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# Biosorption of Cadmium(II) Ions from Wastewater using Carabao Grass (*Paspalum conjugatum*): Morphological Characterization and Adsorption Kinetic Studies

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The presence of cadmium(II) in wastewater poses significant risks to human health and the environment, highlighting the need for sustainable and efficient treatment methods. This study aimed to evaluate dried powdered carabao grass as an adsorbent for cadmium by examining its morphology, adsorption capacity and the isotherm and kinetic models governing the adsorption process using a true experimental design. The morphology of the adsorbent was analysed through scanning electron microscopy (SEM), while cadmium concentrations were determined using ICP-OES. SEM images revealed that the adsorbent exhibited an irregular, elongated structure with extensive pores, which contributed to its adsorption performance. The material achieved a maximum adsorption capacity of 0.588 mg $g^{-1}$ and a cadmium removal efficiency of 93.68% at a contact time of 180 min. Adsorption isotherm analysis showed high correlation coefficients for both the Langmuir ($R^2 = 0.9996$) and Freundlich ($R^2 = 0.9883$) models. However, the Langmuir constant ($K_L = -91.554$ L $mg^{-1}$ and $Q_{max} = 0.513$ mg $L^{-1}$) and Freundlich constants ($K_F = 0.468$ mg (L $mg^{-1})^{1/n}$ and $n = -9.862$) showed otherwise. This indicates that neither Langmuir nor Freundlich isotherm model are suitable in describing the adsorption of cadmium(II) ions onto the dried powdered carabao grass. Conversely, the adsorption kinetics followed pseudo-second-order kinetic model ($R^2 = 0.9971$) which resulted to a rate constant of 0.3791 g $mg^{-1}$ $min^{-1}$. Thus, the dried powdered carabao grass was an ideal adsorbent of cadmium governed by chemical adsorption.

**Keywords: Cadmium, Carabao grass, Langmuir isotherm model, Pseudo-second-order kinetic model.**

## INTRODUCTION

Adsorbent is a solid phase substance that can adsorb other substances on its surface. It is usually obtained from agricultural wastes and byproducts, which is a widely used materials for the separation of toxic materials on wastewater due to its economic impact and high efficiency [1]. The use of adsorbent has been used for a while now as an alternative sustainable solution for removing heavy metals ions in wastewater treatment [2]. Heavy metals, specifically cadmium, when released in the environment are highly toxic that pose a great risk to human health as well as to other organisms [3].

In Camarines Norte, Philippines, small-scale gold miners dispose the untreated mining tailings into nearby rivers, which then flow into Mambulao Bay, Philippines. It was found that the sediments in the bay contain a considerable amount of cadmium with a total concentration of 1.4 mg $kg^{-1}$. This resulted in an adverse biological effect on the aquatic biota of Mambulao Bay [4]. Likewise, in Sarangani, Philippines, ~ 0.095 ppm of cadmium was detected on the bottom sediments along the coastline, affecting the fishes near the area [5].

Despite the extensive research on plant-derived materials and agricultural byproducts such as rice husks, banana peels and corn cobs as adsorbents for heavy metal removal [6-8], the potential use of weeds has received comparatively little attention. In particular, studies focusing on carabao grass (*Paspalum conjugatum*) remain limited. Previous studies have mainly focused on the role of *Paspalum conjugatum* in the remediation of heavy metal accumulation in soils [9,10], while its potential application as an adsorbent for wastewater treatment remains largely unexplored.

Addressing this research gap may reveal the broader utility of this widely available weed as a sustainable and low-cost adsorbent for cadmium removal from wastewater. Therefore, this study aims to evaluate its effectiveness in reducing cadmium contamination, which may contribute to protecting aquatic ecosystems, improving drinking water quality and promoting sustainable wastewater management practices bene-

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ficial to both communities and environmental conservation. *Paspalum conjugatum*, commonly known as carabao grass or buffalo grass, belongs to the Poaceae family [11]. It is a stealing perennial grass characterized by long stolons and typically grows to a height of 40-100 cm [12]. The plant is commonly found in wild and urban environments and is widely used as livestock forage and for landscaping purposes [13].

