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Comparative Study on Adsorption Kinetics of Heavy Metals in Produced Water Using Banana Peel and *Luffa Cylindrica* Derived Activated Carbon

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Abstract

This paper investigates the potentials of activated carbon (AC) derived from *Banana peel and Luffa cylindrica* biowaste for the removal of heavy metals such as zinc, copper, nickel, and iron from produced water. Activated carbon was obtained by carbonizing adsorbents (*Banana peel and Luffa cylindrica)*, using an impregnation ratio of 1:3 of H_3PO_4 for 24 hrs. The experimental runs were conducted using the batch adsorption method, where produced water was treated using a 2 g adsorbent dosage for 2, 4, and 6 hours of contact time. Adsorption kinetics were analysed using both the pseudo-first-order and pseudo-second-order model equations. The results show that Luffa *cylindrica*-derived AC achieved up to 85.7, 88.3, 54.7, and 52.2 % removal in Zn, Cu, Ni, and Fe, respectively, while banana peel AC led to 85.4, 70.7, and 35.2% removal in Zn, Cu, Ni, and Fe., respectively. Kinetic data indicated that pseudo-first-order best described Zn, Cu, and Fe adsorption ($R^2 > 0.76$) on both adsorbents, while only Fe adsorption on banana peel AC fitted well with pseudo-second-order ($R^2 = 0.9998$). These findings suggest the potential of these low-cost, sustainable biosorbents for effective treatment of produced water.

Keywords: *Adsorption kinetics; Banana peel; Luffa cylindrica waste; Activated Carbon; Heavy metals, Produced water*

1. Introduction

Petroleum crude is produced with large volumes of wastewater generally referred to as produced water. The amount of produced water could be due to formation water. Formation water is seawater or fresh water that has been trapped for millions of years with oil and natural gas in a geologic reservoir consisting of a porous sedimentary rock formation between layers of impermeable rock within the earth's crust (Olajire, 2020). Produced water, a major byproduct of oil and gas extraction, accounts for billions of gallons generated annually across over 65,000 global oil and gas fields (Peng *et al.,* 2020; Davidson *et al.,* 2014). Daily estimates indicate roughly 250 million barrels of produced water are generated alongside 80 million barrels of oil (Ahmadun *et al.,* 2009). This water often contains toxic heavy metals—such as lead, mercury, and cadmium—originating from subsurface formations (Shamaei *et al.,* 2018). The composition is influenced by reservoir geology and well age. If improperly managed, produced water can pose serious environmental threats, particularly to soil and aquatic ecosystems (Udeagbara *et al.,* 2020).

Adsorption is considered an effective and economically viable method for treating produced water, particularly for the removal of heavy metals. It offers significant advantages over conventional treatment technologies by producing high-quality effluent with minimal environmental impact. The method is cost-efficient, as many adsorbents can be regenerated and reused, making it suitable for large-scale produced water applications (Hussain *et al.,* 2021). Furthermore, adsorption is simple to operate and does not generate harmful byproducts, positioning it as an environmentally friendly solution for managing the complex composition of produced water (Demirbas, 2008).

Despite their proven effectiveness, activated carbons face several limitations in the treatment of produced water such as high production costs, challenges in disposing of spent material, and energy-intensive regeneration processes. These constraints have driven extensive research toward low-cost, non-conventional biosorbents. Among the adsorbents are agricultural wastes such as rice husk, coconut shell, sawdust, corn cobs, banana peels, and sugarcane bagasse have gained significant scientific research investigations. These materials are abundantly available, inexpensive, and environmentally sustainable. Their lignocellulosic structure and diverse functional groups—such as hydroxyl, carboxyl, and phenolic groups—contribute to strong binding affinities for heavy metal ions, making them highly effective for treating produced water (Alalwan *et al.,* 2018; Burakov *et al.,* 2018).

The removal of heavy metals by adsorption using activated carbon is a prominent technology to treat domestic and industrial wastewater due to its easy operating requirements, high regeneration ability, and low cost (Abbas and Alalwan 2019; Jabbari *et al.,* 2016). Activated carbon could be available in both powdered and granular forms, each with distinct properties relevant to produced water treatment. Powdered activated carbon generally has larger pores but a smaller internal surface area, while granular activated carbon offers a higher internal surface area with smaller pores, enhancing its adsorption efficiency. The performance of activated carbon in removing contaminants from produced water is largely determined by its porosity, surface area, and chemical characteristics. However, due to the high cost and challenges associated with regeneration and disposal, there is growing interest in utilizing low-cost alternatives—particularly agricultural wastes—as sustainable and cost-effective adsorbents for treating the complex composition of produced water (Hussain *et al.,* 2021).

