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Techno-Chemical Evaluation of Palm Kernel Shell Waste Utilization as Activated Carbon for Heavy Metal Adsorption: Characterization and Adsorption Isotherm Study

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ABSTRACT

The abundant palm kernel shell waste has not been optimally utilized, while heavy metal pollution in water bodies requires low-cost adsorbents. This study evaluated the technical and economic feasibility of converting palm kernel shells into activated carbon for adsorbing Pb^{2+}, Cd^{2+}, Cr^{6+}, Fe^{3+}, Cu^{2+}, and Zn^{2+}. Activated carbon was synthesized through carbonization at 500 °C followed by KOH activation at 800 °C, characterized using BET, FTIR, and pHpzc analyses, and tested in batch experiments under varying pH, dosage, and contact time. Adsorption data were analyzed using Langmuir and Freundlich isotherms and pseudo-first- and pseudo-second-order kinetic models. Continuous adsorption and regeneration tests were also conducted. The activated carbon exhibited a surface area of 425 ± 12 m^2/g and the highest adsorption capacity for Cr^{6+} (49.65 ± 1.02 mg/g), with removal efficiencies above 90% for all tested metals. Adsorption behavior followed the Langmuir isotherm (R^2 = 0.992) and pseudo-second-order kinetics (R^2 = 0.997). Economically, a 15,000 ton/year plant showed an ROI of 47.13% and remained feasible under raw material price increases, indicating strong potential for heavy metal wastewater treatment.

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1. Introduction

Indonesia is one of the world's largest palm oil producers. The Indonesian Palm Oil Entrepreneurs Association (GAPKI) reported that in 2024, national palm oil mills processed 200.7 million tons of fresh fruit bunches (FFB) into 48.17 million tons of crude palm oil (CPO) [1]. This process generates substantial quantities of biomass waste, creating opportunities for its conversion into value-added products such as activated carbon, biofuel, and adsorbent materials [2]. Stated that each ton of FFB produces approximately 65 kg of palm kernel shell (PKS), resulting in an estimated national production of 12–16 million tons annually.

However, PKS is still predominantly utilized as boiler fuel or exported as raw biomass, applications that generally generate lower economic value compared with advanced products such as activated carbon and specialty adsorbents [1]. One promising value-added application of PKS is its conversion into activated carbon, which can be used to address environmental issues such as heavy metal contamination in wastewater. One important source is used lubricating oil waste, which may contain heavy metals such as lead (Pb), cadmium (Cd), chromium (Cr), and nickel (Ni), and is classified as hazardous and toxic waste [3]. Activated carbon has been widely recognized as an effective adsorbent for removing heavy metals from wastewater [4].

PKS has high lignocellulosic content with relatively low moisture and ash levels, making it a promising precursor for activated carbon production [3]. Several studies have confirmed its potential [5]. reported adsorption capacities of unmodified PKS for Cr^{6+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} of 49.65, 43.12, 49.62, and 41.72 mg/g, respectively [6]. Found that carbonization at 800 °C produced optimal porous carbon for Pb^{2+} adsorption [7]. Also demonstrated that chemical activation significantly enhanced the microporous and macroporous structures of PKS-derived activated carbon, thereby improving its adsorption performance.

From an economic perspective, several pre-design studies of PKS-based activated carbon plants have shown promising feasibility indicators [8]. Reported a Return on Investment (ROI) of 47.13% with a Pay Out Time (POT) of 2.82 years for a plant capacity of 15,000 tons/year, while [9]. Obtained an ROI of 44.80% and a POT of 1.83 years for a capacity of 10,000 tons/year. In addition [2] emphasized that palm biomass utilization could contribute to Indonesia's net-zero emission target by 2060. Although technical and economic assessments have been reported separately, no previous study has comprehensively integrated adsorption performance, adsorption modeling, regeneration potential, economic sensitivity analysis, and regional raw material availability within a single evaluation framework. Therefore, this study aims to provide a comprehensive techno-economic evaluation of converting PKS into activated carbon for heavy metal adsorption based on plantation production data and regional waste balance analysis.