## EXPERIMENTAL

**Plant collection:** The carabao grass was collected from Barangay Magsaysay, New Bataan, Davao de Oro, Philippines, placed in a resealable bag and then authenticated by the qualified botanist of the Department of Agriculture – RFO XI.

**Preparation of carabao grass extract:** The carabao grass was washed thoroughly with tap water multiple times to remove any dust and dirt. This would be followed by a final rinse with distilled water, which ensures that there are no unwanted particles that hindered the experiment. The collected grass was dried in a dehydrator at 50 °C for 4 h to remove moisture. The dried material was then ground into a fine powder using a grain-milling machine to enhance its adsorption potential [14]. The powdered sample was sieved to obtain a uniform particle size of 250 μm and the resulting particles were stored in a desiccator until further use.

**Adsorption process:** In an Erlenmeyer flask, 2 g of dried powdered carabao grass was brought into contact with 1 L of 1 ppm cadmium solution. The pH of the aqueous solution was adjusted to pH 3.5 using 0.1 M NaOH solution. The flasks were then horizontally agitated using an orbital shaker at 200 rpm for 3 h at room temperature [15]. The concentration of the solution was tested at 20 min time interval to analyze the cadmium removal over time. The experiment was conducted in triplicate to ensure reliability and consistency of the results [16].

**Adsorption capacity:** To understand the adsorbate uptake on the surface of the powdered carabao grass, the adsorption capacity at time (t) and at equilibrium, was calculated using the following equation:

$$Q_t = \frac{V \times (C_o - C_t)}{m} \quad (1)$$

$$Q_e = \frac{V \times (C_o - C_e)}{m} \quad (2)$$

where the $Q_e$ and $Q_t$ were the adsorption capacity (mg g$^{-1}$) at equilibrium and time; V as the volume of aqueous solution (L); m as the mass (g) of adsorbent added; $C_o$ as the initial concentration of cadmium solution; $C_e$ as the concentration at equilibrium; and $C_t$ as the concentration of cadmium at time [17].

### Adsorption isotherm study

**Langmuir isotherm model:** The Langmuir isotherm model was used to predict the maximum adsorption capacity of the dried powdered carabao grass, assuming that the adsorbate molecules form a monolayer on the surface of the adsorbent. This relationship was described using the following linear equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max}} C_e + \frac{1}{Q_{max} K_L} \quad (3)$$

where $Q_{max}$ represents the maximum adsorption capacity (mg/g) of the adsorbent and $K_L$ is the Langmuir equilibrium constant (L/mg). The values of $Q_{max}$ and $K_L$ would be calculated through linear regression analysis and by plotting $C_e/Q_e$ *versus* $C_e$ [18].

**Freundlich isotherm model:** The Freundlich isotherm model assumed that the adsorbates form a multilayer on the surface of adsorbent and described by the following linear relation (eqn. 2):

$$\log Q_e = \frac{1}{n} \log C_e + \log K_F \quad (4)$$

where $K_F$ is the Freundlich constant, an indicative of the adsorption capacity of the adsorbent and n is the Freundlich exponent depicting adsorption intensity. The $K_F$ and n would be identified through linear regression and by plotting log $Q_e$ *versus* log $C_e$ [19]. The model that exhibits the highest $R^2$ would be considered the best-fitted isotherm model.

### Adsorption kinetics study

**Pseudo-first-order (PFO) kinetic model:** The adsorption rate constant was determined using the pseudo-first-order kinetic model, which is commonly associated with physical adsorption and is expressed by the following linear equation (eqn. 2):

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 t \quad (5)$$

where $Q_t$ is the amount of cadmium ions adsorbed at a given time; $Q_e$ is the amount of $Cd^{2+}$ ions adsorbed at equilibrium; t is the contact time (min) and $k_1$ is the rate constant (min$^{-1}$) [20]. The value of $k_1$ was obtained from the linear relationship between $Q_t$ and t through regression analysis [19].

