

An Efficient Adsorption Approach For Sustainable Removal of Heavy Metals From Wastewater Using Biochar Derived From Cowpea Husk

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Abstract- Heavy metal contamination in wastewater poses significant environmental and health hazards, necessitating efficient removal strategies. Industrial discharges contribute to the accumulation of toxic and carcinogenic heavy metals in aquatic ecosystems, leading to severe consequences for both human and marine life. Among the various remediation techniques, adsorption has emerged as a highly effective, cost-efficient, and environmentally sustainable method for heavy metal removal. This study explores the potential of biochar derived from cowpea husk powder through KOH-assisted pyrolysis as a novel adsorbent for heavy metal remediation. The high surface area and enhanced adsorption capacity of biochar significantly improve metal removal efficiency. Experimental findings demonstrate a 93% removal efficiency for heavy metals at an initial concentration of 10 ppm and pH 8. The study further investigates the impact of key operational parameters, including adsorption time, pH variation, feed concentration, and adsorbent dosage, on metal removal efficiency. The results underscore the viability of biochar as a sustainable alternative to conventional adsorbents for wastewater treatment, offering a promising solution for mitigating heavy metal pollution.

Keywords- Heavy metal removal, wastewater treatment, adsorption, biochar, cowpea husk, pyrolysis, eco-friendly adsorbent, KOH activation, metal remediation, sustainable water treatment.

I. INTRODUCTION

Heavy metal contamination in wastewater has emerged as a serious environmental and public health challenge due to its toxic, persistent, and bioaccumulative nature. Unlike organic pollutants that can degrade over time, heavy metals such as lead (Pb), cadmium (Cd), chromium (Cr), mercury (Hg), and arsenic (As) are non-biodegradable and tend to accumulate in the soil, water, and living organisms, resulting in severe ecological and human health risks. Chronic exposure to these metals can lead to neurological disorders, liver and kidney dysfunction,

respiratory issues, immune system suppression, and increased carcinogenic risks. Industrial activities such as mining, electroplating, battery manufacturing, fertilizer production, and chemical processing are the primary contributors to heavy metal contamination, releasing significant amounts of these hazardous elements into water bodies. Due to their high toxicity, even trace amounts of heavy metals in drinking water or agricultural irrigation systems can pose long-term threats to ecosystem stability and human well-being. Therefore, it is crucial to develop effective, sustainable, and economically viable methods for the removal of heavy metals from wastewater to protect both the environment and public health. Several conventional techniques have been employed for heavy metal removal from wastewater, including chemical precipitation, ion exchange, membrane filtration, coagulation-flocculation, and electrochemical treatments. While these methods can achieve high removal efficiencies, they often suffer from high operational costs, secondary waste generation, energy-intensive processes, and limited metal selectivity. In contrast, adsorption technology has emerged as a cost-effective, efficient, and environmentally sustainable approach for heavy metal removal. Adsorption is widely preferred due to its simplicity, scalability, reusability, and high selectivity for metal ions, making it an ideal candidate for large-scale wastewater treatment applications.

Among various adsorbents, biochar-based materials derived from agricultural waste and biomass have gained significant attention as low-cost, renewable, and high-performance sorbents for heavy metal removal. Biochar is a carbon-rich material obtained through pyrolysis (thermal decomposition) of organic biomass under limited oxygen conditions. The physicochemical properties of biochar, including high surface area, porosity, surface functional groups (-OH, -COOH, -NH₂), and cation-exchange capacity, enhance its ability to chelate, adsorb, and immobilize heavy metals in contaminated water. By utilizing agricultural waste for biochar production, this approach also contributes to waste valorization and circular economy initiatives, making it a green and sustainable solution for environmental remediation.

Despite the potential of biochar for heavy metal adsorption, its performance varies significantly based on feedstock type, pyrolysis conditions, and surface modifications. In this study, cowpea husk powder was selected as a biomass precursor for biochar synthesis due to its abundance, low cost, and high carbon content. The pyrolysis process was KOH-assisted, which enhances the porosity, surface functionality, and adsorption efficiency of the resulting biochar. The key objectives of this study include:

1. Synthesis and Characterization of Cowpea Husk Biochar: Investigating the effect of KOH activation on surface morphology, functional groups, and adsorption capacity using techniques such as Scanning Electron Microscope with Energy Dispersive X-Ray Spectroscopy
2. Adsorption Kinetics and Isotherm Studies: Applying Langmuir model to understand the adsorption mechanism and capacity of cowpea husk biochar.