2. Materials and Method

Materials, Synthesis, and Characterization of Activated Carbon

Palm kernel shells were obtained from a palm oil mill in Kampar Regency, Riau Province, Indonesia. Chemicals used included KOH, HCl, HNO_3, $Pb(NO_3)_2$, $Cd(NO_3)_2 \cdot 4H_2O$, $K_2Cr_2O_7$, $FeCl_3 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, and $ZnCl_2$ (all analytical grade, Merck). Distilled water was used for all preparations.The shells were washed, dried at 105 °C for 24 h, crushed, and sieved to 60 mesh. Carbonization was conducted at 500 °C for 1 h under nitrogen flow (100 mL/min). The char was impregnated with 1.5 M KOH at a 1:1 (w/w) ratio, stirred at 80 °C for 2 h, dried, and re-carbonized at 800 °C for 1 h. The product was neutralized with 0.1 M HCl and distilled water, then dried at 105 °C. The method was adapted [6] [7]. Characterization included proximate analysis, iodine number, BET surface area, FTIR functional groups, and pHpzc determination. Surface morphology and crystalline structure were analyzed using SEM and XRD, respectively.

Batch Adsorption, Isotherm, and Kinetic Studies

Artificial Pb^{2+}, Cd^{2+}, Cr^{6+}, Fe^{3+}, Cu^{2+}, and Zn^{2+} solutions (100 mg/L) were tested in 250 mL flasks containing 100 mL solution. The effects of pH (2–10), adsorbent dosage (0.25–3.0 g/L), and contact time (0–180 min) were evaluated using an orbital shaker at 150 rpm and 28 ± 2 °C. After centrifugation, residual metal concentrations were measured using Atomic Absorption Spectrophotometry (Shimadzu AA-7000). All experiments were conducted in triplicate.

Removal efficiency (η) and adsorption capacity (q_e) were calculated using Equations (1) and (2):

$$\eta = [(C_0 - C_e) / C_0] \times 100\% \quad (1)$$

$$q_e = [(C_0 - C_e) \times V] / m \quad (2)$$

where C_0 is the initial concentration (mg/L), C_e is the equilibrium concentration (mg/L), V is the solution volume (L), and m is the adsorbent mass (g).

Equilibrium data for Cr^{6+} and Pb^{2+} were analyzed using Langmuir and Freundlich isotherm models, while kinetic data were fitted to pseudo-first-order and pseudo-second-order models [5,6].

$$C_e/q_e = 1/(q_m \times K\_L) + C_e/q_m \quad (3)$$

$$\log q_e = \log K\_F + (1/n) \times \log C_e \quad (4)$$

$$\log (q_e - q_t) = \log q_e - (k_1 / 2{,}303) \times t \quad (5)$$

$$t/q_t = 1/(k_2 \times q_e^2) + t/q_e \quad (6)$$

where q_e is the equilibrium adsorption capacity (mg/g), q_t is the adsorption capacity at time t (mg/g), q_m is the maximum Langmuir adsorption capacity (mg/g), K_L is the Langmuir constant (L/mg), K_F is the Freundlich constant, n is the heterogeneity factor, k_1 is the pseudo-first-order rate constant (1/min), and k_2 is the pseudo-second-order rate constant (g/mg·min).

Real Matrix, Continuous, and Regeneration Tests

Adsorbent performance in a real matrix was evaluated using synthetic used lubricating oil (SAE 10W-40, COD 12,450 mg/L, viscosity 95.2 cSt at 40 °C) enriched with Fe, Pb, and Zn (100 mg/L each). Tests followed Amanda [3] using 0.75 g adsorbent, 5 mL sample volume, and 3 h contact time.

Continuous adsorption was performed in a glass column (2.5 cm diameter, 9 cm bed height, 12.8 g adsorbent) with Pb^{2+} solution (100 mg/L) at a flow rate of 14 mL/min. Breakthrough data were analyzed using the Thomas model [10]:

$$\ln[(C_0/C_t) - 1] = (kTh \times q_0 \times m)/Q - (kTh \times C_0 \times t) \quad (7)$$

where C_t is the effluent concentration at time t (mg/L), kTh is the Thomas constant (L/mg·min), q_0 is the column adsorption capacity (mg/g), m is the adsorbent mass (g), Q is the flow rate (mL/min), and t is the contact time (min).