Kinetic models are essential for understanding the mechanisms involved in the adsorption of metal ions and for assessing the performance of various adsorbents. Numerous kinetic models have been developed to describe the rate and dynamics of heavy metal adsorption processes. In the present study, the adsorption kinetics of zinc (Zn^{2+}), copper (Cu^{2+}), nickel (Ni^{2+}), and iron (Fe^{2+}) onto activated carbon derived from banana peel and Luffa cylindrica would be investigated using pseudo-first-order and pseudo-second-order kinetic models.

Therefore, the aim of this study was to investigate heavy metal removal from produced water using banana peel and *Luffa cylindrica*-derived activated carbon The kinetic parameters of the adsorption process were examined by applying both pseudo-first-order and pseudo-second-order models, enabling a detailed understanding of the adsorption mechanism and improving the efficiency of produced water treatment.

2. Materials and Method

Banana peels and *Luffa cylindrica* were obtained from Ibadan, Oyo State, Nigeria. Produced water samples were collected from an oilfield located in the Niger Delta region. All reagents utilized in the study were of analytical grade to ensure experimental accuracy.

2.1. Activated carbon preparation

Banana peels and *Luffa cylindrica* samples were thoroughly rinsed with distilled water to remove impurities. Then, the rinsed samples were cut into smaller pieces and air-dried for seven days. Subsequently, the samples were oven-dried at 100 ^{o}C for 5 hr and 3 hr respectively, for banana peels and *Luffa cylindrica* in order to remove residual moisture. The dried samples were pulverized into powder form and stored in airtight containers until further use. Chemical activation pulverized samples were carried out to enhance the adsorptive properties. The powdered samples were impregnated with a phosphoric acid (H_3PO_4) solution at a specified impregnation ratio (1:3 by mass) and left to stand for 24 hours at room temperature. After impregnation, the samples were dried and subjected to carbonization in a muffle furnace at temperature of 450°C for 1 hour and 30 mins under an inert atmosphere (nitrogen flow) to prevent combustion. Following carbonization, the activated carbon was washed with distilled water until neutral pH was achieved, then oven-dried and stored for subsequent experiments.

2.2 Adsorbent characterization

The physicochemical properties of the activated carbon samples were evaluated using established standard procedures. Moisture content, ash content, and volatile matter were determined in accordance with the methods described by Oladimeji et al. (2021). Additionally, bulk density and surface area were measured based on the method explained by Sugumaran *et al.,* (2012).

2.3 Batch Adsorption Analysis

A fixed dosage of 1 gram of activated carbon derived from the adsorbents was added to 50 mL of produced water in separate test tubes. The mixtures were subjected to agitation on a mechanical shaker for varying contact times of 2, 4, and 6 hours. After agitation, the mixtures were filtered using Whatman filter paper to separate the filtrate from the spent adsorbent. The filtrates were collected in labelled sample bottles for analysis, while the spent adsorbents (residues) were wrapped in aluminium foil and stored in a desiccator for further laboratory analysis. The concentrations of heavy metals in the filtrates were measured using an Atomic Absorption Spectrophotometer (AAS; PerkinElmer Analyst 200). The efficiency of heavy metal removal by the Banana peels and *Luffa cylindrica* derived-activated carbon was calculated using the Equation (1). This equation quantifies the percentage of each heavy metal removed by the adsorbents during the adsorption process.

$$\%\, removal\ efficiency = \frac{C_o - C_t}{C_o} \times 100 \qquad (1)$$

Where:
C_o = initial concentration of the heavy metal in produced water (mg/L)
C_t = concentration of the heavy metal in the filtrate after treatment (mg/L)

2.4 Adsorption Kinetic

The adsorption kinetics experiments were carried out using a batch technique under limited bath conditions. Typically, 1 g of each adsorbent was introduced into 50 mL of produced water. Samples were collected at time intervals of 2, 4, and 6 hours for analysis. The concentrations of metal ions remaining in solution were determined using atomic absorption spectroscopy (AAS). The extent of adsorption was quantified using the fractional attainment of equilibrium, expressed by Equation (2).

$$F = \frac{q_t}{q_e} \qquad (2)$$

where qt (mg/g) is the amount of metal adsorbed at time t, and qe (mg/g) is the amount adsorbed at equilibrium.