**Pseudo-second-order (PSO) kinetic model:** The pseudo-second-order kinetic model was used to estimate the adsorption rate constant, assuming a chemisorption mechanism, and is repressented by eqn. 3:

$$\frac{1}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (6)$$

where $k_2$ is the PSO rate constant (g mg$^{-1}$ min$^{-1}$) [20]. The $k_2$ would be determined through linear regression analysis by plotting $t/Q_t$ *versus* t [19].

## RESULTS AND DISCUSSION

**Morphological studies:** Fig. 1 shows the SEM micrograph of the dried powdered carabao grass, revealing an irregular and elongated morphology with a rough and highly porous surface. The abundance of pores and surface cavities indicates a large specific surface area and a high density of potential adsorption sites, which are favourable for cadmium ion uptake. Enhanced adsorption performance can be attributed to the porous and irregular morphology of plant-derived adsorbents, which provides increased surface area and more active sites for contaminant attachment [21].

The rough and porous surface texture plays a significant role in the adsorption mechanism by facilitating the diffusion of cadmium ions from the aqueous phase to the interior and

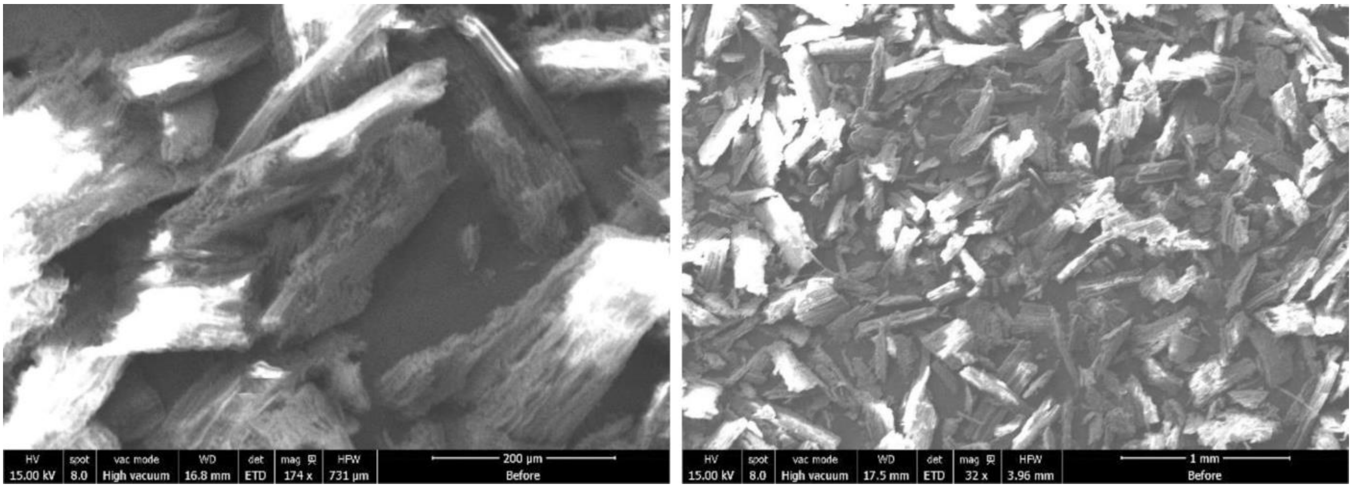

Fig. 1. SEM images of the shape of dried and powdered carabao grass

surface of the adsorbent particles. The irregular morphology increases surface heterogeneity, thereby promoting physical adsorption and enhancing the accessibility of active sites for cadmium binding. This observation is consistent with previous findings showing that surface roughness improves adsorption capacity by providing more contact points for metal ion attachment [22]. Furthermore, the interconnected pore structure shortens diffusion pathways and accelerates the mass transfer of cadmium ions toward the adsorption sites [23]. The combined effects of increased surface area, surface roughness and pore distribution enhance cadmium-adsorbent interactions, resulting in higher cadmium uptake and improved removal efficiency. These results demonstrate that the favourable surface morphology of dried powdered carabao grass plays a crucial role in governing cadmium adsorption from aqueous solutions.

