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BIOCHAR-MEDIATED REMEDIATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN WASHING EFFLUENT FROM AUTOMOBILE SERVICE STATION SOIL

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Introduction

Petroleum hydrocarbon contamination resulting from human activities including spills, industrial manufacturing, and fossil fuel disposal is a global environmental issue. Considering the contamination of soils by petroleum oil, it has been discovered of a major challenge to the environment. The surge in the automobile industry has increased automobile service stations, especially in developing countries. As per the studies, it was revealed that service stations often discharge wastewater containing over 600 mg/L of oil and grease, contributing to soil contamination [1].

One of the hazardous pollutants of huge concern is Polycyclic Aromatic Hydrocarbons (PAHs), known for their persistence, hydrophobicity, and ability to accumulate in the environment. PAHs, characterized by their molecular structure comprising two to six conjugated aromatic rings, pose significant health risks and have gained increasing attention from the scientific community. The US Environmental Protection Agency (EPA) has identified 16 PAHs as priority contaminants with potential carcinogenic effects, including pyrene (PYR). Pyrene is a dominant PAH resulting from incomplete combustion of oil and its by-products, often found in soil due to its low degradability and volatility. The EPA has recommended a PYR concentration in drinking water of less than 0.2 μg/L. Particularly, PAHs may negatively impact the flora and fauna of impacted environments, leading to their uptake and accumulation in the food chain and, in certain circumstances, to severe health issues and genetic changes in people. Various cleanup techniques have been developed to address the growing concern of PAH contamination. Sorption-based methods are gaining popularity due to their nonflammability, chemical inertness, cost-effectiveness, and widespread availability. Among these methods, the use of biochar or carbon-based materials has emerged as a promising approach to remove industrial chemicals, including PAHs like naphthalene, phenanthrene, and pyrene.

Although biochar has primarily been used as a soil amendment to enhance soil fertility, its potential as an innovative tool for cleaning up contaminated sites has garnered increased interest in recent years. The excellent affinity of biochar for organic contaminants like PAHs makes it attractive for soil remediation. However, despite numerous studies investigating the use of biochar, particularly from various sources, for oil spill cleanup, no research has been conducted on the use of waste-derived dendro biochar for the removal of oil from contaminated soil. Dendro biochar is formed from *Gliricidia sepium* and is a byproduct of dendro power industries. Previous studies have shown that biochar produced at high temperatures such as as 500 ^{0}C, removes PAHs efficiently. [2]. The focus of this research is on investigating soil contamination in automobile service stations, with particular attention to detecting the presence of PYR, a representative PAH, in the contaminated soil. Additionally, the study aims to assess the potential of dendro biochar as a treatment agent for the wastewater effluents discharged from these service stations.

Materials and Methods

Sample collection and preparation of EBC

Contaminated soil samples were collected from ten automobile service station sites in Sri Lanka (Kegalle, Kurunegala, Kalutara, Bandarawela, Galle, Wijayaramaya, Vavuniya, Uragasmanhandiya). Biochar (EBC) was collected from the bioenergy industry in Embilipitiya. The EBC was generated as a byproduct during the power generation process using *Gliricidia sepium* wood, which was pyrolysis at around 350 °C, followed by thorough washing to remove impurities and drying at 60 °C, overnight. The crushed EBC particles were then sieved through a 1 and 2 mm metal mesh and particles retained on the 1 mm mesh were used for further analysis.

Characterization of oil and Biochar

The chemical composition of the extracted oil was analyzed using a Fourier transform infrared spectrometer (FT-IR, PerkinElmer Spectrum Two), with wavelength ranging from 500 to 4500 cm^{-1}. The surface physical-morphological structure and microstructure of the biochar adsorbent were investigated using a field emission Scanning Electron Microscope (SEM, SU6600 FESEM; Hitachi, Ltd. located in Tokyo, Japan) at an acceleration voltage of 10 kV.

Soil washing experiment

The most contaminated sample (200 g/L) was added to soapy water (50 mL) made with different amounts of dishwashing liquid to create the washing effluents. The mixture was constantly stirred at 250 rpm for 12 hours. Dishwashing detergent was used in a range of 0 to 25% v/v to study the best ratio of detergents to distilled water for dishwashing detergent [3].