The pseudo-first-order kinetic model (Equation (3)) initially proposed by Lagergren 1898, assumes that the rate of adsorption is proportional to the number of available adsorption sites. $\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (3)$

After integration and applying boundary conditions, the linear form becomes

$$In(q_e - q_t) = Inq_e - k_1 t \qquad (4)$$

The linearised Lagergren pseudo-second-order kinetic model, which assumes chemisorption as the rate-limiting step may be represented in Equation (5) (Aly and Luca, 2013):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (5)$$

Integrating and applying boundary conditions to Equation (6) yields

$$\frac{q}{qt} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \qquad (6)$$

3. Result and Discussion

3.1.Physicochemical properties of the adsorbents

The physicochemical characteristics of the phosphoric acid (H_3PO_4)-activated adsorbents are presented in Table 1. As shown in the table, the ash content of the activated carbon samples ranged from 2.8 to 3.23%, indicating that the original biomass was predominantly organic with minimal inorganic residue after thermal treatment. Low ash content is desirable, as it reflects reduced mineral contamination and contributes to higher adsorbent purity and performance.

The total carbon content of banana peel and *Luffa cylindrica* AC adsorbents were found to be 86.5±0.3 and 91.0±0.3 respectively, confirming the effectiveness of banana peel and *Luffa cylindrica* as suitable precursors for bio-adsorbent production. High carbon levels typically correlate with improved structural integrity, thermal stability, and reactive surface functionality—qualities that are essential for efficient contaminant removal in water treatment processes.

The bulk density values were between 0.28 and 0.32 g/cm³, and within the range (0.32 g/cm³) of previous study (Ekpete *et al*., 2017) for phosphoric acid-activated plantain stem carbon but marginally lower than 0.39–0.56 g/cm³ reported by Ziezio *et al.,* (2020) for coffee grounds. Bulk density plays a critical role in adsorption system design, especially for fixed-bed or column operations, as it affects bed packing and mass transfer rates.

The specific surface area of banana peel-derived activated carbon was 920.0 m²/g from 2.275 m²/g while *Luffa cylindrica*-derived carbon exhibited a surface area of 830.0 m²/g from 1.189 m²/g. These high values show significant pore development during activation, which is vital for maximizing adsorption performance. A larger surface area implies a greater number of available active sites for binding contaminants. These results aforementioned results exceed the 361.86 m²/g reported by Ramutshatsha-Makhwedzha *et al*., (2022) and are comparable to the surface areas (720 m²/g) achieved by Ziezio *et al*., (2020) using similar activation techniques.

In summary, the high surface area, low ash content, and favorable bulk density of these chemically activated agricultural waste materials highlight their promise as sustainable and cost-effective adsorbents for the treatment of produced water and broader water purification applications.

Table 1: Characteristics of produced adsorbent^

Parameter	Banana peel activated carbon	*Luffa cylindrica* activated carbon
Moisture Content (%)	8.4 ± 0.1	8.0 ± 0.2
Volatile Matter (%)	0.8 ± 0.1	0.6 ± 0.1
Total Carbon (%)	86.5 ± 0.3	91.0 ± 0.3
Total Fixed Carbon (%)	74.6 ± 0.2	79.2 ± 0.2
Total Ash (%)	2.8±0.2	3.2 ± 0.3
Bulk Density (Packed) (g/cm³)	0.3	0.3
Surface area (m²/g)	920	830

^: Akinsete *et al*. (2022).

3.2 Heavy water removal

Table 2 presents the results of laboratory analysis carried out using Atomic Absorption Spectrophotometry (AAS) to quantify the concentrations of selected heavy metals in the produced water sample. The analysis focused on four key metals—zinc (Zn^{2+}), copper (Cu^{2+}), nickel (Ni^{2+}), and iron (Fe^{2+})—to assess the adsorption potential of activated carbon derived from banana peel and Luffa cylindrica. The measured concentrations were 0.258 mg/L for Zn^{2+}, 0.144 mg/L for Fe^{2+}, 0.300 mg/L for Ni^{2+}, and 3.600 mg/L for Cu^{2+}. These results indicate a significant level of heavy metal contamination, underscoring the necessity for effective treatment of produced water before environmental discharge or potential domestic use.

Table 2: Concentrations of heavy metals in produced water

Heavy Metal	Concentration (mg/L)
Zn	0.258
Cu	0.144
Ni	0.300
Fe	3.600

3.3 Effect of contact time on heavy metal removal

The concentrations of heavy metals obtained after PW treatment with banana peel and *Luffa cylindrica* at 2, 4, ad 6 hr contact times are presented in Table 3. The table shows a substantial reduction in the concentrations of metal ions in treated PW. Thus, the increase in adsorption can be attributed to the availability of free and highly unsaturated adsorbent sites at the beginning of the process (Ullah *et al*., 2023).