The outcomes of this study demonstrate the feasibility of cowpea husk-derived biochar as an efficient, low-cost, and environmentally friendly adsorbent for wastewater treatment. By integrating waste biomass valorisation and sustainable water purification, this research provides a scalable and practical solution for mitigating heavy metal contamination in industrial effluents and natural water systems.

The rest of this paper is structured to provide a comprehensive understanding of the study's methodology, findings, and implications. The Materials and Methods section details the preparation of cowpea husk biochar, its physicochemical characterization, and the experimental setup used for adsorption studies. This section also outlines the procedures followed to assess adsorption efficiency under varying conditions, including pH, contact time, initial metal concentration, and adsorbent dosage. The Results and Discussion section presents the key findings of the study. Finally, the Conclusion and Future Scope section summarizes the major findings, emphasizing the feasibility of using biochar as a sustainable solution for heavy metal removal. Additionally, this section discusses potential industrial applications and future research directions to further enhance biochar's adsorption efficiency and scalability in wastewater treatment systems

II. MATERIALS AND METHODOLOGY

The Mechanism of the suggested process was illustrated in this section,

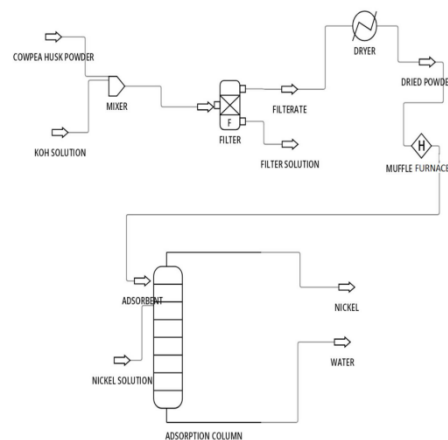


Fig. 1 Schematic representation of the suggested mechanism

The process flow diagram(See figure 1) illustrates the preparation of biochar from cowpea husk and its application in nickel adsorption from wastewater. In the biochar preparation stage, cowpea husk powder is mixed with KOH solution for chemical activation, followed by filtration to remove excess solution. The solid residue is dried and then transferred to a muffle furnace for pyrolysis, producing activated biochar with enhanced adsorption properties.

In the adsorption stage, the prepared biochar is packed into an adsorption column, where it treats nickel-contaminated wastewater. The nickel solution enters the column, and the biochar adsorbs the metal ions, allowing purified water to exit while nickel is retained in the adsorbent. This process provides a sustainable and cost-effective method for wastewater treatment using agricultural waste-derived adsorbents.

2.1 Collection of Cowpea Husk

The cowpea husk (*Vigna unguiculata*) used in this study was collected from local agricultural sources. Cowpea is a widely cultivated leguminous crop, particularly in semi-arid regions of Africa and Asia, due to its ability to grow in sandy soil with minimal rainfall. The husk, a byproduct of cowpea processing, is typically discarded as waste but holds potential as a raw material for activated carbon production.

Before use, the husks were thoroughly cleaned to remove dust, soil, and foreign particles. The cleaned husks were then sun-dried for 24 hours to remove surface moisture before being mechanically ground into a fine powder, ensuring a consistent particle size for further processing.

2.2 Preparation of Activated Carbon

The preparation of activated carbon from cowpea husk involved multiple steps, including chemical activation and thermal treatment.

First, the ground husk powder was impregnated with a potassium hydroxide (KOH) solution in a 1:2 weight ratio. The impregnated mixture was subjected to ultrasonication for 30 minutes to enhance the penetration of KOH into the husk matrix. Following ultrasonication, the material was placed in a rotary shaker for 4 hours to facilitate chemical interaction. The treated husk was then dried in a microwave oven at 120°C for 2 hours to remove excess moisture. After drying, the material underwent carbonization in a muffle furnace at 600°C for 2 hours under a nitrogen atmosphere to prevent unwanted oxidation.

The resulting activated carbon was washed with deionized water and diluted hydrochloric acid (HCl) to remove residual chemicals and neutralize pH. Finally, the washed carbon was oven-dried at 105°C and stored in airtight containers for further use.

2.3 Experimental Procedure

The adsorption experiments were conducted using batch adsorption methods by varying different parameters to assess the effectiveness of the activated carbon in nickel (II) ion removal.

