad Kawasan Nasaruddin Belia, Perak in Malaysia. The chemicals including H₃PO₄, NaOH and ZnCl₂ were purchased from
Avantis Laboratory Supply. PW was collected from an oil and gas company operating in Southeast Asia.

2.2. Synthesis of OPLAC

The OPLAC was prepared in three steps. The steps included pre-processing of OPL, processing of OPLAC synthesis and post-processing of OPLAC. In a pre-processing step, the OPL were washed, air dried, cut into small pieces, ground and sieved to 0.5 mm particle size.

In the processing step of OPLAC preparation, the leaf mass was activated using three chemicals and carbonized using three impregnation ratios and temperatures. The purpose was to prepare the OPLAC with the highest surface area and carbon content. As activation agent plays major role in forming the well sized pores and increasing the surface area of ACs, the surface area was considered as evaluation criteria for selection of activation agents. The carbonization majorly depends on the pyrolysis temperature and IR of the material. Therefore, it was considered as the evaluation criteria for the carbon content. The processing steps are shown in Figure 1. Briefly, the leaf mass was chemically activated by wet impregnation technique using an acidic (H₃PO₄), basic (NaOH) and oxidizing agent (ZnCl₂). The leaf mass was soaked overnight in chemical solutions of 0.25 M H₃PO₄, 0.1 M NaOH and 0.1 M ZnCl₂ with impregnation ratio of 1:1 (w/w). The soaked OPL mass was carbonized in a tube furnace (MTI Corp, Model: OTF-1200X-S) at 800 °C for 2 h with a heating rate of 10 °C/min in the presence of N₂ gas purged at 150 cm³/min. The prepared ACs were named OPLAC-HP, OPLAC-NO and OPLAC-ZC based on activating agents H₃PO₄, NaOH and ZnCl₂, respectively. Among three OPLACs, the OPLAC with the highest surface area was further tested for carbon content by varying temperatures from 400–800 °C and impregnation ratio from 1:0.5–1:3. The surface areas of OPLACs were determined using Brunauer–Emmett–Teller (BET) TriStar II 3020 V1.04. The moderate temperature range of 400–800 °C was selected to avoid incomplete carbonization at low temperatures and higher ash content at high temperatures [21]. The carbon content was determined using a scanning electron microscope equipped with energy-dispersive X-ray spectroscopy (SEM-EDX) technique.

In the post-processing step, the prepared OPLACs were washed repeatedly using 0.1 M HCl and dried in an oven at 105 °C for 12 h. The OPLACs were stored in air-tight storage bottles for further use.

The yield of OPLACs can be calculated using the following equation [35]:

\[
\text{Yield of OPLAC} = \frac{\text{g of OPLAC}}{\text{g of dried OPL}} \times 100
\]
Prepare OPLAC using 3 chemical agents
(800 °C, 1:1)
H$_3$PO$_4$, NaOH, ZnCl$_2$

Select OPLAC with highest surface area

Preparation of OPLAC at 3 carbonization temperatures
400 °C, 600 °C, 800 °C

Select OPLAC with highest carbon content

Preparation of OPLAC at 3 impregnation ratio
1:0.5, 1:1, 1:2, 1:3

Select OPLAC with highest Carbon content

The OPLAC with highest surface area and carbon content is used for adsorption of COD in WW.

Figure 1. Schematic diagram of OPLAC preparation.

2.3. Characterization of AC and PW

The surface functional groups of OPLAC were analyzed by Fourier transformed infrared spectroscopy (FTIR). The Nicolet Magna 550 spectrometer in KBr was used to obtain FTIR spectra of 5 mg finely ground sample with a scan range of 400–4000 cm$^{-1}$. Elemental composition was found by Zeiss EVO LS15 SEM-EDX under high vacuum condition and 15 kV EHT. The surface areas and pore volumes of OPLACs were determined using BET analysis on isotherm obtained by nitrogen adsorption-desorption experiment. The sample was first degassed at 300 °C for 240 min with 10 °C/min ramp rate under
vacuum environment. Then nitrogen adsorption-desorption experiment was conducted for up to 13 selected equilibrium points. The quantitative and qualitative analysis of the chemical composition of OPLACs was conducted using X-ray photoelectron spectroscopy (XPS) (Micromeritics, Tristar II) with Al K alpha source and background spot of 400 µm. The crystalline properties of OPLAC were determined by X-ray diffraction (XRD) analysis using a Panalytical X'pert3 powder diffractometer. The scanning angle (2θ) was 2–79.99° with a step size of 0.026 s/step.