Adsorption dosage study

The adsorption of PYR was studied by varying the EBC dose from 4 g/L to 120 g/L, while keeping the PYR concentration in the soil washing effluent constant at the value (0.05 mg/L). This concentration value was selected based on the soil washing experiment results. Erlenmeyer flasks with biochar and soil washing effluent were placed on the mechanical shaker to agitate the sample at 150 rpm and shaken continuously for 6 h by allowing sufficient time for adsorption. The adsorption capacity and removal efficiency were measured by the following equations.

$$\text{Adsorption capacity } (q_e) = \frac{C_0 - C_e}{m} \times V \quad (1)$$

$$\text{Removal efficiency (R\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where C_0 is the starting PYR concentration expressed in mg/L, q_e is the PYR sorbed amount (Adsorption capacity) in mg/g , C_e is the equilibrium PYR concentration expressed in mg/L, V is the volume of the solution in L and m is the amount of sorbent in g [4]. High-performance liquid chromatography (HPLC) was employed to analyze the pyrene concentrations in the soil-washing effluent.

Results and Discussion

As per the results, sites are heavily contaminated with petroleum oil, the highest contaminated site (Kegalle) had 121 g/kg (12.06 % wt/wt soil) of oil in the soil and the least contaminated site (Bandarawela) had oil at 3.40 g/kg (0.34 % wt/wt) in the contaminated soil. So, the highest contaminated soil (Kegalle) was used for the soil washing experiment and dosage experiment.

Characterization of EBC

This SEM image of EBC (Figure 1-a) showed the formation of a porous structure with micro-pores ranging from 5-50 µm. Increased porosity enhances the oil adsorption capacity by facilitating surface adsorption through a larger surface area and a pore-filling mechanism. The Figure 1b showed, as new bonds with hydrocarbons formed, the intensity of the peaks at about ~1033-1581, ~2920, and ~3478 cm^{-1} in the Fourier transform infrared (FTIR) spectra in spent biochar increased, indicating interactions between oil and biochar. Broad separate peaks about ~3400 cm^{-1} are attributed to carboxylic acid, phenol, or alcohol -OH stretching vibrations. Strong peaks are observed in the spent biochar (Batch) at ~2920 cm^{-1}. These peaks were related to the hydrocarbons, adsorbed by the EBC.

These high-intensity peaks indicate the presence of aliphatic hydrocarbons with CH_2 and CH_3 groups in the spent biochar whereas the peak at ~1432,1433 cm^{-1} indicated bending vibrations of CH and CH_2 units in biopolymers.

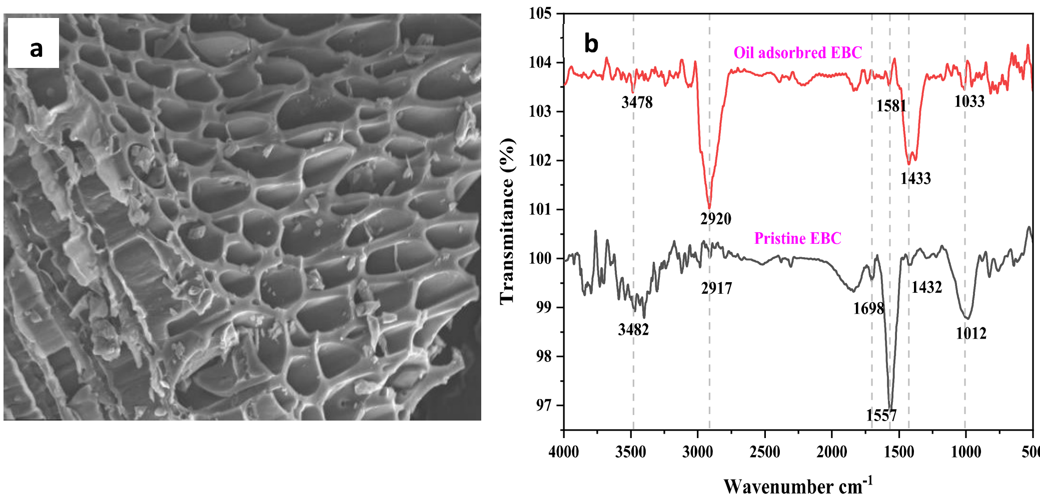

Figure 1: a) The SEM image of EBC at magnification ×1000, b) FT-IR spectra for pristine EBC and spent EBC

