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Coffee ground biosorbent for nitrite and nitrate recovery and soil nutrient

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Abstract. Nitrate (NO_3^-) and nitrite (NO_2^-) are two forms of nitrogen that contribute to the occurrence of eutrophication if found in excess concentrations. Conversely, nitrogen is one of the major macronutrients required for healthy plant growth. The purpose of this work is to evaluate the recovery of NO_3^- and NO_2^- from aquaculture wastewater (AW) by adsorption using coffee grounds (CG) as a biosorbent. The influence of carbonization temperatures (200 – 700 °C) was studied. The result postulates that CG carbonized at 200 °C was the most effective in NO_3^- and NO_2^- recovery from AW, having more than 80 and 70 %, respectively. The potential of the spent CG for soil conditioning was also investigated by evaluating the germination index (GI). The findings showed that spent CG from AW resulted in high GI with 105.6 % after 72 h of incubation. CG biosorbent is a potential sorbent to recover nitrate and nitrite from wastewater. The spent or nitrate and nitrite recovered biosorbent can be reutilized as soil nutrient.

Keywords: Coffee grounds, Biosorbent, Nitrate, Nitrite, Recovery, Aquaculture wastewater, Plant growth

1. Introduction

Nitrate (NO_3^-) and nitrite (NO_2^-) are two forms of dissolved solid nutrients that are present in aquaculture effluents or aquaculture wastewater (AW). However, the discharge of the untreated AW containing high concentrations of these nutrients can contribute to eutrophication, which can be detrimental to aquatic life and negative impacts on the environment (Nagaraju et al., 2022). On the other hand, nitrogen in the form of NO_3^- is essential for plant growth in terms of nutrient uptake in agriculture (Humayro et al., 2021). There are numerous physical-chemical and biological methods developed to treat NO_3^- and NO_2^- in water and wastewater such as precipitation, coagulation, ion-exchange, reverse osmosis membrane filtration, adsorption, anaerobic processes, and sequencing batch reactors. However, adsorption is relatively low-cost with simple operation and also efficient in removing heavy metals, dyes, and other organic pollutants (Singh et al., 2018; Wong et al., 2018).

In addition to that, the coffee industry is responsible for the abundance of coffee ground waste (CG) generated due to its growing popularity in recent years (Nguyen et al., 2021). CG's various functional groups have contributed to effective adsorption applications. Recent studies have reported that biochar or biosorbent derived from CG showed significant removal (> 99%) of lead and tetracycline, respectively (Kim et al., 2014; Oladipo et al., 2016). Additionally, it was reported that chemically modified CG biochar manifested high adsorption for ammonium with maximum adsorption capacity of 51.52 mg/g in aqueous solution (Nguyen et al., 2021). However, none has been reported on nitrate and nitrite. The intent of this study is to investigate the effectiveness of CG biosorbent prepared at different carbonization temperatures for nitrate and nitrite recovery. Additionally, the germination study using spent CG was evaluated to justify the spent CG as an alternative source of nutrients for plant growth.

2. Materials and Methods

2.1. Materials

CG was retrieved from a local Starbucks Chain located in Kampar, Perak, Malaysia. The collected CG was placed onto a tray for oven drying for 24 h at 105 °C, which was considered as raw sample and denoted as CG105.

2.2 GC105 carbonization

The CG105 was sieved to a size of < 250 μm prior to the carbonization process. A tubular carbonization unit with tubular reactor was used to carbonize 60 g of CG105 at various temperatures *i.e.* from 200 to 700 °C under a constant nitrogen gas flow rate for a certain hour. The carbonized biosorbents were denoted as CGB200, CGB300, CGB400, CGB500, CGB600, and CGB700.