Table 3: Heavy metals concentration in produced water after treatment

Adsorbent	Time (hours)	Metal concentration (mg/l)			
		Zn	Cu	Ni	Fe
Untreated PW	-	0.26	0.14	0.30	3.60
Luffa cylindrica activated carbon	2	0.20	0.09	0.29	3.44
	4	0.20	0.09	0.24	3.37
	6	0.15	0.05	0.21	3.05
Banana Peel activated carbon	2	0.26	0.14	0.27	3.34
	4	0.17	0.11	0.25	3.34
	6	0.17	0.06	0.15	3.33

Luffa cylindrica-derived AC achieved highest Zn (89.1%) and Cu (85.4%) reductions. Zn removal by *Luffa cylindrica* AC of 89.1% exceeds insert reported by Aly *et al*., (2014) for PAN adsorbents (~80%), while Banana peel carbon showed superior Ni adsorption (up to 100%). Both Banana peel carbon's Cu (86.1%) and Ni (100%) removals are comparable to those achieved by modified sugarcane bagasse (Burakov *et al.,* 2018). These results align with findings by (Popoola *et al.,* 2022), who reported >90% Cu removal using *Citrullus lanatus* peel.

Although the produced water used in this study contained higher concentrations of heavy metals than reported (Zn 0.01 mg/l, Cu 0.02 mg/l, Fe < 0.01 mg/l; Zn 0.125 mg/l, Cu 0.076 mg/l, Fe 0.552 mg/l, Ni 0.035; Zn 0.101, Cu 0.009, Fe 0.048) in recent studies from the Niger Delta area of Nigeria (Okologume & Olayiwola 2019; Udeagbara *et al*., 2021; Popoola *et al*. 2022), the obtained results showed that bio-adsorbent have great efficiency of reducing the concentration of heavy metal in produced water.

3.4 Adsorption kinetics studies

The data obtained from the pseudo-first-order and pseudo-second-order for both adsorbent is shown in Figure 1 – 4. The figure generally shows that the banana peel and *Luffa cylindrica* activated carbon showed higher adsorption capacity for Zn, Cu, and Fe with contact times. The pseudo-second-order plots for both banana peel and Luffa cylindrica activated carbon exhibit strong linear relationship between the log of the difference in equilibrium and time dependent adsorption and contact time, indicating an excellent fit to the model and suggesting that chemisorption governs the adsorption process. In contrast, the pseudo-first-order plots show lower linearity and weaker lines of best fit, suggesting a less accurate representation of the adsorption behavior. Moreover, Table 4 presents the result using pseudo-first-order and pseudo-second-order kinetic models for investigating adsorption mechanism of Zn, Cu, Ni, and Fe from the PW using banana peel and *Luffa cylindrica* activated carbon.

The rate constants (k_1, k_2), equilibrium adsorption capacities (q_1, q_2), and the correlation coefficients (R^2) were provided to assess the fit of each model to the experimental data. The correlation coefficients, R^2, values being close to 1 in the Psuedo-first order calculations, confirms that chemisorption governs adsorption process. This suggests that electron sharing or exchange occurs between the adsorbate and adsorbent surfaces, aligns with findings by (Musti *et al.,* 2024; Demirbas 2008; and Al-Kaabi *et al.,* 2021).

Table 4: Adsorption kinetics constant for heavy metals using banana peel and *Luffa cylindrica* adsorbents

Adsorbent	**Heavy Metal**	**Pseudo-first order**			**Pseudo-second order**		
		k_1 (g/mg.h)	**q_e (mg/g)**	**R^2**	**K_2 (g/mg.h)**	**q_e (mg/g)**	**R^2**
Luffa cylindrica activated carbon	Zn	0.5446	0.0112	0.7632	0.0207	0.00885	0.4554
	Cu	0.5301	0.0101	0.7719	0.0206	0.00835	0.4508
	Ni	0.6598	0.0179	0.9724	74.708*	-0.00175*	0.731
	Fe	1.0474	0.3021	0.7864	0.283*	-0.11701*	0.0673
Banana peel activated carbon	Zn	0.6905	0.0100	0.8574	1771.426*	-0.0001*	0.742
	Cu	0.677	0.0166	0.8468	350.912*	-0.00046*	0.8533
	Ni	0.7489	0.000059	0.781	5.277*	-0.0109*	0.1813
	Fe	0.2452	0.0150	0.9461	535.91	0.0138	0.9998