Soil washing experiment

Table 1: Pyrene concentration in washing effluents with different proportions of dishwashing agent

Dishwashing agent %	PYR concentration (mg/L)	PYR (mg/Kg)
0	0.007	0.012
2	0.057	0.095
3	0.083	0.138
4	0.095	0.158
5	**0.107**	**0.178**
10	0.063	0.105
15	0.067	0.112
25	0.032	0.053

The best removal of PYR from the soil was accomplished when a 5% (v/v) solution of soapy water was used, as shown in Table 1. Pyrene levels decreased as the amount of dishwashing liquid increased after 5%(v/v) because the creation of bubbles impeded the extraction procedure. Therefore, the best ratio (5%) of dishwasher was used to make the soil washing effluent.

Dosage experiment

The adsorption capacities were measured for each dosage, and it was found that the highest adsorption capacity of 0.0052 mg/g was achieved at the lowest dosage of 4 g/L. However, as per the Figure 2, a clear removal efficiency trend was observed before 20 g/L of adsorbent dosages. For increased experimental precision, the procedure was replicated twice.

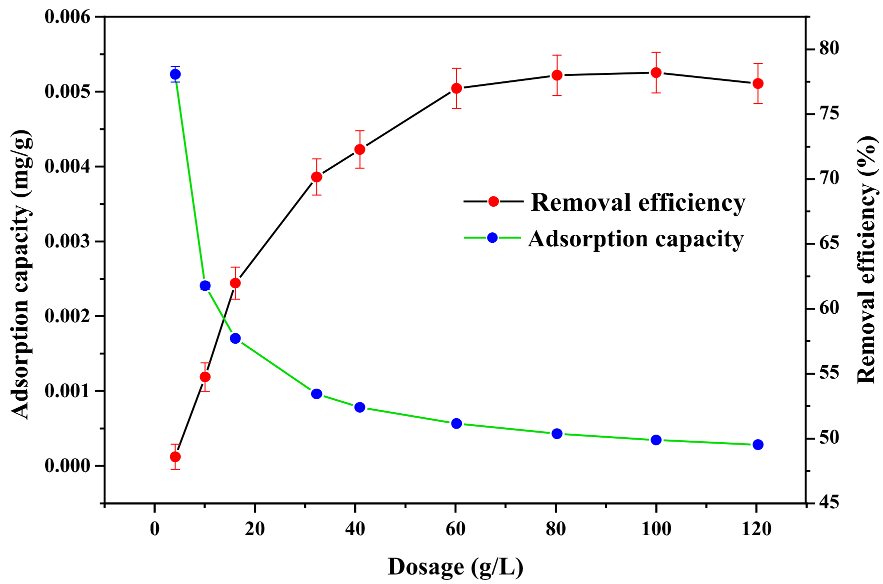

Figure 2: PYR removal efficiency and adsorption capacity of EBC at 4-120 g/L of dosages

This phenomenon was in line with previous reports, indicating that an excessive dosage of adsorbent might lead to a decrease in adsorption capacity. It was proposed that this could be attributed to a saturation of active adsorption sites on the adsorbent surface, resulting in diminished PYR uptake. Additionally, it was noticed that after reaching an adsorbent dosage of 16 g/L, further increments did not significantly enhance Pyrene removal. This suggests that there might be a limit to the number of available active sites, beyond which additional adsorbent does not contribute to a considerable increase in removal efficiency [6]. Furthermore, particle aggregation at higher EBC dosages was identified as another potential cause for reduced adsorption capacity. Such aggregation could lead to a decrease in the total surface area of the adsorbent, thereby limiting the contact points available for PYR molecules to adsorb. Based on the findings from Figure 2, subsequent experiments were conducted at an adsorbent dosage of 16 g/L for 6 h, which appeared to strike a balance between effective PYR removal and optimal utilization of the adsorption capacity.

Conclusions and Recommendations

The research highlights the crucial role of adsorbent dosage in PYR adsorption using EBC and emphasizes the importance of an appropriate dosage for achieving efficient pollutant removal to the optimal adsorbate dosage was 16 g/L. EBC biochar's can be used as a treatment agent for the wastewater effluents discharged from these service stations. To assess overall sorption performances, adsorption isotherm and kinetic studies will be further investigated needed.

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