The water quality parameters of PW are given in supplementary information in Table S1. The PW was mainly analyzed for COD content using HACH DR spectrophotometer and high range COD vials. Briefly, 2 mL of PW sample was poured to the COD vial and kept in a heated digester at 150 °C for 2 h. A blank was also prepared using similar method. The COD concentration (mg/L) was measured after 2 h using USEPA method 800 under programme 430 [36]. The total COD content of PW was 2000 mg/L, whereas the dissolved COD content was 1344 mg/L. Suspended COD was removed using suction filtration unit.

2.4. Adsorption Batch Experiments

To examine the dissolved COD removal capability of OPLAC, batch experiments were conducted at various pH, dosage of AC and contact times. PW was filtered through Whatman filter paper of 45 mm Ø, using suction filtration unit to remove the suspended particles. The experiments were conducted using a hot plate with magnetic stirrer, taking 50 mL of PW in a beaker. Adsorption capacity was evaluated at pH range of 2–12, contact time of 10 min–24 h and adsorbent dosage of 10–3000 mg/L. The samples were placed for stirring at 220 rpm at 25 ± 1 °C. After termination of the stirring time, samples were taken out, filtered with 0.45 µm syringe filter and tested for final COD amount using spectrophotometer.

2.5. Adsorption Isotherm Modelling

To analyze the experimental data from adsorption equilibrium investigations, the Langmuir isotherm model (LIM) and Freundlich isotherm model (FIM) were employed. The experiments were performed for 10–3000 mg/L OPLAC dosages at 25 ± 1 °C.

LIM is the simplest adsorption model and applies to ideal conditions. The model is applicable for monolayer physical adsorption of fluids [37]. Its assumptions include; (i) the adsorption is deemed complete when a monolayer covers all active sites, (ii) each site can hold one molecule that has been adsorbed, the surface is homogeneous and all active sites are identical and, (iii) the occupancy of adjacent sites has no effect on the adsorption of a molecule at a given site [38]. Equation (2), below, represents the linear form of LIM [39]:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_{\text{max}}} + \frac{C_e}{q_{\text{max}}}
\]

where \(q_e\) represents the mg of adsorbate adsorbed per gram of adsorbent and \(C_e\) represents the equilibrium adsorbate concentration in solution. \(K_L\) (L/mg) is the Langmuir constant, and \(q_{\text{max}}\) is the maximum adsorption capacity of adsorbate (mg/g) [40].

The FIM is mostly applied to characterize the non-ideal adsorption properties of heterogeneous surfaces [41]. It considers that there are various types of accessible sites operating at the same time, each with a different sorption energy [42]. Equation (3) represents the linear form of the FIM [43], shown here:

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

where \(K_f\) is FIM constant (mg/g) and \(n\) is adsorption intensity. When \(\frac{1}{n} = 1\), it shows that partitioning between the two phases is unaffected by concentration. When \(\frac{1}{n} < 1\), the adsorption is normal. Conversely, a value of \(\frac{1}{n} > 1\) implies cooperative adsorption [44].
2.6. Adsorption Kinetic Modelling

Pseudo-first order (PFO), pseudo-second order (PSO) and Weber and Morris (WM) intraparticle diffusion models were used to study the kinetics of COD removal by OPLAC. Batch experiments were conducted from 10 min to 24 h duration. All kinetic models were evaluated based on the $R^2$ value to compare their performance in describing the kinetics of COD removal by OPLAC.