*Not valid due to negative slope

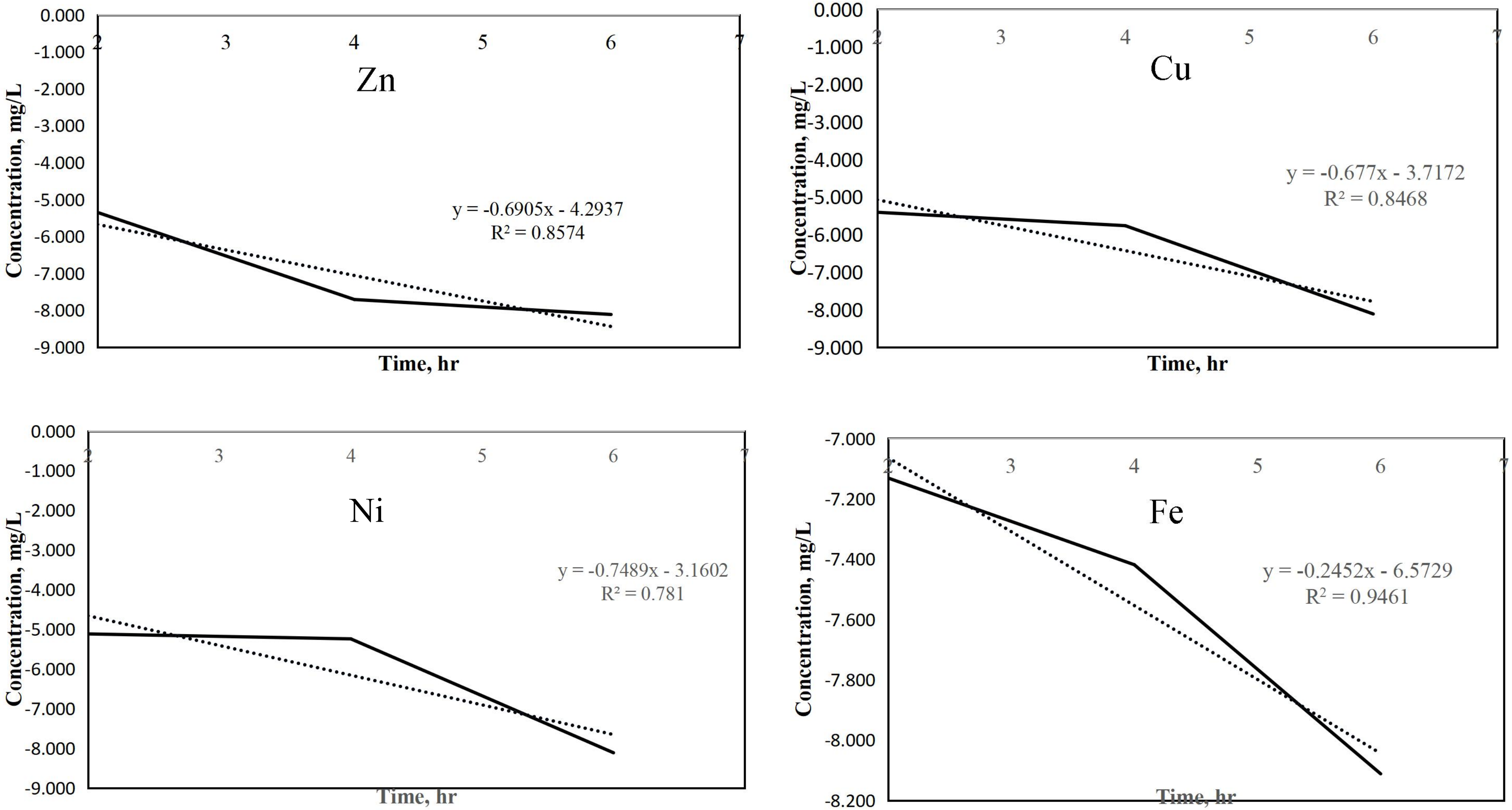

Figure 1:Pseudo-first order plot of Banana peel activated carbon for PW treatment