**Optimization of the adsorption parameters:** The adsorption study was conducted at pH 3.5, which was chosen to optimize cadmium ions removal while minimizing interference with hydrogen ions. At this acidic pH, the surface functional groups of carabao grass, such as hydroxyl and carboxyl groups, remain available for binding cadmium ions without excessive protonation, enhancing adsorption efficiency. Maintaining pH below the $Cd(OH)_2$ precipitation limit ensures that $Cd^{2+}$ removal is mainly attributed to adsorption rather than precipitation. Adsorption of $Cd^{2+}$ onto biomass and carbon-based adsorbents increases with pH (typically between 3 and 7) due to reduced proton interference and greater deprotonation of functional groups, whereas higher pH may induce $Cd(OH)_2$ precipitation, complicating the adsorption process [24].

The cadmium(II) concentration was determined by ICP-OES instrument to evaluate removal efficiency. As shown in Table-1, cadmium concentrations were monitored every 20 min for 3 h. From an initial concentration of 1.256 mg/L, 90.95% removal occurred within 20 min, followed by minor changes until equilibrium was reached at 180 min with 93.68% removal. The initial rapid uptake is attributed to the abundant unoccupied active sites on the irregular, porous surface of dried powdered carabao grass, providing a large effective surface area [17,25]. The subsequent fluctuations reflect a dynamic desorption–re-adsorption process, where weakly bound $Cd^{2+}$ ions temporarily disengage due to site saturation and rebind when sites become available [2]. The maximum adsorption efficiency was achieved after 180 min, when the available adsorption sites became saturated [3,16].

TABLE-1
CONCENTRATION OF Cd(II) (mg/L) AND CALCULATED PERCENT REMOVAL IN THE SOLUTION AT 20 min INTERVAL

| Time (min) | Mean Cd conc. (mg/L) | Std. Dev. | Removal (%) |
|---|---|---|---|
| 0 (initial) | 1.256 | 0.014 | 0.00 |
| 20 | 0.114 | 0.013 | 90.95 |
| 40 | 0.156 | 0.022 | 87.58 |
| 60 | 0.158 | 0.022 | 87.45 |
| 80 | 0.148 | 0.027 | 88.19 |
| 100 | 0.143 | 0.018 | 88.61 |
| 120 | 0.144 | 0.005 | 88.54 |
| 140 | 0.157 | 0.021 | 87.53 |
| 160 | 0.129 | 0.029 | 89.76 |
| 180 | 0.079 | 0.059 | 93.68 |

**Adsorption capacity:** Table-2 summarizes the time-dependent adsorption capacity ($Q_e$) and removal efficiency of cadmium onto dried powdered carabao grass. The data show a gradual increase in adsorption capacity over time, reaching a maximum of 0.588 mg $g^{-1}$ at 180 min, with a corresponding removal efficiency of 58.8%.

TABLE-2
ADSORPTION CAPACITY ($Q_e$) AND REMOVAL EFFICIENCY OF CADMIUM ONTO DRIED, POWDERED CARABAO GRASS OVER TIME

| Time (min) | $Q_e$ (mg/g) ± SD | 95% CI (mg/g) | Removal efficiency (%) ± SD | 95% CI (%) |
|---|---|---|---|---|
| 20 | 0.571 ± 0.003 | 0.565-0.578 | 57.1 ± 0.3 | 56.5-57.8 |
| 40 | 0.550 ± 0.005 | 0.540-0.560 | 55.0 ± 0.5 | 54.0-56.0 |
| 60 | 0.549 ± 0.014 | 0.490-0.608 | 54.9 ± 1.4 | 49.0-60.8 |
| 80 | 0.553 ± 0.017 | 0.484-0.622 | 55.3 ± 1.7 | 48.4-62.2 |
| 100 | 0.556 ± 0.013 | 0.495-0.616 | 55.6 ± 1.3 | 49.5-61.6 |
| 120 | 0.555 ± 0.008 | 0.526-0.584 | 55.5 ± 0.8 | 52.6-58.4 |
| 140 | 0.549 ± 0.012 | 0.506-0.592 | 54.9 ± 1.2 | 50.6-59.2 |
| 160 | 0.563 ± 0.018 | 0.493-0.633 | 56.3 ± 1.8 | 49.3-63.3 |
| 180 | 0.588 ± 0.031 | 0.508-0.667 | 58.8 ± 3.1 | 50.8-66.7 |

Based on Table-2, low SD and moderate 95% CI values confirm the reproducibility and statistical reliability of the results. Rapid adsorption occurred during the early stage (20-60 min) due to the availability of active sites, followed by a slower approach to equilibrium between 100 and 180 min. These statistical indicators show minimal variation among replicates, and therefore provides a reliable basis for subsequent kinetic analysis.