PFO kinetic model explains the relationship between the rate at which adsorbent sorption sites are occupied and the number of empty sites [45]. The model is based on the premise that adsorption rate is governed by adsorbate diffusion. Equation (4), shown below, is the linear form of the PFO kinetic model:

$$\ln(q_e - q_t) = \ln q_e - K_1 t$$  \hspace{1cm} (4)

where $K_1$ is rate constant of PFO adsorption (min$^{-1}$), $q_t$ is adsorption capacity at time $t$ (mg/g) and $q_e$ is equilibrium adsorption capacity (mg/g). The model’s parameter $K_1$ and $q_e$ are calculated by plotting $\ln(q_e - q_t)$ vs. $t$.

The PSO kinetic model, which is represented by Equation (5), explains the dependence of the adsorbent’s adsorption capacity on time [46]. The model assumes that the chemical adsorption is the rate limiting step due to surface adsorption interactions. Equation (5) is shown below:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (5)

where $K_2$ is second order rate constant of adsorption (g/mg/min). The model’s parameter $K_2$ and $q_e$ are calculated by plotting $\frac{t}{q_t}$ vs. $t$.

Weber and Morris (WM) Intraparticle diffusion model is used to understand the intraparticle diffusion process and to find out the rate controlling step [47]. Equation (6) shows the linear form of the model. When intraparticle diffusion is the governing mechanism, the plot of $q_t$ versus $t^{1/2}$ is a straight line that passes through origin. Otherwise multiple processes are involved to regulate the adsorption [48]. Equation (6) is shown below:

$$q_t = K_i t^{1/2} + C$$  \hspace{1cm} (6)

where $K_i$ is rate constant of intraparticle diffusion (mg/g/min$^{1/2}$) and $C$ (mg/g) is intercept of intraparticle diffusion. The model’s parameters $K_i$ and $C$ are calculated by plotting $q_t$ vs. $t^{1/2}$.

3. Results and Discussion

3.1. Surface Areas of OPLACS

The three ACs, viz., OPLAC-HP, OPLAC-NO and OPLAC-ZC were characterized for their surface area, total pore volume, pore size and percentage yield (Table 1). The results showed that OPLAC-ZC had the largest BET surface area, pore volume and pore size, compared to the other prepared ACs. A larger surface area indicated the availability of more adsorption sites for OPLAC-ZC, compared to OPLAC-HP and OPLAC-NO.

| Activated Carbon | BET Surface Area (m²/g) | Total Pore Volume (cm³/g) | Average Pore Size (nm) | Yield (%) |
|------------------|-------------------------|---------------------------|------------------------|-----------|
| OPLAC-HP         | 255.840                 | 0.166                     | 2.5                    | 42        |
| OPLAC-NO         | 267.719                 | 0.0521                    | 0.8                    | 46        |
| OPLAC-ZC         | 331.153                 | 0.206                     | 2.5                    | 42        |

3.2. Surface Functional Groups of OPLAC-ZC

OPLAC-ZC not only had dominant surface properties but also surface functional groups, evident from the FTIR spectra. For the analysis of functional groups present at the
surfaces, the three ACs were characterized using FTIR. The results are given in Figure 2. The FTIR spectra of OPLAC-HP, OPLAC-NO and OPLAC-ZC showed broad peaks around 3414, 3437 and 3424 cm$^{-1}$, respectively, suggesting the presence of a $-\text{OH}$ stretching vibration in the hydroxyl groups [49]. The peaks for OPLAC-ZC had the lowest transmittance values, showing the presence of higher hydroxyl groups at the surface, compared to OPLAC-HP and OPLAC-NO. An intense peak of C=O stretching compounds including esters, aliphatic ketones and aldehydes was observed for OPLAC-ZC (1725 cm$^{-1}$), compared to OPLAC-HP (1730 cm$^{-1}$) and OPLAC-NO (1733 cm$^{-1}$) [50]. The other peaks, around 1078, 1089, and below 470 cm$^{-1}$ wavenumbers suggested the presence of C-O and C=O stretchings and other complex deformations at the surface of the OPLACs [51]. The transmittance values were lower for OPLAC-ZC, indicating the presence of a higher number of functional groups at the surface. It indicated that OPLAC modified by ZnCl$_2$ had superior surface properties for the adsorption of organic pollutants forming COD, compared to the other two OPLACs.