2.3 Adsorption experiment

The collection of AW was done from an aquaculture farm situated in Kampar, Perak, Malaysia, and the adsorption tests were conducted using the collected AW. 1.0 g of carbonized biosorbents at various temperature levels were added to 200 ml of AW solution containing an initial concentration of 4.5 and 0.05 mg/L for NO_3^- and NO_2^-, respectively. The suspension was agitated at 150 rpm for 2 h min at room temperature (25 °C) using an orbital shaker. The suspensions were subsequently filtered with a cellulose acetate syringe filter (0.45 µm), and the final concentration of NO_3^- and NO_2^- were then analyzed. The concentrations of NO_3^- and NO_2^- were determined using the Vis-spectrophotometer (HACH DR3900) using the cadmium reduction method using powder pillows (8039) and diazotization method (10031) vial tests. All experiment works were conducted in duplicates and average values were reported. The recovery efficiency of the biosorbents was calculated based on Eq.(1) below:

$$Recovery\ efficiency\ (\%) = \frac{(C_0 - C_e)}{C_0} \times 100\ \% \qquad (1)$$

where C_0 represents the initial concentration (mg/L) whereas C_e represents the final concentration (mg/L).

2.4 Characterization

The presence of functional groups in the biosorbents prepared were identified using Attenuated total reflectance (ATR-IR) spectroscopy. Measurements were made within the 400 – 4000 cm^{-1} spectral range at room temperature.

2.5 Germination study

The biosorbent with the best performance in the adsorption test was chosen to examine the possibility of using the spent biosorbent as a soil conditioner for plant growth. The germination test helps characterize the acute toxicity or phytotoxicity of a sample based on the germination index (GI) (Oktiawan et al., 2018). The experimental conditions were adopted and modified from Baderna et al. (2015); however, okra seeds (*Abelmoschus esculentus*) were used instead. 5 g of the spent CGB was placed in a 9 cm petri dish and dampened with 5 mL of distilled water, filter paper is then set atop. Distilled water (control) and AW solution were used as liquid extracts; similarly, filter paper was placed on top and wetted with 5 mL of each solution. Next, 10 okra seeds were placed on the surface of the filter paper for the respective Petri dish and parafilm was used to seal the petri dish. All the petri dishes undergone 72 h of incubation in darkened conditions maintained at 25 °C. GI was determined using equations (2),**Σφάλμα! Το αρχείο προέλευσης της αναφοράς δεν βρέθηκε.** and **Σφάλμα! Το αρχείο προέλευσης της αναφοράς δεν βρέθηκε.** as shown:

$$RSG\ (\%) = \left(\frac{\overline{N}_{GS,i}}{\overline{N}_{GS,control}}\right) \times 100 \qquad (2)$$

$$RL\ (\%) = \left(\frac{\overline{L}_{GS,i}}{\overline{L}_{GS,control}}\right) \times 100 \qquad (3)$$

$$GI\ (\%) = \frac{(RSG \times RRL)}{100} \qquad (4)$$

where, RSG and RRG corressponds to the relative germination of seed (%) and the relative root growth (%). $\overline{N}_{GS,i}$ and $\overline{N}_{GS,control}$, respectively, are the mean number of seeds germinated in respective petri dish and in control; $\overline{L}_{GS,i}$, and $\overline{L}_{GS,control}$ are the mean root length of seeds germinated in respective petri dish and in control.

3. Results and Discussion

3.1 Influence of carbonization temperature

Based on the findings illustrated in **Figure 1,** CG200 biosorbent exhibited the highest recovery efficiencies of 80.7 and 71.4 % for NO_3^- and NO_2^-, respectively, from AW. CG105 showed high recovery for NO_3^- at 76.8 %, nonetheless, the recovery efficiency for NO_2^- is relatively low at 50 %. CG biosorbents prepared at higher carbonization temperatures (300°C and above) have no affinity for NO_3^- and significantly lower NO_2^- adsorption. The surface functional groups are associated with high recovery efficiencies of NO_3^- and NO_2- from AW. At a higher carbonization temperature, the functional groups are diminished. Thus, the recovery was mainly due to the active functional groups of CG biosorbents (Nguyen et al., 2021).