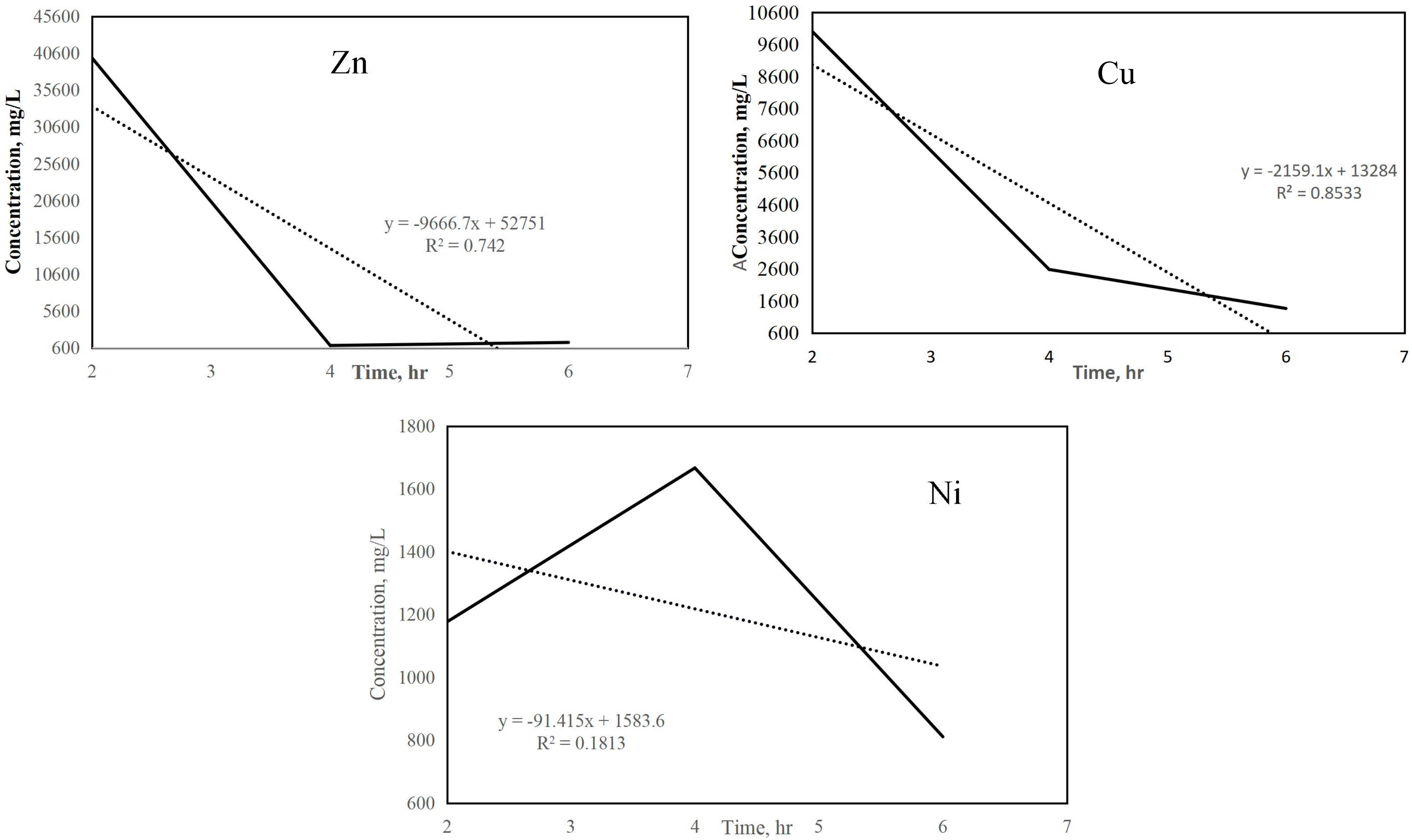

Figure 2: Pseudo-second order plot of Banana peel activated carbon for PW treatment