Table 1. Physical properties of OPLACs.

| Activated Carbon | BET Surface Area (m$^2$/g) | Total Pore Volume (cm$^3$/g) | Average Pore Size (nm) | Yield (%) |
|------------------|-----------------------------|-----------------------------|------------------------|-----------|
| OPLAC-HP         | 255.840                     | 0.166                       | 2.5                    | 42        |
| OPLAC-NO         | 267.719                     | 0.0521                      | 0.8                    | 46        |
| OPLAC-ZC         | 331.153                     | 0.206                       | 2.5                    | 42        |

3.3. Elemental Composition of OPLAC-ZC

OPLAC-ZC was further characterized for its carbon content at various temperatures and impregnation ratios. Temperature ranging from 400–800 °C was used for the pyrolysis of ZnCl$_2$ impregnated OPL biomass (1:1). The carbon content was determined using SEM-EDX mapping. The results (Table 2) showed that increasing the temperature, from 400 °C to 800 °C, increased the carbon content of OPLAC-ZC, from 68.3% to 81.2%. The temperature was not increased beyond 800 °C, to avoid higher ash content in OPLAC-ZC. Therefore, 800 °C was considered to be the most suitable temperature for the preparation of OPLAC-ZC.
Table 2. Elemental composition of OPLAC-ZC at various temperatures and impregnation ratios.

| Elements | C   | O   | Zn  | Si  | Ca  |
|----------|-----|-----|-----|-----|-----|
| Temperature °C |     |     |     |     |     |
| 400      | 68.3| 20.2| 2.8 | 1.2 | 0.4 |
| 600      | 74.2| 14.29| 3.2 | 2.2 | 0.9 |
| 800      | 81.2| 9.6 | 4   | 4.2 | 1.1 |

| Impregnation ratio |     |     |     |     |     |
|--------------------|-----|-----|-----|-----|-----|
| 1:0.5              | 76.4| 11.3| 0.8 | 6.6 | 3   |
| 1:1                | 81.2| 9.6 | 4   | 4.2 | 1.1 |
| 1:2                | 70.9| 15.9| 1.7 | 6.1 | 1.9 |
| 1:3                | 68.3| 11.6| 7.4 | 5.4 | 4.3 |

The carbon content of OPLAC-ZC was analyzed further using various impregnation ratios at 800 °C. The highest carbon content, of 81.2%, was observed at an impregnation ratio, i.e., OPL biomass to ZnCl$_2$ ratio of 1:1 (Table 2).

Figure 3 shows the SEM images of OPLAC-ZC at the three temperatures and impregnation ratios. The images show that the porous structure was more apparent when the temperature was increased from 400 to 800 °C and at an impregnation ratio of 1:1. Hence, OPLAC-ZC modified by ZnCl$_2$, with an impregnation ratio of 1:1 and carbonized at a pyrolysis temperature of 800 °C, was considered the most suitable adsorbent prepared from OPL.

