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Adsorption Of Humic Acid from Leachate by Zeolite, Activated Carbon and Biochar with Their Effects on Plant Growth

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Abstract: Adsorption process has been widely used for removing pollutant from water because it is simple, fast, cost-effective and environmentally friendly. This study was conducted to investigate the optimum conditions for humic acid (HA) adsorption from leachate by zeolite, activated carbon and biochar. The results showed the optimum conditions were 60 min contact time, 50 g/L adsorbent dosage and solution pH of 3. The HA removal efficiencies of zeolite, activated carbon and biochar were 52.77%, 99.65% and 79.90% respectively. The effects of humic acid-zeolite (HAZ), humic acid-activated carbon (HAC) and humic acid-biochar (HAB) on plant growth within 10 days (early stage) and 5 weeks (late stage) were also studied. HAZ had shown the best performance in effects on plant growth. Biochar was suggested in this study as it possesses reasonable HA removal efficiency, acceptable effects on plant growth with low purchase price.

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1. Introduction

Humic acid (HA), a significant component of humic substances (HS), is commonly found in leachate and impacts water quality through its colour, taste, and odour [1]. Although not directly toxic, HA reacts with disinfectants during water treatment, forming carcinogenic by-products such as trihalomethanes (THMs). Effective removal of HA is critical for ensuring safe water treatment and environmental protection [2].

Several methods have been explored for HA removal, including membrane filtration, coagulation, advanced oxidation, and adsorption [3]. Among these, adsorption is preferred due to its simplicity, cost-effectiveness, and scalability [4]. Recent advancements have focused on optimizing adsorbents such as activated carbon [5], zeolite [6], and biochar [7], owing to their distinct physicochemical properties. Activated carbon, with its highly developed porosity, remains a benchmark for adsorbent performance. Zeolite, a natural aluminosilicate, exhibits excellent cation exchange and molecular sieving properties, making it an economical choice capabilities [8]. Meanwhile, biochar, derived from biomass pyrolysis, has garnered attention for its sustainability and effectiveness in removing HA and other organic pollutants from water [9]. Activated carbon is an amorphous form of elemental carbon with the highly developed porous structures and widely used adsorbent for wastewater treatment. Activated carbon is famous with its superior ability for removal of wide variety of organic and inorganic pollutants dissolved in aqueous media [10]. While considerable research has focused on HA removal from water, studies targeting its removal from leachate a complex, highly polluted wastewater are limited. Moreover, HA's known benefits for plant growth, such as enhanced nutrient uptake and improved soil fertility, suggest potential dual applications in wastewater treatment and agriculture.

This study investigates the optimum conditions for HA adsorption from leachate, exploring the effects of adsorbent type, dosage, pH, and contact time. Additionally, the impact of HA-treated adsorbents zeolite (HAZ), activated carbon (HAC), and biochar (HAB) on plant growth is evaluated, providing insights into integrated environmental management strategies.

2. Methodology

2.1 Materials and Chemicals

Standard HA was purchased from Aldrich Chemical Co. and raw leachate samples were collected from Seelong Sanitary Landfill, Malaysia, stored at 4°C in the dark to maintain quality. Zeolite, activated carbon (produced from coconut shell), and biochar (derived from rice husk) were obtained from local suppliers. The solution pH was adjusted using 37 % hydrochloric acid (HCl) and 99 % potassium hydroxide (KOH) was purchased from QRëC™, Malaysia.

2.2 Isolation of Humic Acid from Leachate

Leachate was filtered through 1.2 µm pore-size filter paper. HA was isolated via an acid-base method: adjusting pH to 10 with KOH, centrifuging at 5000 rpm for 10 minutes, acidifying to pH 2 with HCl, and storing overnight for precipitation. The precipitate was recovered by centrifugation and dissolved in 0.1N KOH.

2.3 Adsorption Study

Adsorption studies were conducted under batch conditions by varying contact time (0–60 minutes), adsorbent dosage (10–50 g/L), and pH (3–11). The experiments were performed using 35 mL leachate in vials at room temperature (25–30°C), agitated at 200 rpm. After treatment, the samples were filtered, and HA concentrations were analysed using a UV-Vis spectrophotometer (Shimadzu UV-1280) at 254 nm. Adsorption capacity and removal efficiency were calculated using standard equations:

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

where C_o and C_t are the concentrations of HA in solution at initial time and at time t, respectively (mg/L); V is the volume of solution (L); m is the mass of adsorbent (g). The HA removal efficiency was calculated using the following equation:

$$Removal\ efficiency\ (\%) = (\frac{C_o - C_t)}{C_o} \times 100\% \quad (2)$$

After that, treatments of leachate by zeolite, activated carbon and biochar under optimum condition were conducted in order to compared the HA adsorption performance among adsorbents.

