Malaysian Journal of Catalysis
http://mjcat.utm.my/
MJCat
Research Article

Luffa Cylindrica Fibers Unveiled: A Sustainable Approach for 4-Nitrophenol Removal in Aqueous Solutions through Activated Carbon Utilization

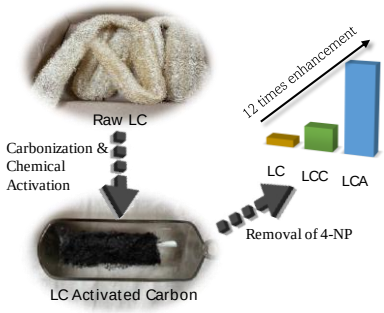
Nurfatehah Wahyuny Che Jusoh[1,2]*, Nurhanani Mohd Azani[1], Nawal Abd Ghafar[1] and Khairunnisa Mohd Paad[1]

[1] *Department of Chemical and Environmental Engineering (ChEE), Malaysia-Japan International Institute of Technology (MJIIT), Universiti Teknologi Malaysia Kuala Lumpur, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia.*
[2] *Center of Hydrogen Energy, Universiti Teknologi Malaysia Kuala Lumpur, Jalan Sultan Yahya Petra, 54100, Kuala Lumpur, Malaysia.*

**Corresponding Author: nurfatehah@utm.my*

Article history:
Received 4 November 2023
Accepted 24 December 2023

GRAPHICAL ABSTRACT



ABSTRACT

The prevalence of mutagenic and highly toxic compounds, such as 4-Nitrophenol (4-NP) and its derivatives, in industrial wastewater poses a significant environmental threat. This study emphasizes the critical need for public authorities to prioritize combating organic compound pollution for sustainable development. The focus of this research is the preparation and evaluation of activated carbon adsorbents derived from *Luffa cylindrica* fibers (LC) for the efficient removal of 4-NP from aqueous solutions. The preparation involved the carbonization process by heating LC in an argon furnace at 800 °C, resulting in carbonized *Luffa cylindrica* fibers (LCC). Subsequently, chemical activation is performed using a potassium hydroxide (KOH) solution, denoted as LCA. The properties of the adsorbent are identified through X-ray diffraction (XRD). To assess the removal efficiency of 4-NP, various parameters, such as pH, adsorbent dosage, and 4-NP solution concentration, are investigated. Optimal conditions for maximum 4-NP removal are achieved at a concentration of 50 mg/L, an adsorbent dosage of 0.75 mg/L (LCA), and a solution pH of 5. These conditions result in an impressive 99.9% removal of 4-NP in 60 minutes. This study demonstrates the feasibility of utilizing locally available raw materials, such as LC fibers, to prepare an adsorbent with a robust adsorptive capacity for toxic pollutants like 4-NP. The findings underscore the potential of eco-friendly solutions for addressing environmental challenges and promoting sustainable practices in wastewater treatment.

Keywords: *Luffa Cylindrica, 4-Nitrophenol, Activated Carbon, Sustainable, Wastewater*

| eISSN 0128-2581 |

1. INTRODUCTION

The persistent challenge of various organic and inorganic constituents present in industrial effluents, particularly in Malaysia's surface and wastewater, remains a longstanding environmental concern. Phenol, known for its high solubility in water, oils, carbon disulfides, and various organic solvents, is a significant contributor to this issue [1]. Originating from both natural and chemical processes associated with industrial or human activities, the introduction of phenol and phenolic compounds into water poses a significant threat to the environment and ecosystems. Phenol, a crucial organic synthetic raw material, finds widespread application in the production of dyes, plasticizers, pharmaceuticals, and antioxidants [2].

One such phenolic compound, 4-Nitrophenol (4-NP), characterized by functional groups NN and OH on the benzene ring, is well-known for its presence in industrial effluents, contributing to unpleasant odors and tastes that can lead to carcinogenic problems. Acute exposure to 4-NP has been linked to various health issues, including blood disorders, kidney and liver damage, skin and eye irritation, anemia, and systemic poisoning in humans [3]. Consequently, governments have enacted laws to monitor and control 4-NP levels in both drinking water and effluents discharged from factories.