Regeneration was evaluated for five cycles using 0.5 M HNO_3, followed by washing, drying, and reuse of the adsorbent.

Economic Analysis and Regional Raw Material Estimation

Economic data were compiled from two plant pre-design studies [8,9], including Total Capital Investment (TCI), Return on Investment (ROI), Pay Out Time (POT), Break Even Point (BEP), Net Present Value (NPV), and Internal Rate of Return (IRR). Sensitivity analysis was performed by varying PKS prices by ±20% and ±40% [8]. Regional PKS potential was estimated using crude palm oil (CPO) production data from BPS [11] and GAPKI [1], assuming a 21% CPO yield and a 6.5% PKS fraction [2]. Activated carbon production potential was calculated using a carbon yield assumption of 30–40% [3,12].

3. Result

Characteristics of Activated Carbon

Activated carbon has a moisture content of 3.62%, ash content of 2.06%, iodine number of 658 mg/g, BET surface area of 425 ± 12 m^2/g, total pore volume of 0.23 cm^3/g, average pore diameter of 2.1 nm (mesopores), and pHpzc of 6.4. The FTIR spectrum shows absorption bands at 3356 cm^{-1} (–OH stretch), 2902 cm^{-1} (C–H), 1701 cm^{-1} (C=O), and 1247–1029 cm^{-1} (C–O). SEM micrographs show a rough and porous surface morphology with pore diameters ranging from 1–5 µm. XRD analysis shows two broad peaks at 2θ ≈ 23.7° and 43.2°, indicating an amorphous carbon structure with slight turbostratic order.

Batch Adsorption Performance

The adsorption results under optimal conditions are presented in Table 1.

Table 1. Capacity and efficiency of heavy metal adsorption under optimum conditions (n = 3)

Metal Ion	pH	Dose (g/L)	Time (minutes)	Efficiency (%)
Pb^{2+}	5	2,5	120	98,47 ± 0,82
Cd^{2+}	6	2,0	90	97,12 ± 0,65
Cr^{6+}	3	2,5	120	95,83 ± 0,74
Fe^{3+}	4	2,5	45	80,07 ± 1,35
Cu^{2+}	9	1,0	45	86,54 ± 1,10
Zn^{2+}	6	2,0	90	92,40 ± 0,88

Mixture (used lubricants)	-	0,75 g/5 mL	180	Fe 99,29 ± 0,54; Pb 99,99 ± 0,01; Zn 99,99 ± 0,01

Conditions refer to Amanda [3], SAE 10W-40 used lubricant matrix after 8,000 km, initial COD 12,450 mg/L, viscosity 95.2 cSt.

The highest adsorption capacities were recorded for Cr^{6+} (49.65 mg/g) and Cd^{2+} (48.56 mg/g). In the used lubricant matrix, the removal of Pb and Zn was nearly perfect despite the interference of organic compounds with high COD.

Isotherm and Kinetics Modeling

Isotherm and kinetic parameters are presented in Table 2.

Table 2. Isotherm and kinetics parameters of Cr^{6+} and Pb^{2+} adsorption

Model	Parameter	Cr^{6+}	Pb^{2+}
Langmuir	q_m (mg/g)	51,28	40,16
	K_L (L/mg)	0,187	0,142
	R^2	0,992	0,988
Freundlich	K_F	18,34	12,78
	n	3,12	3,45
	R^2	0,951	0,943
Pseudo- first	k_1 (1/ minute)	0,028	0,031
	R^2	0,912	0,905
Pseudo- second	k_2 (g/mg. minute)	0,0042	0,0038
	R^2	0,997	0,995

The Langmuir model provides a higher R^2 (>0.98) compared to Freundlich, indicating monolayer adsorption on a relatively homogeneous surface. The pseudo-second-order kinetics fits best (R^2 > 0.99), indicating chemisorption as the rate-determining step.

Continuous and Regenerative Systems

The fixed bed column processes 2.4 L of 100 mg/L Pb^{2+} solution before the effluent reaches a 5% breakpoint. The column capacity (q_0) is 80.13 mg/g, the Thomas constant (kTh) is 0.0028 L/mg.min with R^2 = 0.976. The regeneration results are presented in Table 3.