2.3.1 Effect of Contact Time

The effect of contact time on nickel adsorption was determined by preparing a 10 ppm nickel (II) solution using nickel sulfate (NiSO_4). A 10 mL portion of this solution was mixed with 0.1 g of activated carbon in a conical flask. The flask was placed in a rotary shaker at 200 rpm, and samples were collected at 30-minute intervals (30, 60, 90, 120, 150, and 180 minutes). After each interval, the solutions were filtered using Whatman filter paper, and the residual nickel ion concentration in the filtrate was analyzed using a UV-Visible spectrophotometer at a wavelength of 470 nm.

2.3.2 Effect of pH

The effect of solution pH on nickel adsorption was studied by adjusting the pH of the 10 ppm nickel solution using dilute hydrochloric acid (HCl) and sodium hydroxide (NaOH). Six solutions with pH values ranging from 2 to 12 were prepared. Each solution was mixed with 0.1 g of activated carbon and shaken at 200 rpm for 60 minutes. After

adsorption, the solutions were filtered, and the residual nickel concentrations were measured using a UV-Visible spectrophotometer.

2.3.3 Effect of Initial Nickel Concentration

To examine the effect of initial nickel concentration on adsorption efficiency, six nickel solutions were prepared with concentrations of 10, 20, 30, 40, 50, and 60 ppm. Each solution was treated with 0.1 g of activated carbon and shaken for 60 minutes at 200 rpm. The mixtures were then filtered, and the remaining nickel ion concentration in the filtrate was determined using UV-Visible spectrophotometry.

2.3.4 Effect of Adsorbent Dosage

The effect of adsorbent dosage was evaluated by preparing six samples containing 10 mL of 10 ppm nickel solution. The amount of activated carbon added varied between 0.2 g, 0.4 g, 0.6 g, 0.8 g, 1.0 g, and 1.2 g. The solutions were shaken at 200 rpm for 60 minutes. After the adsorption process, the solutions were filtered, and the residual nickel content was measured.

2.4 Adsorption Isotherms and Kinetics Studies

To understand the adsorption mechanism, the experimental data were analyzed using Langmuir and Freundlich isotherm models.

2.4.1 Langmuir Isotherm

The Langmuir adsorption model is represented by the equation:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad \#(1)$$

where q_e is the amount of nickel adsorbed per unit mass of adsorbent, C_e is the equilibrium concentration, q_{\max} is the maximum adsorption capacity, and K_L is the Langmuir constant.

2.4.2 Freundlich Isotherm

The Freundlich adsorption model is given by:

$$q_e = K_F C_e^{1/n} \quad \#(2)$$

where K_F and n are Freundlich constants indicating adsorption capacity and intensity.

2.7 Statistical Analysis

All experiments were conducted in triplicate, and the results were expressed as mean \pm standard deviation. Statistical analysis, including ANOVA and regression analysis, was performed using SPSS software to determine significant differences between experimental conditions.

III.RESULT AND DISCUSSION

This section presents the results obtained from the adsorption experiments and provides an in-depth discussion of the findings. The adsorption efficiency of cowpea husk-derived activated carbon for nickel (II) removal was analyzed based on varying contact time, pH, initial nickel concentration, and adsorbent dosage. The adsorption mechanism was further studied using isotherm models and kinetic analysis.

After the samples were tested with UV spectroscopy to measure the absorbance of the nickel in the sample and the results were came out for those four parameters test and calculation were done.

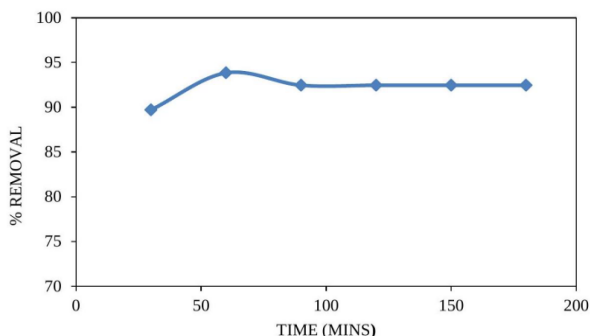


Fig. 2 Effect of time on HM removal: Initial con. 10 ppm, 200rpm, dosage 0.1 g

The graph shows that nickel removal increases with contact time, reaching a peak at **60 minutes** before stabilizing. This suggests that the initial rapid adsorption is due to the availability of active sites on the adsorbent, while the equilibrium phase occurs as the sites become saturated. Beyond 60 minutes, no significant improvement in removal efficiency is observed, indicating equilibrium adsorption.