Several techniques have been developed to address the removal of 4-NP from contaminated water, such as adsorption, chemical oxidation, electrocoagulation, solvent extraction, and membrane separation. Among these, the adsorption process stands out for its efficiency in removing certain organic matter from waste effluents, boasting advantages such as initial cost-effectiveness, flexibility, and ease of operation. Activated carbons, renowned for their exceptional adsorption capabilities for organic pollutants, have been widely utilized, although their high initial cost and

the need for a costly regeneration system pose economic challenges. Consequently, researchers have explored low-cost, readily available alternatives, turning their attention to agricultural waste or industrial by-products as potential adsorbents.

For instance, Lv et al (2020) reported the preparation of activated carbon using rice husk via pyrolysis and potassium hydroxide (KOH)-activation. The rice husk-activated carbon possesses a high adsorption capacity for the removal of phenol. (325.27 mg/g) [4]. Additionally, Liu et al (2020) produce corn cob-activated carbon with have ability to remove 97.2% of mercury, Hg (II) in 120 min [5]. This shift is attributed to the economic and practical viability of adsorption by agricultural by-products, demonstrated in the removal of various pollutants, including phenol derivatives.

In this context, Luffa cylindrica fibers (LC), primarily composed of cellulose, hemicelluloses, and lignin in a proportion of 60%, 30%, and 10% by weight, respectively, emerge as a promising alternative adsorbent for the removal of 4-NP from aqueous solutions [6].

2. EXPERIMENTS

2.1 Preparation of *Luffa cylindrica* (LC) fibers, carbonized LC (LCC) and activated LC (LCA)

Luffa cylindrica fibers (LC) were obtained from a local market in Petaling Jaya, Malaysia. LC was cut into smaller pieces and washed multiple times to remove any adhering dirt and seeds with deionized water. Next, LC was dried in an oven under 100 ℃ for 12 hours. After that, the LC was flattened using a cold-press machine and placed in a sample boat to undergo the carbonization process in a furnace under an argon atmosphere. The LC was heated at a rate of 10 ℃/min and carbonized at 800 ℃ for 1 hour. The obtained sample was denoted as LCC.

Then the LCC was activated using potassium hydroxide (KOH) by mixing in a mass ratio of 1:2 in 30 mL of deionized water for 10 hours, then dried in an oven at 80 ℃. The mixture was heated again in an argon furnace at 700 ℃ at a rate of 10 ℃/min for 1 hour. Then, it was washed thoroughly with 1 M hydrochloric acid (HCl) to remove any inorganic salts. The sample will be washed a second time with deionized water to remove the acid and dried in an oven at 80 ℃ overnight. Thus, the activated sample was denoted as LCA.

2.2 Characterization

The structures of the adsorbent were determined by the X-ray diffraction (XRD) method with Cu-kα radiation, λ = 1.54 Å as an X-ray source at 25°C using the Empyrean Multi-Purpose Research X-Ray Diffractometer. The accelerating voltage was 40 kV, and the applying current was 40 mA.

2.3 Removal of 4-Nitrophenol (4-NP)

Adsorbent activity was evaluated in the adsorption of 4-Nitrophenol (4-NP) through a series of batch experiments. Various concentrations of 4-NP solution (ranging from 10 to 100 mg/L) were stirred (200 rpm) at room temperature, ensuring even dispersion of the adsorbent (dosages between 0.25 to 1.00 g/L). The pH of the solution was adjusted to the desired level using 0.1 M HCl or 0.1 M NaOH. At predetermined intervals, 3 ml aliquots were withdrawn, centrifuged, and then analysed using a UV-Vis spectrophotometer (Shimadzu UV-2600i, Japan) at 318 nm and 400 nm for acidic and basic samples, respectively, to determine the remaining concentration of 4-NP. Each experimental set was conducted in triplicate, and the removal percentage was calculated using the formula provided,

$$Removal\ [\%] = \frac{C_0 - C_t}{C_0} \times 100$$

where C_0 and C_t represent the initial and time-dependent concentrations of 4-NP, respectively.

3. RESULTS AND DISCUSSION

3.1 Characterization

The XRD analysis was conducted on LC, LCC, and LCA adsorbents. Figure 1 illustrates the XRD patterns obtained for each of these samples.