2.4 Effect on Plant Growth

A 100 g portion of each adsorbent was added to 1000 mL of raw leachate at optimal pH and stirred for the designated optimal contact time. The mixture was then filtered using a sintered glass filter, and the resulting filter cake was dried in an oven at 100°C for 60 minutes. The dried cakes, referred to as humic acid-zeolite (HAZ), humic acid-activated carbon (HAC), and humic acid-biochar (HAB), were prepared for use. For the 10-day study, maize seeds were directly planted in four plastic containers, each containing 20 g of HAZ, HAC, or HAB, while one container served as a control. Plant heights were measured daily, and growth conditions were compared after 10 days.

For the 5-week study, maize seeds were planted in soil within four polybags. After two weeks, 20 g of HAZ, HAC, or HAB was added weekly to three respective bags, while the fourth remained as a control. Weekly measurements of plant height were recorded, and after five weeks, plant height, stem and root diameter, fresh weight, and dry weight were measured. The plants were placed in a sunny, wind-protected area and watered daily to ensure optimal growth conditions.

3. Results and Discussions

3.1 Adsorption Study

The removal of HA from leachate was evaluated using zeolite, activated carbon, and biochar as adsorbents. Factors such as contact time, solution pH, and adsorbent dosage were found to play significant roles in determining the efficiency of the adsorption process (Fig. 1). The optimal conditions for maximum HA removal were identified as a contact time of 60 minutes, an adsorbent dosage of 50 g/L, and a solution pH of 3. Among the tested adsorbents, activated carbon achieved the highest HA removal efficiency of 99.65%. This exceptional performance is due to its extensive surface area and highly developed porous structure, which provide abundant active sites for HA molecules to bind. Its surface functional groups further enhance adsorption through mechanisms like hydrogen bonding and π-π stacking interactions [4].

Biochar, with a removal efficiency of 79.90%, demonstrated moderate performance. Its mesoporous structure and surface chemistry facilitated electrostatic interactions and hydrogen bonding, which are effective but not as robust as activated carbon's mechanisms [11].

Zeolite exhibited the lowest removal efficiency at 52.77%, primarily due to its microporous structure, which is less suitable for larger HA molecules. However, its ion-exchange capabilities contributed to its performance, albeit less effectively than the other adsorbents [12].

These findings emphasize the importance of adsorbent properties, such as pore size, surface area, and functional groups, in optimizing HA removal. Each material's unique characteristics make it suitable for specific applications, highlighting the need for careful selection based on treatment goals.

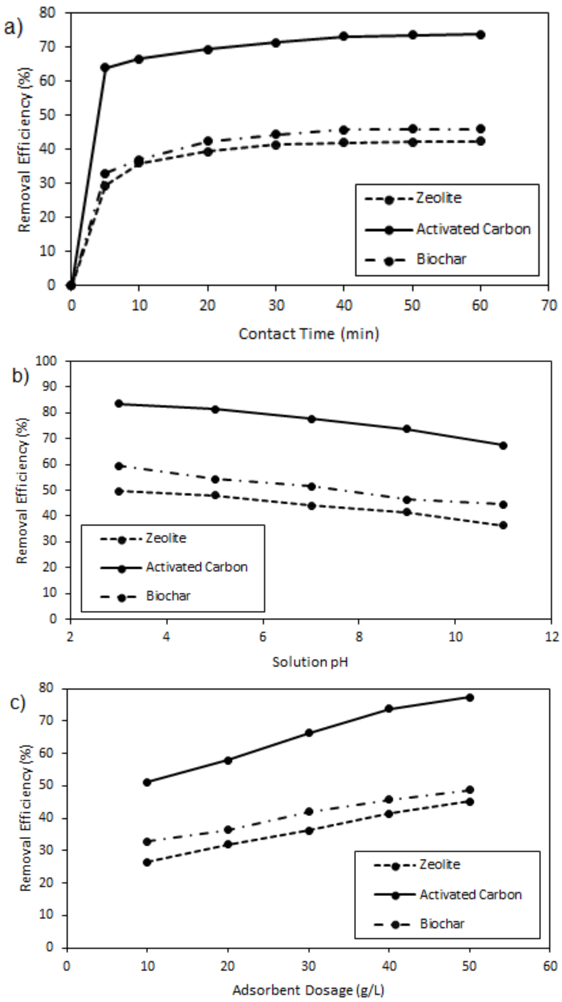

Fig. 1 - (a) Effect of Contact Time, (b) Effect of Solution pH, (c) Effect of Adsorbent Dosage on HA Removal Efficiency