3.4. Chemical Composition and Crystallinity of OPLAC-ZC

Figure 4a represents the XPS analysis of OPLAC-ZC, where larger peaks of C and O can be observed at the surface. Figure 4b represents the C1s XPS spectra of the OPLAC-ZC, showing binding energies within a range of 284–289 eV. The peaks were assigned to C-C (284.98 eV), C-O/C-COO (286.28 eV), C-N/C-CON (287.28) and C=O/O-C=O.
The O1s spectra of OPLAC-ZC showed peaks at 531.18 eV, 532.18 eV, 533.18 eV and 532.28 eV (Figure 4c). The peaks were assigned to ZnO, C=O, O and C-O functional groups, respectively. The crystallinity of OPLAC-ZC was studied by XRD analysis, which is represented in Figure 4d. The multiple broad peaks in the range of 20–50 °C represented the 0 0 2 and 1 0 0 planes, reflecting the graphitic lattice structure of OPLAC-ZC [53]. The percentage of crystallinity is found by taking the ratio of the area of the crystalline peaks and the area of all the peaks in the XRD graph. The percentage of crystallinity was found to be 64.57%, using OriginPro. The broader peaks showed the presence of amorphous carbon rings at the surface [54].

3.5. Effect of Initial Solution pH on Removal of COD

The pH of a solution is a key parameter that affects an adsorbent’s effectiveness [55]. The adsorbate surface charge and degree of ionization of the adsorbent material are affected by the pH value of the solution and it has a significant impact on the adsorption process [56]. The adsorbent surface will be totally saturated with H+ ions under acidic conditions and the positively charged organic pollutants will be unable to compete for adsorption sites. The resistance from protons decreases as pH rises, allowing the positively charged organic pollutants to be adsorbed at the negatively charged sites on the adsorbent.
Batch experiments were conducted to study the effect of initial pH levels on adsorptive removal of COD in PW. The initial COD content of PW was 1344 mg/L. It was treated with OPLAC-ZC at various initial pH values, ranging from 2–12, at a dosage of 1000 mg/L and contact time of 60 min at 25 ± 1 °C. The initial pH of PW was adjusted using 0.01 M H₂SO₄ and NaOH. The final COD was measured after each experiment and the impact of pH on adsorptive removal of COD was studied. Figure 5a shows the results of the final COD in PW, with a change in the initial pH value. The results showed that COD in PW reduced from 1344 mg/L to 588 ± 5 mg/L (56.25 ± 5%), with an increase in pH from 2 to 7. A further increase in pH, from 8 to 12, slightly changed the COD amount. Hence, pH 7 was considered as optimum for the adsorption of COD using OPLAC-ZC. The pH value at which the net charge on the adsorbent’s surface is zero is called the point of zero charge (pH_{ZPC}). The surface is positively charged below pH_{ZPC} and functional groups are protonated. At a higher pH, the surface gets deprotonated and the negative charge predominates [57]. The pH_{ZPC} of OPLAC-ZC was found as a pH of 9 (Figure 5b). Higher COD adsorptive removal was observed at pH < pH_{ZPC}, when the surface of OPLAC-ZC was positively charged. It indicated that COD was highly favorable to be removed, due to protonated oxygenated functional groups, involving a π–π interaction between OPLAC-ZC and organic pollutants in PW. Many studies have reported that a pH value of 7–8 is the most suitable value for the removal of COD from wastewater [58].

![Figure 5. Effect of (a) pH; (b) pH_{ZPC}; (c) dosage of OPLAC-ZC; (d) contact time on adsorption of COD in PW.](image)

### 3.6. Effect of OPLAC-ZC Dosage on Removal of COD

The effect of the dosage of OPLAC-ZC on the removal of COD is shown in Figure 5c. The dosage was varied from 10–3000 mg/L, at a pH of 3 and contact time of 60 min. A significant decrease in the final COD amount occurred with the increase in dosage, up to 1000 mg/L. Increasing the dose further did not result in an increase in COD removal. Therefore, 1000 mg/L dosage of OPLAC-ZC was found to be the optimal dosage for the removal of COD. The final COD concentration was 542 ± 5 mg/L (removal efficiency 59.6 ± 5%) at this dosage.
3.7. Effect of Contact Time on Removal of COD

The effect of contact time on the removal of COD is shown in Figure 5d. The adsorptive removal of COD was considerably increased when the contact time was increased from 5 to 90 min. Increasing the contact time further did not improve the adsorption capacity. The adsorption rate was quicker at first because there were more accessible active sites on the OPLAC-ZC surface; however, the adsorption rate gradually declined as the active sites were gradually occupied until they became saturated. Hence, a contact time of 90 min was the optimal time for the removal of COD. The final COD concentration was $593 \pm 5$ mg/L (removal efficiency $55.8 \pm 5\%$) at this contact time.