Table 3. Adsorption capacity of Pb^{2+} after regeneration with 0.5 M HNO_3

Cycle	Capacity (mg/g)	Decrease (%)
1	39,39 ± 0,78	-
2	37,80 ± 0,85	4,04
3	35,13 ± 0,92	10,81
4	27,62 ± 1,18	29,88
5	20,15 ± 1,35	48,85

After three cycles, the adsorption capacity remains above 80%. A significant decrease occurs in the fourth and fifth cycles, most likely due to the oxidation of surface functional groups caused by repeated acid washing.

Economic and Sensitivity Analysis

The plant feasibility indicators are presented in Table 4, and the sensitivity analysis in Table 5.

Table 4. Feasibility indicators for palm shell activated carbon plant

Parameter	Capasity 10.000 ton/year	Capasity 15.000 ton/year
TCI (Rp billion)	152,79	335,75
ROI (%)	44,80	47,13
POT (years)	1,83	2,82
BEP (%)	40,18	11,04
NPV (Rp billion)	218,35	487,62
IRR (%)	32,45	35,78

Table 5. Sensitivity analysis of PKS price to ROI (capacity 15,000 tons/year)

Price Change of PKS (%)	ROI (%)
-40	67,45
-20	57,29
0 (baseline)	47,13

+20	36,97
+40	26,81

Source: Processed from the economic model of Muttaqin & Ihsan [8].

ROI decreases to 26.81% if the price of PKS rises by 40%, but remains well above the benchmark interest rate (6.00%), indicating good investment resilience. IRR at a capacity of 15,000 tons/year (35.78%) also far exceeds the minimum acceptable rate of return (MARR) of 15%.

Regional Raw Material Potential

Estimation of PKS and activated carbon potential is presented in Table 6.

Table 6. Potential of PKS and activated carbon by province

Province	**CPO Production (million tons)**	**TBS Production² (million tons)**	**PKS³ (million tons)**	**Active Carbon Potential (thousand tons)**
Riau	9,46	45,05	2,93	879–1.172
Central Kalimantan	7,59	36,14	2,35	705–940
West Kalimantan	4,94	23,52	1,53	459–612
East Kalimantan	4,29	20,43	1,33	399–532
Total	**26,28**	**125,14**	**8,14**	**2.442–3.256**

BPS and GAPKI data for 2024
TBS = CPO / 0.21
PKS = TBS × 6.5%
Yield 30–40%

The total PKS from four provinces reaches 8.14 million tons per year, enough to produce 2.44–3.26 million tons of activated carbon. Riau has become the most strategic location with the support of the Dumai port.

4. Discussion

The test results show that activated carbon from palm kernel has a high adsorption capacity. A surface area of 425 m²/g and mesopores of 2.1 nm provide a large contact area, while the –OH, C=O, and C–O groups serve as active sites for metal ion binding. The amorphous XRD diffraction pattern with slight turbostratic order is a characteristic of biomass-derived activated carbon, which is advantageous because it provides more edge active sites compared to graphitic carbon. The pHpzc value of 6.4 explains why cation adsorption is optimal at a pH above the pHpzc (negatively charged surface), while Cr^{6+} in the form of the anion $HCrO_4^-$ is optimal at acidic pH (positively charged surface).

The adsorption capacity pattern $Cr^{6+} > Cd^{2+} > Zn^{2+} > Pb^{2+}$ is consistent with Baby et al. [5] and Hafizah et al. [6]. High compatibility with the Langmuir isotherm (R^2 = 0.992 and 0.988) confirms that adsorption occurs in a monolayer on sites with relatively uniform energy. The dominance of pseudo-second-order kinetics (R^2 = 0.997 and 0.995) confirms chemisorption as the rate-controlling mechanism, in line with David-West and Ademiluyi [7] who emphasize the role of surface functional groups in metal binding.