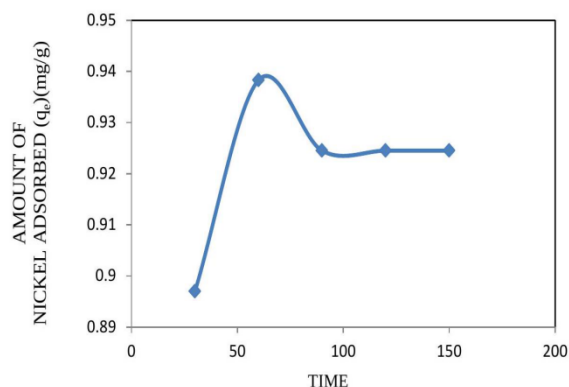


Fig. 3 Effect of time on amount of nickel adsorbed

The adsorption capacity (q_{eq_eqe}) follows a similar trend, increasing sharply and peaking at 60 minutes before stabilizing. The initial rise is due to fast adsorption on available active sites, and the subsequent decline or stabilization suggests that the adsorbent has reached its maximum adsorption capacity, limiting further nickel uptake.

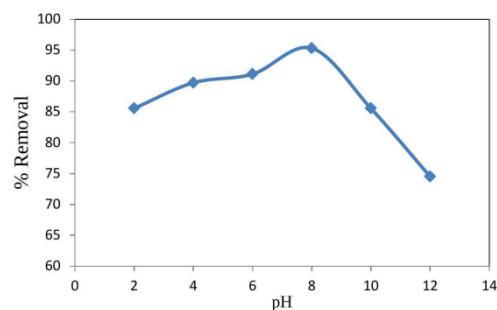


Fig. 4. Effect of pH on HM removal: Initial con. 10 ppm, 200rpm, dosage 0.1 g

The removal efficiency is highly dependent on pH, with **maximum adsorption at pH 8**. At lower pH levels, competition between H^{+++} ions and nickel ions for active sites reduces adsorption efficiency. At pH values above 8, the removal efficiency drops sharply due to the precipitation of $Ni(OH)_2$, reducing the availability of free nickel ions in solution.

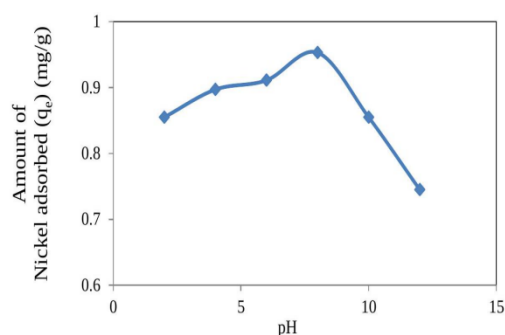


Fig. 5 Effect of pH on amount of nickel adsorbed

The adsorption capacity follows the same trend as removal efficiency, increasing with pH and peaking at **pH 8**. Beyond this, the decline is attributed to metal precipitation rather than adsorption, which reduces the effectiveness of the adsorbent in removing nickel from the solution

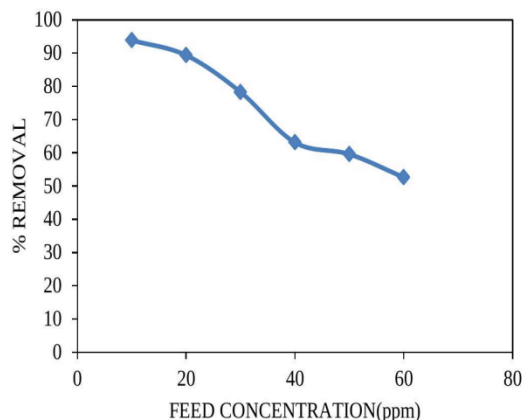


Fig. 6 Effect of feed concentration on HM removal: Initial con. 10 ppm, 200rpm, Time 60 min.

As the feed concentration increases, the percentage of nickel removal decreases. This is because, at higher concentrations, there are more nickel ions competing for the same number of available adsorption sites, leading to a lower removal percentage. However, the adsorbent remains effective at lower concentrations.