**Adsorption isotherms:** The Langmuir isotherm constants ($K_L$ and $Q_{max}$), Freundlich isotherm constants ($K_F$ and n), pseudo-first-order constant ($k_1$) and pseudo-second-order constant ($k_2$) were calculated using the linear regression analysis and the results are shown in Table-3.

TABLE-3
ISOTHERM PARAMETERS OF Cd(II) ADSORPTION ONTO CARABAO GRASS (*P. conjugatum*)

| Model | Parameter | Value |
|---|---|---|
| Langmuir | $Q_{max}$ (mg $g^{-1}$) | 0.513 |
| | $K_L$ (L $mg^{-1}$) | -91.554 |
| | $R^2$ | 0.9996 |
| Freundlich | $K_F$ (mg(L $mg^{-1})^{1/n}$) | 0.468 |
| | n | -9.862 |
| | $R^2$ | 0.9883 |
| Pseudo-first-order | $k_1$ ($min^{-1}$) | 0.0124 |
| | $R^2$ | 0.3259 |
| Pseudo-second-order | $k_2$ (g $mg^{-1}$ $min^{-1}$) | 0.3791 |
| | $R^2$ | 0.9971 |

The Langmuir model initially showed a very high correlation with the experimental data ($R^2 = 0.9996$), which would normally indicate monolayer adsorption on the uniform surface sites. The Freundlich model also produced a strong correlation coefficient ($R^2 = 0.9883$), suggesting the presence of heterogeneous surface interactions and possible multilayer adsorption. However, closer examination of the calculated isotherm parameters reveals inconsistencies with the theoretical requirements of these models. In the Langmuir isotherm, the constant 'b' must be positive to represent the favourable monolayer adsorption. The negative value obtained in this study is physically unrealistic, indicating that the Langmuir model does not adequately describe the adsorption behaviour [26].

A similar inconsistency is observed for the Freundlich model. The adsorption intensity parameter 'n' generally exceeds 1 for favourable adsorption. In this case, the calculated value of $n < 1$, contradicts this condition, suggesting that the Freundlich model is also unsuitable for explaining the adsorption mechanism of Cd(II) in this system [27]. Therefore, despite the relatively high correlation coefficients, the unrealistic parameter values indicate that neither the Langmuir nor the Freundlich isotherm provides an appropriate description of Cd(II) adsorption onto dried powdered carabao grass.

Adsorption kinetics were evaluated using the pseudo-first-order (PFO) and pseudo-second-order (PSO) models. The PFO model relates the adsorption rate to the availability of vacant adsorption sites and is generally associated with physical adsorption. In contrast, the PSO model assumes that the adsorption rate is controlled by chemical interactions between the adsorbate and the adsorbent surface. The kinetic results showed that the PSO model provided a much better fit to the experimental data ($R^2 = 0.9971$) than the PFO model, with a calculated rate constant $k_2$ of 0.3791 g $mg^{-1}$ $min^{-1}$. This strong agreement suggests that the adsorption of $Cd^{2+}$ onto dried powdered carabao grass is mainly governed by chemisorption processes [17,25], such as ion exchange or surface complex formation. Similar PSO-type kinetic behaviour has also been reported for $Cd^{2+}$ ions removal using various plant derived adsorbents, where ion-exchange interactions between $Cd^{2+}$ ions and functional groups on the adsorbent surface play an important role in the adsorption mechanism [21].