3.2 Characterization of biosorbents

The surface functional group distribution of GC105, CGB200, CGB300, CGB400, CGB500, CGB600 and CGB700 are illustrated in **Figure 2**. The noticeable broad adsorbance peak at 3350 cm^{-1} from CG105 and CGB200 was attributed to OH groups (alcohols) (Shin et al., 2023); however, the peak gradually decreased as the carbonization temperature increased from 300 to 700 °C. Similarly, the intense peak at 1742 cm^{-1} that correspsonds to the stretching of C=O, carboxylic groups (Pavlović et al., 2014), are no longer present after high carbonization temperatures (above 300 °C). Furthermore, CG105 and CGB200 exhibited an intensive peak at 1100 to 1020 cm^{-1} that is strongly associated with the C-O stretching vibration can be attributed to incomplete decomposition of cellulose, hemicellulose, and lignin (Han et al., 2021). Thus, this suggest that the surface functional groups may be the main driver for the recovery of NO_3^- and NO_2^- from AW.

3.3 Germination test

The response of okra seeds, *Abelmoschus esculentus,* to the toxicity of spent GC200 and raw AW in relative seed GI and relative root elongation is summarized in **Table 1**. The spent CGB200 showed a higher GI value (105.6) compared to exposing the seeds in raw AW with GI of 81.6 after 72 h.

Table 1 Germination index (GI) and root length of *Abelmoschus esculentus* seed after 72 h of incubation

Condition	Germination Index (%)	Average Root Length (cm)
AW	81.6	1.86 ±0.517*

Spent CG200	105.6	2.16±0.29*

*Values represent standard deviation of mean

The higher GI of the spent GCB200 also corresponds to a higher average root length at 2.16±0.29. This finding shows that GCB200 has a high potential to improve plant growth as a soil conditioner. The results contradict the claim made by Humayro et al. (2021) that spent CG in general has strong phytotoxic characteristics due to caffeine content, implying that it can impact the germination rate test.

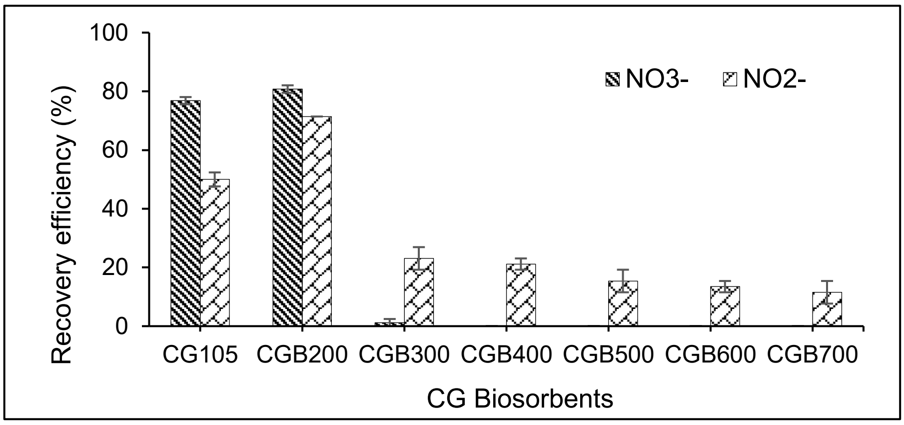

Figure 1. The influence of carbonization temperature on CG biosorbent preparation for NO_3^- and NO_2^- recovery from AW