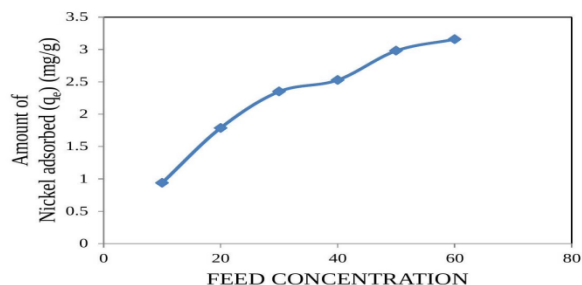


Fig. 7 Effect of feed conc. on amount of nickel adsorbed

Unlike removal efficiency, the adsorption capacity increases with increasing initial nickel concentration. This suggests that higher concentrations provide a stronger driving force for mass transfer, allowing the adsorbent to capture more nickel ions per gram of adsorbent, even though the overall percentage removal decreases.

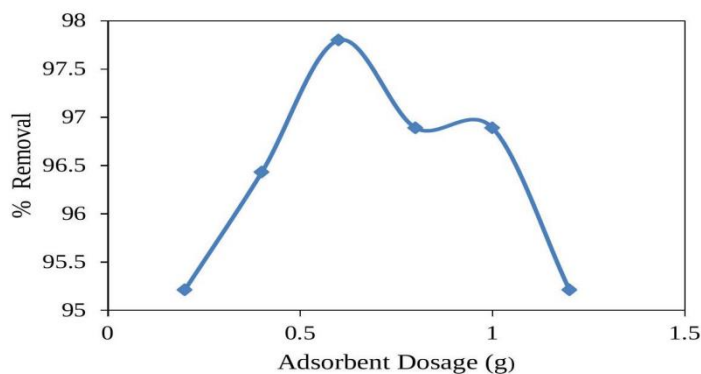


Fig. 8 Effect of adsorbent dosage on HM removal: Initial con. 10 ppm, 200rpm, Time 60 min.

The removal efficiency increases with adsorbent dosage, reaching a maximum at **0.6 g**, after which it declines. This indicates that increasing the adsorbent amount initially provides more active sites, but beyond the optimal dosage, particle aggregation occurs, reducing the effective surface area for adsorption.

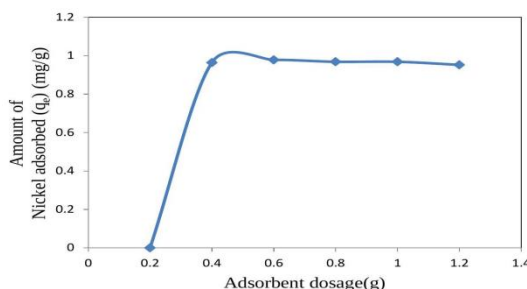


Fig. 9 Effect of adsorbent dosage on amount of nickel adsorbed

Adsorption capacity increases with adsorbent dosage up to **0.6 g**, beyond which it stabilizes. This suggests that after reaching saturation, additional adsorbent does not contribute to increased adsorption but rather leads to reduced efficiency due to overlapping or blocked active sites.

Fig. 10 Material balance around Adsorption Column

The schematic illustrates the adsorption process, highlighting the influent and effluent conditions. The system treats 300 L of water with an initial nickel concentration of 180 mg/L, reducing it to 11.6 mg/L after treatment. The mass balance calculations confirm the adsorbent dosage of 3 kg, with a calculated adsorption capacity of 16840 mg/kg, ensuring efficient removal of nickel ions.

Table 1: Adsorption column design parameters

| Parameter | Value |
|-------------------------------|-----------------------|
| Mass of adsorbent | 3 kg |
| Volume of adsorbent per cycle | 0.00450m ³ |
| Volume of adsorption tank | 0.380m ³ |
| Selected reactor size | 0.550m ³ |
| Diameter of tank | 0.623 m |
| Area of tank | 0.493m ² |
| Height of tank | 1.36 m |

This adsorption column design ensures efficient heavy metal removal while maintaining an economical and scalable treatment process.

These results confirm that cowpea husk-derived activated carbon is an efficient and cost-effective adsorbent for nickel removal, with optimized conditions at pH 8, 60 minutes contact time, and 0.6 g adsorbent dosage.

IV. DISCUSSION

The cowpea husk-derived activated carbon has better adsorption capacity for nickel (II) ions and hence can be used as an adsorbent for the removal of nickel (II) ions from wastewater as reported in the study. The factors that affect the adsorption process were contact time, pH, initial concentration of nickel and dosage of adsorbent. This indicated that adsorption improved with time and reached a condition of equilibrium after 60 min, since the removal was not significant when the time exceeded 60 min. This indicates that fast uptake occurred due to the availability of vacant adsorption sites, and the latter saturation phase was a result of site occupation and interaction between adsorbed nickel ions and those in solution.