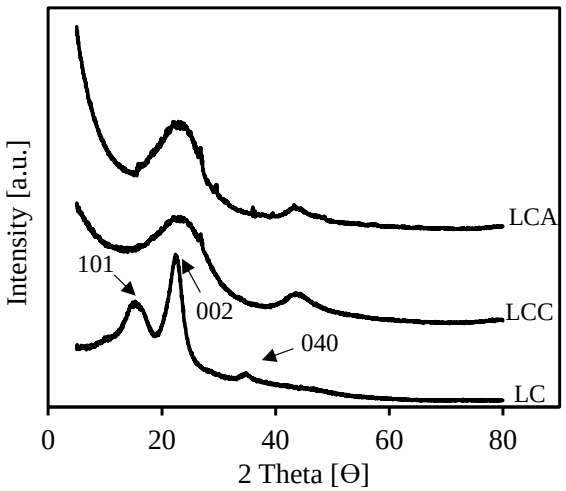


Figure 1. XRD pattern of LC, LCC and LCA adsorbents

The XRD pattern of LC displays characteristic features synonymous with cellulose, featuring well-defined diffraction signals at 2θ=15.4°, 22.5°, and 34.2°, corresponding to specific crystallographic planes, namely (101), (002), and (040), respectively [7]. Notably, two relatively broad diffraction peaks are observed around 23° and 44°, indicating the amorphous nature of both LCC and LCA samples.

Furthermore, the XRD analysis reveals distinctions between LCA and LCC. LCA exhibits a relatively intense peak compared to LCC, suggesting an increased degree of graphitization in the sample following the activation process. This enhanced graphitization signifies structural changes and modifications in the activated carbon, highlighting the impact of the activation process on the crystalline properties of the adsorbent [8].

3.2 Adsorption Study

The adsorption study encompassed a comprehensive exploration of the impacts of different factors, including the type of adsorbents, pH variations, adsorbent dosage, and 4-NP concentration. Within the effect of adsorbents, a comparative analysis was conducted among the three distinct adsorbents—LC, LCC, and LCA. The results, as depicted in Figure 2, revealed a distinctive adsorption behavior characterized by an initial rapid adsorption phase within the first 3 mins, followed by a slower adsorption phase that persisted until reaching a plateau at approximately 60 mins.

It is noteworthy that LC exhibited the lowest removal efficiency for 4-NP (8%). However, the carbonization process resulted in a notable improvement in adsorption properties, as evidenced by LCC, which exhibited a considerable increase to 25%. The subsequent activation process further enhanced the graphitization of the absorbent in LCA, leading to a remarkable 12-fold increment in 4-NP removal, a significant improvement compared to the initial LC adsorbent performance (95%).

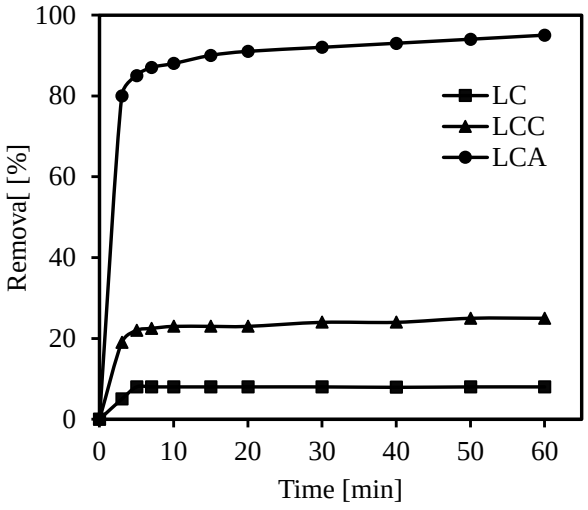


Figure 2. Effect of adsorbents (LC, LCC and LCA adsorbent) on removal of 4-NP [pH=5, adsorbent dosage=0.50 g/L, initial 4-NP concentration=50 mg/L, time=60min]

These results point out the significance of carbonization and activation steps in an argon atmosphere. The strength of adsorption is thought to be improved in the presence of argon, which promotes a greater internal porosity and higher effective surface area than raw LC [9, 10]. This has considerable value for specialized absorbents in practical applications to remove pollutant entities from solution or atmospheres. [9].