3.8. Adsorption Isotherm Modeling

The study of isotherm models is an important step in choosing the best model to represent the adsorption process. Figure 6 shows the LIM and FIM for the adsorption of COD for OPLAC-ZC. The $R^2$ values of the linear regression lines produced from the FIM and LIM were 0.92 and 0.707, respectively, suggesting a much better fit for the FIM. The fitting of the adsorption data to the Freundlich model suggested that COD adsorptive removal took place on a heterogeneous surface, and may entail a multilayer adsorption process [59]. The FIM suggested that organic pollutants forming COD adsorbed on active sites, with different activation energies [34]. Other investigations have found similar findings for COD adsorptive removal in wastewaters [60]. Table 3 states the parameters of the isotherm models. A $1/n$ value was observed between 0 and 1, showing a favorable adsorption process.

Table 3. Isothermal adsorption modeling parameters for adsorption of COD onto OPLAC.

| Model | Parameters | Units | Values  |
|-------|------------|-------|---------|
| LIM   | $q_{\text{max}}$ | mg/g  | 4.62    |
|       | $K_L$      | L/mg  | 0.0025  |
|       | $R^2$      |       | 0.707   |
| FIM   | $K_F$      | mg/g  | 1.67505 |
|       | $1/n$      |       | 0.98    |
|       | $R^2$      |       | 0.92    |

Figure 6. Cont.
3.9. Adsorption Kinetic Modeling

The study of kinetics is essential in the treatment of wastewaters because it offers significant information about the adsorption mechanism. In 90 min, the COD adsorptive removal process reached equilibrium, and OPLAC-ZC became saturated, as shown in Figure 5c. It shows that one of the advantages of employing OPLAC-ZC as an adsorbent might be the ability to quickly absorb organic pollutants, measured as COD in PW. The kinetics of COD removal onto OPLAC-ZC were investigated using PFO, PSO and WM intraparticle diffusion models. Figure 6 shows that the PSO model best explained the COD adsorptive removal onto OPLAC-ZC, indicating that chemisorption controlled the process.

Table 4 shows the parameters of the three kinetic models employed in this study. The $R^2$ value obtained from the PSO kinetic model was higher than that obtained from the PFO kinetic model (Table 4). The adsorption capacity of 746.27 mg/g determined through the PSO model was also closer to the experimentally determined adsorption capacity of 802 mg/g. The model implied that chemical adsorption occurred while forming chemical bonds between the adsorbate and OPLAC-ZC’s surface functional groups, as well as electron transfer between them occurred [61]. The WM intraparticle diffusion model implied that the adsorption on the surface of the OPLAC-ZC was followed by a diffusion step and intraparticle adsorption process. Figure 6e shows that multiple steps were involved in
intraparticle diffusion of organic pollutants forming COD on to OPLAC-ZC, using the WM model. If the intraparticle diffusion plot showed a straight line, the intraparticle diffusion would be the single mechanism responsible for the adsorption process [62]. However, as seen in Figure 6e, three linear portions influenced the adsorption process, implying that three stages were involved in the adsorption process. The first, steeply sloping stage was related to surface diffusion, in which a high quantity of COD was immediately adsorbed through OPLAC-ZC’s surface active sites. The organic pollutants forming COD adsorbed to the inner surface of OPLAC-ZC pores, when almost all of the surface functional groups of the OPLAC-ZC were occupied, resulting in the second stage, which was the rate-limiting step [43]. The equilibrium state was achieved last, i.e., the third stage. In conclusion, according to the kinetic models, both chemisorption and intraparticle diffusion between the active sites of OPLAC-ZC and organic pollutants forming COD had an influence on the adsorption process.