Nickel adsorption was highly dependent on the solution pH: maximum efficiency was reached at pH 8. The low pH stage hydrogen ion compete with Ni²⁺ ions for active sites, leading to decreased adsorption; while at high pH, corrosion precipitation of nickel hydroxide and - decrease of removal efficiency. Results for nickel removal percentage_Initial concentration were also reported, and the values decreased with an increase in Initial concentration, however, the mg/g adsorbed increased with an increase in Initial concentration, which illustrates the transition from high active sites during low concentrations to saturation state at higher concentrations. The maximum removal of 97.8% was obtained at an adsorbent dose of 0.6 g. The lowering effect became negligible beyond this dose, as an increase in the amount of adsorbent leads to agglomeration of adsorbent particles, reducing available surface area.

The Langmuir isotherm model provided a good fit for the adsorption data, and confirmed that adsorption was a monolayer onto a surface. Results indicated a relatively high correlation coefficient, which suggests that adsorption takes place at certain binding sites that favors the chemisorption mechanism. The pseudo-second-order model fit the experimental results well, suggesting that the adsorption mechanism was governed by chemical reactions rather than diffusion. The model of the adsorption column was created based on the experimental results, having optimal dimensions of 0.380 m³, while the adsorbent quantity obtained per cycle was 3 kg. A reactor volume of 0.550 m³ was selected, indicating the potential for process scaling for practical application for wastewater treatment.

The adsorption performance of cowpea husk adsorbent was found to be more effective compared to various agricultural waste-derived adsorbents such as derived from rice husk biochar and yield from sugarcane bagasse. showing its promise as an inexpensive and effective material for remediating heavy metals. Nevertheless, additional studies are required to investigate its applicability to actual industrial effluents, assess its regeneration potential following several sorption/desorption cycles, and ascertain optimal continuous flow systems for wide-scale application. These results also support the use of activated carbon from agricultural waste as a green adsorbent that is competitive with commercial adsorbents towards a sustainable and cost-effective way to purify water.

V. CONCLUSION

Results showed that activated carbon derived from cowpea husk can be used as an effective and inexpensive adsorbent for nickel (II) ions removal from wastewater. The contact time, pH of the solution, initial nickel concentration and adsorbent dosage played to large extent in the adsorption process with the highest removal efficiency of 97.8%, which took place with the use of 0.6 g adsorbent dosage while maximum adsorption of 95.3% nickel removal was obtained at pH 8 thus, indicating that the solution pH was vital for optimizing the adsorption efficiency. The specific adsorption equilibrium categories were reached after 60 minutes with 93.83% of nickel removed in the contact time experiments. The maximum adsorption capacity was determined as 16840 mg/kg, indicating that even though nickel removal efficiency decreased at higher initial concentrations, the amount of nickel adsorbed subsequently increased.

The adsorption of ZnO was better expressed by the Langmuir isotherm models which indicated monolayer adsorption on a surface having homogeneous sites. Kinetic

studies showed that the adsorption process obeyed the pseudo-second-order model, suggesting that chemisorption was the governing mechanism in the adsorption of OSA-L in influsing solutions. The adsorption column design calculations gave a reactor size of 0.380 m³ and determined a reactor size of 0.550 m³ to ensure practical up-scaling [1534, 1536]. The calculated amount of adsorbent needed was found to be 3 kg per cycle, indicating the feasibility of the process for treating industrial wastewater.

Although the high adsorption efficiency has been demonstrated, the study needs further validation in practical industrial wastewater containing diverse competing ions. Particularly, future studies should encompass regeneration studies via repeated adsorption-desorption cycles as these results will inform the feasibility of these adsorbent materials in terms of their economics and long-term reutilization. Moreover, continuous flow adsorption experiments in fixed-bed columns need to be developed for the optimization of adsorption parameters for an industrial application of the adsorption process. Devise modifications for improving adsorbent stability and selectivity towards the practical implementation.

Overall, this study shows that activated carbon derived from cowpea husks could be an industrially viable, low-cost and more environmentally friendly alternative to conventional adsorbents for wastewater treatment applications. The high performance with the low cost of agricultural waste materials also confirms using as an effective biosorbent for heavy metals removal, which could lead to a sustainable bioecosystem in biosorption and sustainable wastewater treatment systems.

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