The subsequent parameter investigated in the adsorption study was the impact of solution pH on the removal of 4-NP using the LCA adsorbent. Solution pH plays a pivotal role in adsorption studies, as it has the potential to influence the surface charge of the adsorbent, as highlighted in previous research [11]. For this investigation, solution pH levels of 3, 5, 8, and 11 were selected. Figure 3 illustrates that the removal efficiency of 4-NP reached its maximum and remained relatively unaffected when the initial pH of the solution was within the range of 3 to 5. However, a noticeable decrease occurred as the pH of the solution increased beyond this range. This finding suggests that the adsorption of 4-NP is more pronounced in acidic solutions compared to basic solutions, and the percentage adsorption of 4-NP diminishes with an increase in the alkalinity of the medium [9]. This insight into the pH effect on adsorption is crucial for optimizing the conditions for the efficient removal of 4-NP in practical applications.

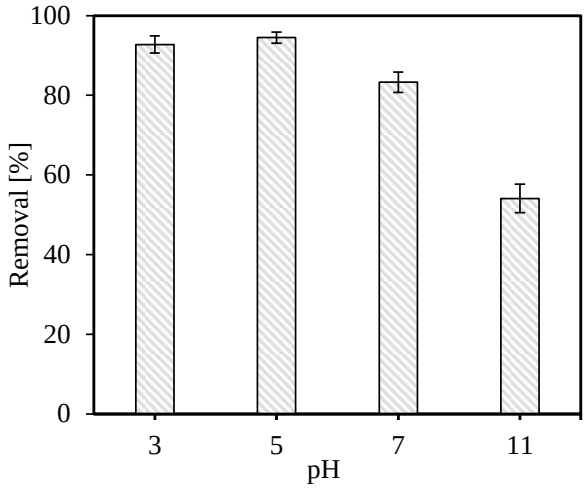


Figure 3. Effect of pH on 4-NP adsorption onto LCA adsorbent [Adsorbent dosage=0.50 g/L, initial 4-NP concentration=30 mg/L, time=60min]

Then, the influence of adsorbent dosage on the adsorption of 4-NP using the LCA adsorbent was investigated. Adsorbent dosage plays a critical role in adsorption studies, serving as the source of active sites for the adsorption of the dye molecules. The process temperature range explored in this study ranged from 0.25 to 1.0 g/L. The graphical representation of the effect of adsorbent dosage on 4-NP adsorption using the LC-A adsorbent is depicted in Figure 4. Notably, the percentage of 4-NP removal exhibited a discernible increase with the rising adsorbent dosage, ranging from 0.25 to 0.75 g/L, resulting in a removal efficiency increase from 89% to 98.5%.

This observed trend can be attributed to the escalating number of sorption sites available at the adsorbent surface as the adsorbent dosage increases, thereby enhancing the percentage of 4-NP removal from the solution [12, 13]. However, it is noteworthy that further increases in adsorption dosage, up to 100 mg, did not yield a significant increment in removal efficiency, stabilizing at 99%. Therefore, 75 mg of adsorbent dosage was deemed optimal for the subsequent investigation into the adsorption of 4-NP at varying concentrations.

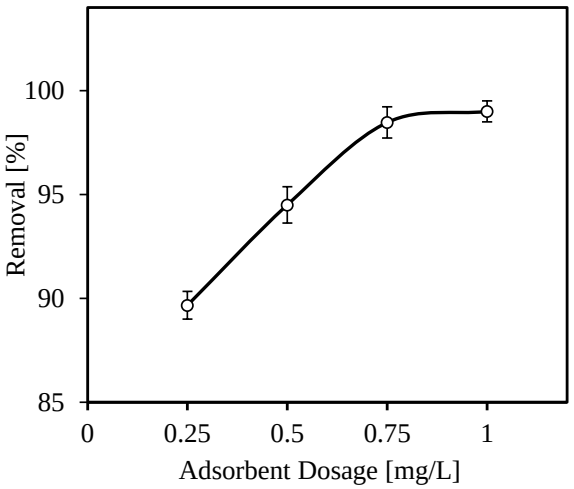


Figure 4. Effect of adsorbent dosage on 4-NP adsorption onto LCA adsorbent [pH=5, and initial 4-NP concentration=30 mg/L, time=60min]

Finally, the impact of the initial 4-NP concentration on the adsorption using the LCA adsorbent was investigated, focusing on a range of initial 4-NP concentrations from 10 to 100 mg/L. The graphical representation of this study is illustrated in Figure 5. Observations from the figure indicate a slight increase in the removal of 4-NP as the initial concentration rises from 10 mg/L to 50 mg/L, resulting in removal efficiencies of 95%, 98%, and 99% for 10 mg/L, 30 mg/L, and 50 mg/L, respectively.