Table 4. Adsorption kinetic modeling parameters for adsorption of COD.

| Model     | Parameters | Units | Values |
|-----------|------------|-------|--------|
| PFO model | $q_e$, exp | mg/g  | 802    |
|           | $q_e$      | mg/g  | 160.737|
|           | $K_1$      | min$^{-1}$ | 0.0008 |
|           | $R^2$      |       | 0.653  |
| PSO model | $q_e$      | mg/g  | 746.26 |
|           | $K_2$      | g/mg/min | 0.000107 |
|           | $R^2$      |       | 0.999  |
| W&M model | $K_i$      | mg/g/min$^{1/2}$ | 119.41 |
|           | $R^2$      |       | 0.98   |

4. COD Adsorption Efficiency of Various Materials

Table 5 summaries the COD removal effectiveness and surface areas of several adsorbents, as reported in earlier research. The findings are compared to OPLAC-ZC’s adsorption efficiency and surface area. When compared to other adsorbents, OPLAC-ZC was more effective than many in reducing COD. A substantial surface area of AC was also observed using oil palm leaves. As a result, it can be concluded that OPLAC-ZC can be effectively utilized to remove COD and perhaps other contaminants in PW.

Table 5. Comparison of COD adsorption capacity of various materials.

| Adsorbent                           | Surface Area (m$^2$/g) | Adsorption Capacity | References |
|-------------------------------------|------------------------|---------------------|------------|
| Eucalyptus bark                     | 6.1178                 | 59%                 | [63]       |
| Palm bark powder biochar            | 1.80                   |                     | [60]       |
| Zeolite Carbon                      | 60.94                  | 3.23 mg/g           | [64]       |
| Palm waste                          | 272                    |                     | [65]       |
| Oil palm leaves carbon              | 122                    |                     | [66]       |
| Activated carbon from red algae     | 0.8950                 |                     | [67]       |
| Coal AC                             | 29.7                   |                     | [68]       |
| Magnetic Coal AC                    | 53.4                   |                     |           |
| Amygdalus scoparia AC               | 209.3                  |                     | [69]       |
| OPLAC                               | 331.153                | 4.62 mg/g, 59.6 ± 5% | This study |
| Sludge magnetic biochar             | 47%                    |                     | [70]       |
| Sugarcane Bagasse AC                | 58.73%                 |                     | [71]       |
| Commercial walnut shell             | 3.93 mg/g              |                     | [72]       |
| Commercial activated carbon         | 99.02%                 |                     | [17]       |

5. Conclusions

The chemical activation technique was used to produce a novel activated carbon (AC), using oil palm leaves (OPL), with various chemical agents to alter its surface properties.
The OPL were chemically activated using three chemical agents, viz., H$_3$PO$_4$, NaOH and ZnCl$_2$. The higher surface area (331.153 m$^2$/g), pore size (2.494 nm) and the chemical structure of OPLAC (C-O and C=O) showed that the synthesis of OPLAC using ZnCl$_2$ was superior in terms of surface properties compared to the others. OPLAC-ZC was synthesized at three pyrolysis temperatures (400 °C, 600 °C and 800 °C) and various OPL to ZnCl$_2$ ratios (1:0.5–1:3). The OPLAC-ZC had a higher carbon content, of 81.2% at 800 °C and 1:1 impregnation ratio. The OPLAC-ZC was used for the removal of COD in PW. The results showed that OPLAC-ZC had good removal efficiency, 4.62 mg/g (59.6 ± 5%), for organic pollutants forming COD in PW. Kinetics showed that the material was able to quickly remove COD (90 min) from PW, following the PSO and WM intraparticle diffusion kinetics. The Freundlich isotherm model best fitted the adsorption data, showing the heterogeneous adsorption behavior. Oxygenated functional groups at the surface of OPLAC-ZC were considered responsible for the chemical adsorption of organic pollutants forming COD, through the electron exchange mechanism in PW.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su14041986/s1, Table S1: The water quality parameters of PW.

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