**Comparative studies:** The comparative data presented in Table-4 summarize recent investigations on plant-derived low-cost biosorbents for the removal of $Cd^{2+}$ ions from aqueous solutions. A wide variation in adsorption capacities is observed, indicating the strong influence of biomass type and surface characteristics on cadmium uptake. Among the reported materials, sugar beet biowaste exhibited the highest adsorption capacity ($Q_{max}$ = 505.6 mg $g^{-1}$), which may be attributed to the presence of abundant surface functional groups and a heterogeneous adsorption surface, as supported by the better fit of the Freundlich isotherm model [29]. Similarly, surfactant-modified guava seeds showed a significantly enhanced adsorption capacity ($Q_{max}$ = 328 mg $g^{-1}$) compared with the natural guava seeds (217 mg $g^{-1}$), confirming that surface modification plays a crucial role in improving the density and accessibility of active binding sites for $Cd^{2+}$ ions [28].

Moderate adsorption capacities were obtained for alkali-treated rice husk biochar (131.58 mg $g^{-1}$) [33] and activated carbon derived from khat stems (78.9 mg $g^{-1}$) [30], for which the equilibrium data were best described by the Langmuir

TABLE-4
CADMIUM ADSORPTION CAPACITY OF RAW/MODIFIED PLANT-DERIVED BIOSORBENTS

| Adsorbate | Plant-Derived Biosorbent | Isotherm model (best fit) | $Q_{max}$ (mg $g^{-1}$) | Ref. |
|---|---|---|---|---|
| $Cd^{2+}$ | Sugar beet biowaste | Freundlich | 505.6 | [28] |
| $Cd^{2+}$ | Surfactant-modified guava seed | Langmuir | 328 | [29] |
| $Cd^{2+}$ | Natural guava seed | Langmuir | 217.4 | [29] |
| $Cd^{2+}$ | Banana, peanut and orange husks | Langmuir/Freundlich | 48.2 (banana), 41.7 (peanut), 36.5 (orange) | [29] |
| $Cd^{2+}$ | Activated carbon from khat stem (*Catha edulis*) | Langmuir | 78.9 | [30] |
| $Cd^{2+}$ | *Luffa cylindrica* peels | Freundlich | 6.711 | [31] |
| $Cd^{2+}$ | Chamomile flower waste | Freundlich | 58.7 | [32] |
| $Cd^{2+}$ | Rice husk biochar (alkali-treated) | Langmuir | 131.58 | [33] |
| $Cd^{2+}$ | Orange peel (mercapto-acetic acid modified) | Langmuir | 136.05 | [34] |

isotherm model, indicating the monolayer adsorption on the relatively homogeneous surfaces. In contrast, untreated agricultural wastes such as banana, peanut and orange husks, as well as luffa peels and chamomile flower wastes, exhibited lower adsorption capacities (6.71-136.05 mg $g^{-1}$) and were generally better fitted by the Freundlich model, suggesting multilayer adsorption on heterogeneous surfaces. In present study, the obtained adsorption capacity ($Q_{max}$ = 0.588 mg $g^{-1}$) is lower than most of the reported values; however, the biosorbent is derived from an abundant and inexpensive raw material and requires minimal processing. This highlights its potential applicability as an environmentally benign and economically feasible adsorbent for the treatment of cadmium contaminated waters, particularly in low-resource settings.

## Conclusion

The findings of this study indicate that dried powdered carabao grass can serve as an efficient biosorbent for Cd(II) removal from aqueous medium. Its irregular and porous morphology provides a large number of accessible adsorption sites, enabling effective cadmium uptake. The $Cd^{2+}$ concentration decreased markedly from 1.256 mg $L^{-1}$ to 0.079 mg $L^{-1}$, demonstrating high removal efficiency at equilibrium. Although the Langmuir and Freundlich isotherm parameter values are not physically meaningful and therefore did not adequately represent the adsorption mechanism, however, the kinetic studies showed that the pseudo-second-order model best described the adsorption behaviour, suggesting that chemisorption controls the process. Based on the results, it can be concluded that dried powdered carabao grass shows promising low-cost and environmentally sustainable material for the cadmium removal from contaminated water.

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## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

## DECLARATION OF AI-ASSISTED TECHNOLOGIES

During the preparation of this manuscript, the authors used an AI-assisted tool(s) to improve the language. The authors reviewed and edited the content and take full responsibility for the published work.

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