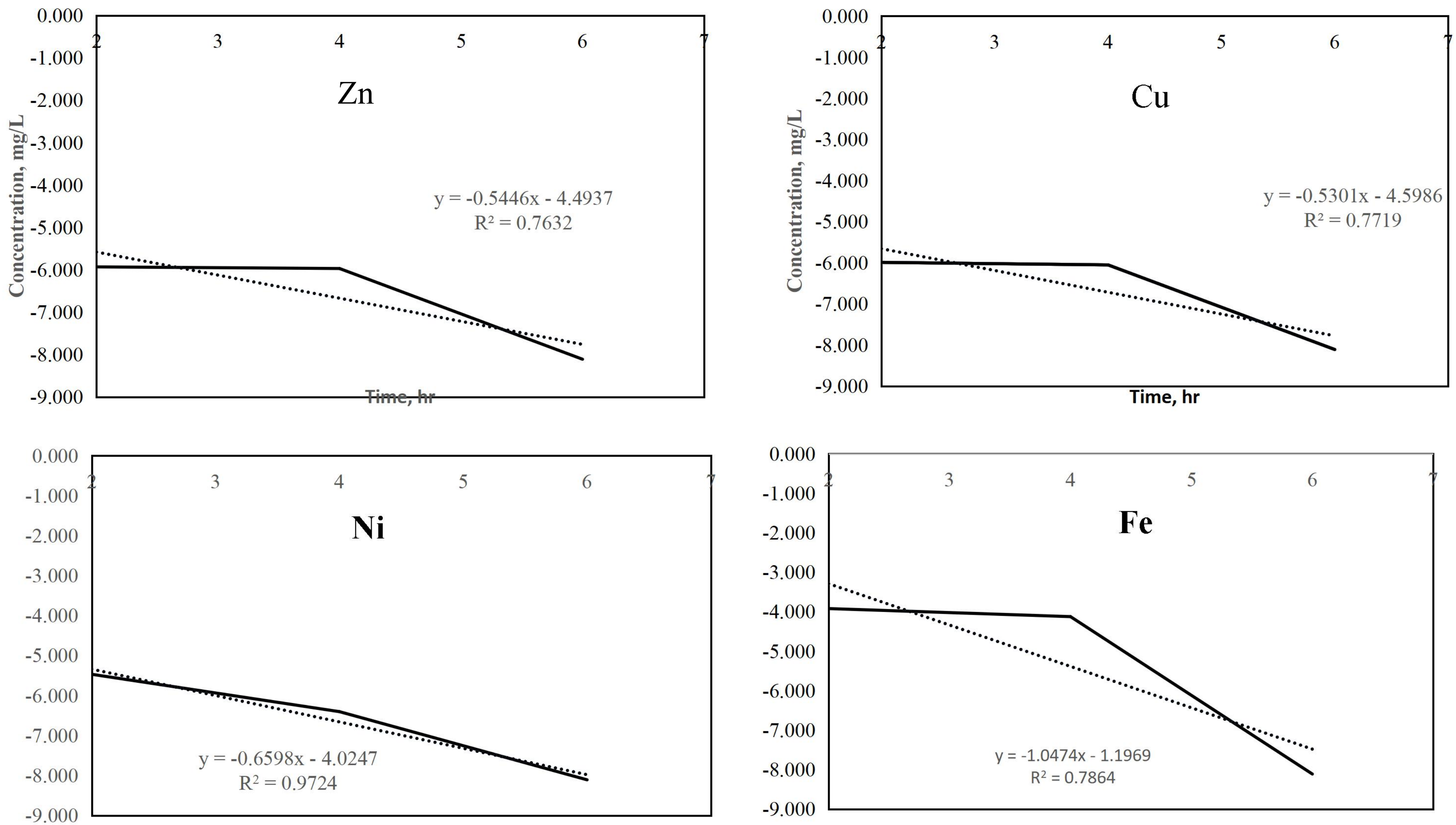

Figure 3: Pseudo-first order plot of Luffa cylindrica activated carbon for PW treatment.