However, further increases in the initial 4-NP concentration, up to 100 mg/L, led to a reduction in removal efficiency from 99% to 94.6%. This decline in removal efficiency with an increase in initial 4-NP concentration can be attributed to the potential saturation of adsorption sites on the LCA adsorbent. As the concentration of 4-NP in the solution rises, the available adsorption sites become saturated, leaving unadsorbed 4-NP in the aqueous solution [14]. These insights are crucial for understanding the behaviour of the adsorption system and for finding the best conditions for practical applications.

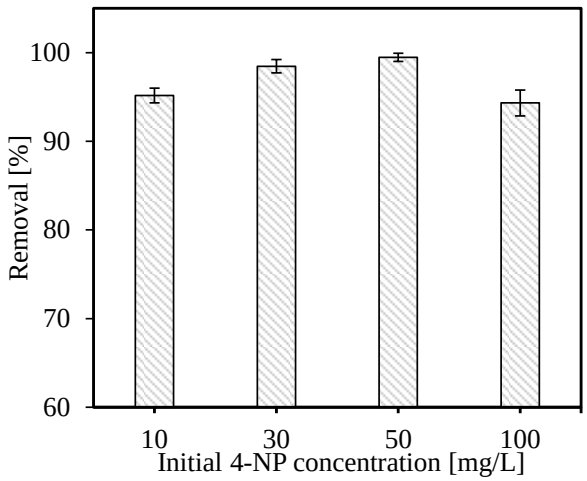


Figure 5. Effect of 4-NP initial concentration on adsorption onto LCA adsorbent [pH=5, and 0.75 mg of adsorbent dosage; time: 60 min]

4. CONCLUSION

This study successfully produced *Luffa cylindrica* fibers (LC) activated carbon adsorbent through carbonization and chemical activation with potassium hydroxide (KOH). The LC activated carbon (LCA) demonstrated remarkable properties, achieving a 99% removal efficiency for 4-NP under optimized conditions (pH=5, adsorbent dosage=75 mg, and initial 4-NP concentration of 50 mg/L). Notably, LCA outperformed LCC and LC, attributed to its chemical activation and heightened adsorption capabilities. The utilization of locally sourced raw materials, like *Luffa cylindrica* fibers, proved effective in creating a highly porous adsorbent with a significant 4-NP removal capacity. This approach, employing low-cost adsorbent, holds promise for environmental sustainability, potentially replacing commercial activated carbon in certain applications and emphasizing the importance of resourceful solutions for environmental challenges.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Higher Education Malaysia under Fundamental Research Grant Scheme, UTM, FRGS/1/2022/STG05/UTM/02/2.

REFERENCES

1. Al-Ananzeh, N., et al., Results in Engineering. **20** (2023) 101404.
2. Yin, H., et al., Microchimica Acta. **169** (2010) 87-92.
3. Serrà, A., et al., Catalysts. **10** (2020) 458.
4. Lv, S., et al., Applied Surface Science. **510** (2020) 145425.

5. Liu, Z., et al., Bioresource Technology. **306** (2020) 123154.
6. Frollini, E., et al., Natural Polymers and Agrofibers Composites. (2000).
7. Nadaroglu, H., S. Cicek, and A.A. Gungor, Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy. **172** (2017) 2-8.
8. Li, Z., et al., Colloids and Surfaces A: Physicochemical and Engineering Aspects. **538** (2018) 28-35.
9. Harimisa, G.E., et al., Chemical Engineering Research and Design. **198** (2023) 325-339.
10. Aghel, B., S. Behaein, and F. Alobaid, Fuel. **328** (2022) 125276.
11. Zhao, R., et al., Colloids and Surfaces A: Physicochemical and Engineering Aspects. **611** (2021) 125866.
12. Saber, S.E.M., et al., Radiation Physics and Chemistry. **209** (2023) 110967.
13. Nitayaphat, W. and T. Jintakosol, Journal of Natural Fibers. **19** (2022) 3365-3377.
14. Ezzuldin M. Saber, S., et al., RSC Advances. **11** (2021) 8150-8162.