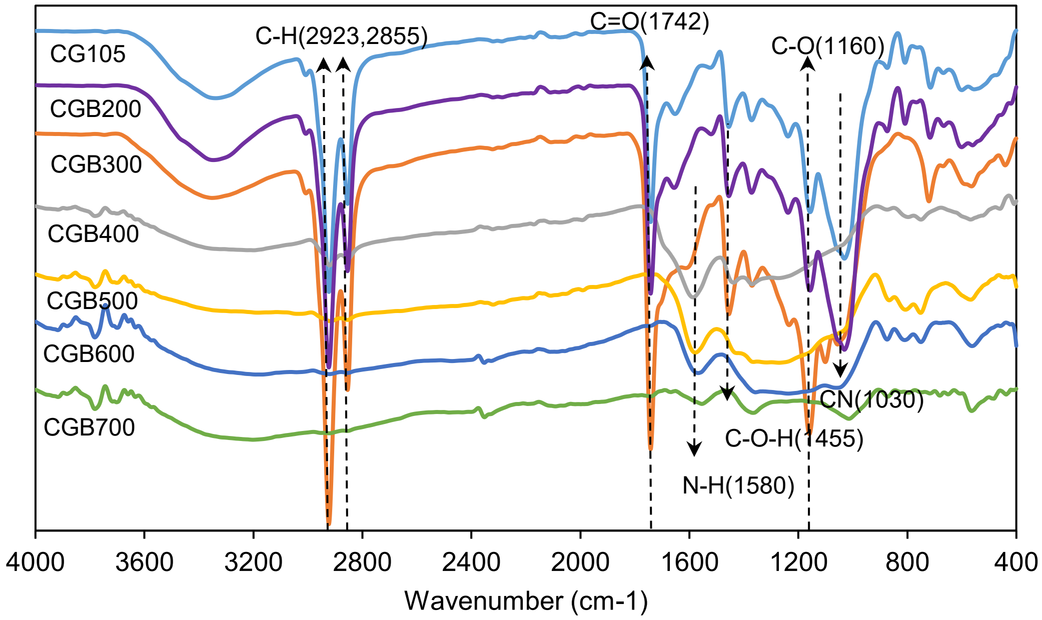

Figure 2. ATR-FTIR spectra of the biosorbents prepared at various temperature.

3.4 Cost-benefit analysis

A cost-benefit analysis (CBA) of biosorbents involves the assessment of economic costs and benefits associated with its production, application, and potential impacts as illustrated in **Table 2**. The cost-benefit ratio was determined using equation 5 (Porter & David, 2019). The CGB200 has an unique selling point whereby it functions as a wastewater adsorbent and also as a soil-conditioner post wastewater treatment.

Table 2 Cost-benefit analysis of CGB200

Cost of Biosorbent Production (per day)	**RM**
Feedstock acquisition	0.00
Energy costs for carbonization process	31.80
Labour costs associated with production	60.00
Total Cost	**91.80**
Expected Benefit	***100.00**
Cost-benefit ratio	**1.089**

*The expected benefit of the optimized CGB200 is an estimation made based on biochar selling price.

$$\boldsymbol{Cost-benefit\ ratio} = \frac{\sum \boldsymbol{Expected\ Benefit}}{\sum \boldsymbol{Associated\ cost}} \quad (3)$$

The total cost was lower compred to the market value and the cost-benefit ratio was slightyly more than 1.0. A reading of 1.0 suggests that the benefits equal the costs. It’s important to note that the specific costs and benefits of biochar can vary depending on factors such as feedstock type, production scale, regional factors, and the specific application.

4. Conclusions

In summary, the preparation of CG biosorbent is environmentally friendly and it does not require any physical or chemical activation to enhance its performance. The preparation of CGB200 was low-cost and the spent CGB200 (by-product generated after recovery of NO_3^- and NO_2^- from AW) is organic and can be easily biodegradable. The adsorption method is relatively easy to operate and less time-consuming compared to the conventional method, i.e., biological treatment method for the removal of NO_3^- and NO_2^- from wastewater. Moreover, the spent CGB200 as soil conditioner can help to reduce the production of chemically synthesized fertilizer in crops production. The cost benefit was positive. The best CG was prepared at 200°C and the spent CG200 has shown excellent germination. Thus, it is evident that CG200 can be reutilized as a soil conditioner for plant growth.

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