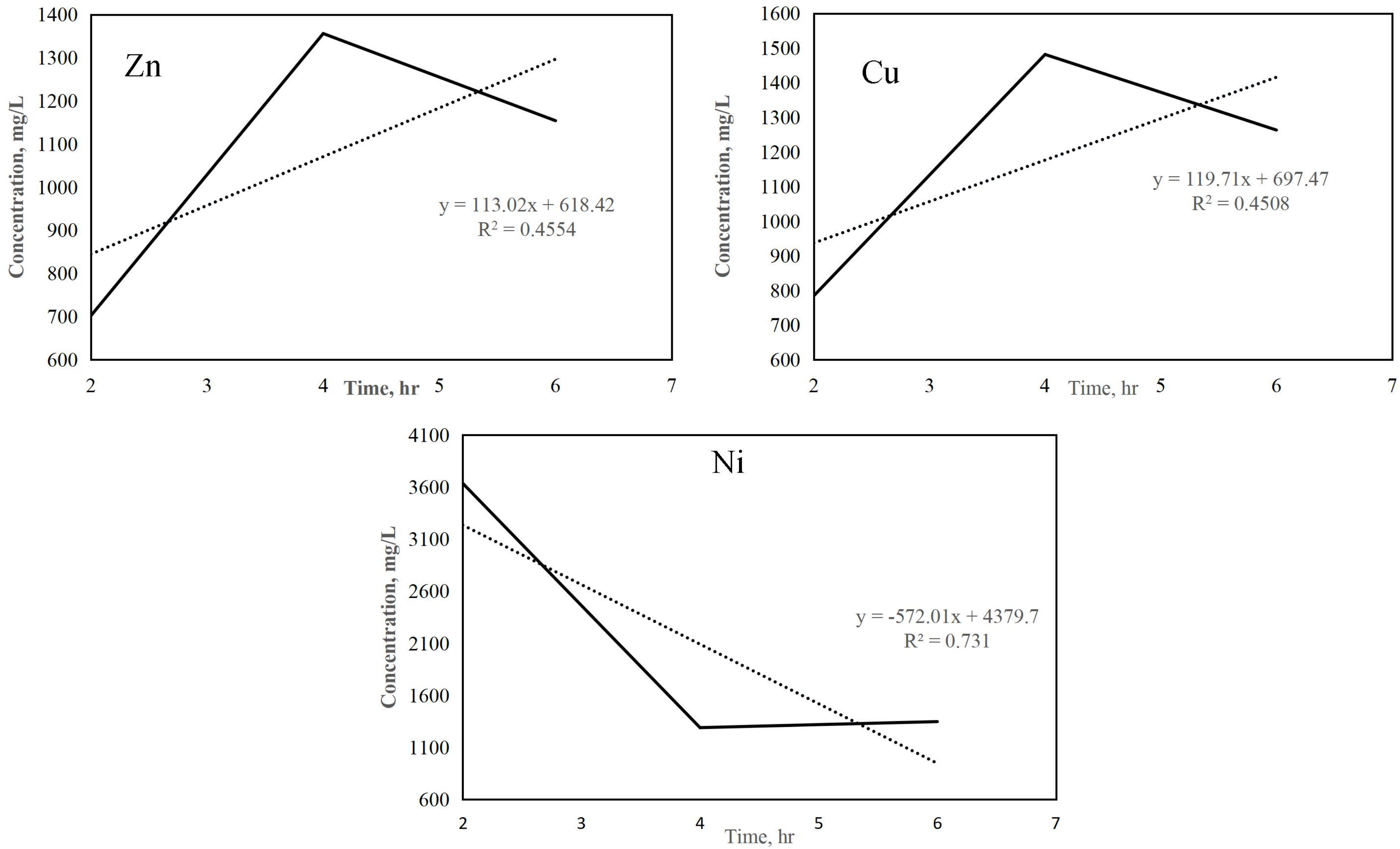

Figure 4: Pseudo-second order plot of Luffa cylindrica activated carbon for PW treatment.

The pseudo-first-order (PFO) model provided a strong fit for Zn, Cu, and Fe adsorption onto both carbons (R^2: 0.76–0.95). Ni on Luffa yielded $R^2 = 0.9724$ ($k_1 = 0.6598\ h^{-1}$, $q_e = 0.0179$ mg/g), while Fe on banana peel achieved $R^2 = 0.9461$. This implies rapid physisorption on accessible surface sites (Hussain et al., 2021).

While in the pseudo-second-order (PSO) kinetic model, Fe adsorption on banana peel ($q_e = 0.0138$ mg/g, $k_2 = 535.91$ g/mg.h), exhibited near-perfect fit (positive slope) with $R^2 = 0.9998$, consistent with chemisorption mechanism (Manirethan *et al*., 2018). However, most metals (Zn, Cu, Ni) showed non-physical negative q_e values (negative slopes) with k_2 = 1771.426, 350.912, 5.277, making the model unsuitable in those cases. This finding is similar to that of Ogidi *et al.,* (2024) who reported a non-physical negative value ($k_2 = -1.8414$) in the treatment of PW using coconut husk activated carbon enhanced with graphene oxide. Similarly, Sandesh *et al.,* (2013 and Dehvari *et al.,* (2017) observed high correlation with both kinetic models, where PSO fit failed due to early saturation or competing ions following PW treatment with cuttlefish bone powder.

In comparison, both banana peel and *Luffa cylindrica* adsorbents showed appreciable heavy metal uptake, but the latter generally displayed higher adsorption capacity for Zn, Cu, and Fe at longer contact times. PFO was found to best describe Zn adsorption on both adsorbents; Luffa carbon achieved $q_e = 0.0112$ mg/g ($R^2 = 0.7632$), compared to banana's $q_e = 0.0100$ mg/g ($R^2 = 0.8574$). Cu was slightly better fit with PSO for banana ($R^2 = 0.8533$), indicating a possible weak chemisorption mechanism. PFO was dominant for *Luffa cylindrica* ($R^2 = 0.9724$) in Ni. However, banana peel AC performed poorly under both models due to low and inconsistent q_e. Ni best modelled by PSO for banana peel ($R^2 = 0.9998$), indicates a strong chemisorption mechanism.

The PFO dominance for Zn, Cu, and Ni suggests physisorption governed by surface diffusion and van der Waals forces was the main mechanism, while the high PSO correlation for Fe on banana peel supports a chemisorption pathway involving ion exchange or complexation with functional groups. These observations were found to be in agreement with previous reports (Demirbas, 2008; Manirethan *et al*., 2018; and Hussain *et al*., 2021). Thus emphasizing the need for metal-specific kinetic analysis. The study has shown time-course data demonstrated a consistent trend: as contact time increased, metal ion concentration decreased significantly. This aligns with the principle that extended contact allows for greater interaction between metal ions and the adsorbent's active sites, enhancing removal efficiency.

4. Conclusion

This study demonstrated that bio-adsorbents *Luffa cylindrica* and banana peel-derived activated carbon), owing to their enhanced surface area and porosity, exhibit high removal efficiencies for Zn, Cu, Ni, and Fe in produced water. Luffa outperformed for Zn and Cu, while banana peel was more effective for Ni and Fe. Kinetic analysis showed pseudo-first-order better described most systems, with exception of Fe on banana peel (PSO fit). Compared to literature benchmarks, these biosorbents offer competitive and sustainable alternatives for water purification.

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