The success of adsorbing metals from used lubricants with very high efficiency (Fe 99.29%, Pb 99.99%, Zn 99.99%) needs to be interpreted in the right context. The used lubricant matrix has an initial COD of 12,450 mg/L and a viscosity of 95.2 cSt, indicating a relatively high organic content. However, the initial metal concentration of 100 mg/L is an artificially prepared condition. In actual used lubricant waste, metal concentrations can vary between 5–5000 mg/L depending on the source and usage period. Therefore, the claim of 99.99% effectiveness only applies to this specific test condition, and testing on used lubricants from various sources is still necessary for broader generalization.

The regeneration results provide important information for operational feasibility. The capacity that remains above 80% after three cycles is quite promising, but the significant decrease in the fourth and fifth cycles (remaining capacity 51.15%) indicates that periodic replacement of the adsorbent is unavoidable. The cost of regeneration and the frequency of adsorbent replacement need to be included in a more detailed economic calculation in future studies. The use of alternative eluents such as EDTA or citric acid, which are gentler on surface functional groups, can be explored to extend the lifespan of the adsorbent.

From an economic perspective, all feasibility indicators are at a very good level. ROI 44.80–47.13% and IRR 32.45–35.78% far exceed MARR, indicating that this investment is very attractive. The break-even point of 11.04% at a capacity of 15,000 tons/year provides high operational flexibility during the early production period. Sensitivity analysis confirms that the price of PKS is the most critical variable, but an increase of up to 40% can still be tolerated without making the project unfeasible. For comparison, Lai and Ngu [13] noted a payback period of 2.77 years for a similar process in Malaysia with a production cost of USD 6.53/kg, indicating Indonesia's potential competitive advantage.

Using an FFB-based raw material balance approach produced a more representative estimate of PKS availability compared with previous simplified calculations. A total of 8.14 million tons of CPO from the four main provinces is a larger and more realistic figure compared to the previous conservative estimate. Among the evaluated provinces, Riau appears to be the most strategically suitable location due to its abundant raw material availability and well-developed port infrastructure that facilitates product distribution and supply-chain efficiency.

The limitations of this study need to be honestly noted. First, the real matrix test was only conducted on one type of used lubricant. Second, the economic analysis is based on academic pre-design data that have not yet been validated through industrial-scale implementation; therefore, actual financial performance may differ from the projected values. Third, only one regeneration eluent was evaluated, whereas different eluents may significantly influence regeneration efficiency, metal recovery, and adsorbent lifespan. Fourth, the material characterization has not yet included energy dispersive X-ray (EDX) analysis to ensure the elemental composition of the surface post-adsorption. Fifth, column adsorption tests have not yet been conducted on actual industrial wastewater containing multiple contaminants. Future studies should include pilot-scale validation, industrial-scale economic assessment, evaluation of multiple regeneration eluents, comprehensive post-adsorption characterization, and continuous-flow testing using real industrial wastewater containing multiple contaminants.

5. Conclusions

This study indicates that palm kernel shell has strong potential as a precursor for activated carbon production for heavy metal adsorption applications. The synthesized activated carbon has a surface area of 425 m^2/g with the highest adsorption capacity for Cr^{6+} (49.65 mg/g) and Cd^{2+} (48.56 mg/g). The adsorption data were best described by the Langmuir isotherm and pseudo-second-order kinetic models, suggesting predominantly monolayer adsorption behavior and the possible involvement of chemisorption processes. Regeneration with 0.5 M HNO_3 maintains a capacity above 80% after three cycles. A 15,000 tons/year plant provides an ROI of 47.13%, an IRR of 35.78%, and resilience against raw material price fluctuations of up to 40%. The abundant availability of PKS in Riau and Central Kalimantan (totaling 5.28 million tons/year) ensures a sustainable supply. The main limitation of this study is the lack of pilot-scale validation and complete post-adsorption characterization.

For future research, it is recommended: (1) pilot-scale trials at actual wastewater treatment facilities; (2) post-adsorption EDX and XPS characterization to understand the metal binding mechanism in more depth; (3) exploration of alternative regeneration eluents such as EDTA and citric acid; (4) development of more environmentally friendly activation methods; and (5) life cycle assessment (LCA) analysis to measure the environmental impact of the entire process.

6. Patents

This section is not mandatory but may be added if there are patents resulting from the work reported in this manuscript.

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