3.2 Effects on Plant Growth

3.2.1 Plant Growth in 10 Days

The influence of HA-treated adsorbents on maize growth was examined over the initial 10-day period. Maize plants treated with HAZ, HAC, and HAB all showed marked improvements compared to the control group (Fig. 2). Among these, HAC demonstrated the most significant enhancement in growth, likely due to its ability to retain HA residuals that enrich the soil with essential nutrients. These residuals may provide immediate availability of critical macro- and micronutrients, promoting vigorous seed germination and shoot elongation. HA's presence in the treated soil not only enhanced nutrient availability but also improved the soil's water-holding capacity and cation exchange properties, creating a more favourable environment for early-stage plant growth. This aligns with previous studies showing that HA enhances soil fertility and stimulates root and shoot development, particularly in nutrient-limited soils [13].

After 10 days, HAC-treated plants displayed visibly healthier and taller shoots compared to those treated with HAZ, HAB, and the untreated control. HAB and HAZ treatments also supported growth, although to a slightly lesser degree, suggesting that their nutrient-release mechanisms are slower but still beneficial [14]. These results highlight the potential of HA-treated adsorbents as dual-purpose materials for wastewater treatment and agricultural improvement. In the short term, HAC emerges as a strong candidate for rapid growth enhancement, particularly for applications where immediate results are required.

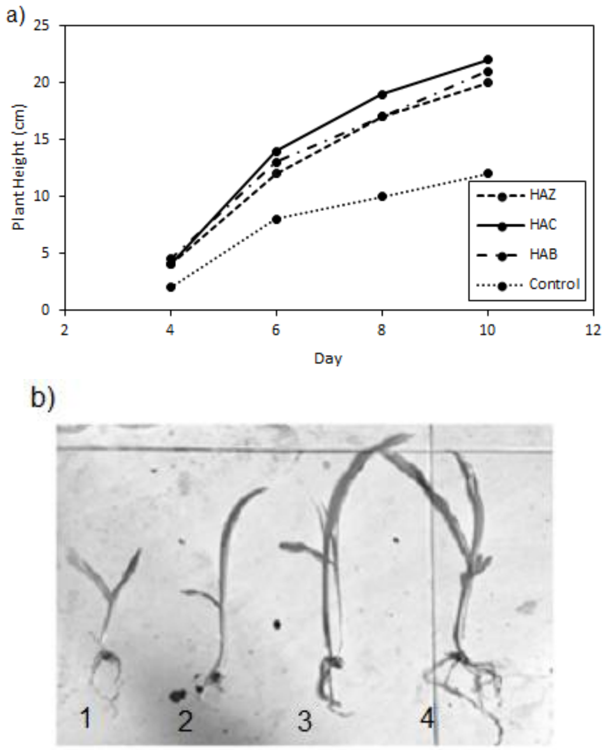

Fig. 2 - (a) Development of Plant Height in 10 Days; (b) Maize Plants after 10 Days (1: Control, 2: HAZ, 3: HAB, 4: HAC)

3.2.2 Plant Growth in 5 Weeks

After five weeks, plants treated with HAZ demonstrated the most vigorous growth among all treatments (Fig. 3, Table 1). The slow and steady nutrient release from zeolite likely supported sustained development, leading to significant improvements in plant height, stem diameter, and root biomass compared to the control. For example, HAZ-treated plants reached an average height of 77 cm, a notable improvement over the 56 cm observed in the control plants. Additionally, root biomass in the HAZ group was more than four times greater, reflecting healthier and more extensive root systems. The other treatments also showed enhanced growth, with HAB and HAC contributing to heights of 72 cm and 66 cm, respectively. Biochar's ability to improve soil water retention and provide essential nutrients likely accounted for its strong performance, while activated carbon's nutrient enrichment from HA residuals contributed to early-stage growth, albeit with a less pronounced long-term effect [15]. These findings underscore the dual role of HA-treated adsorbents: purifying wastewater by removing harmful compounds and serving as effective soil amendments to promote plant growth. This dual functionality offers a sustainable solution for integrated water management and agriculture. By transforming waste-derived adsorbents into resources that enhance crop production, this approach aligns with principles of circular economy and resource efficiency [16].

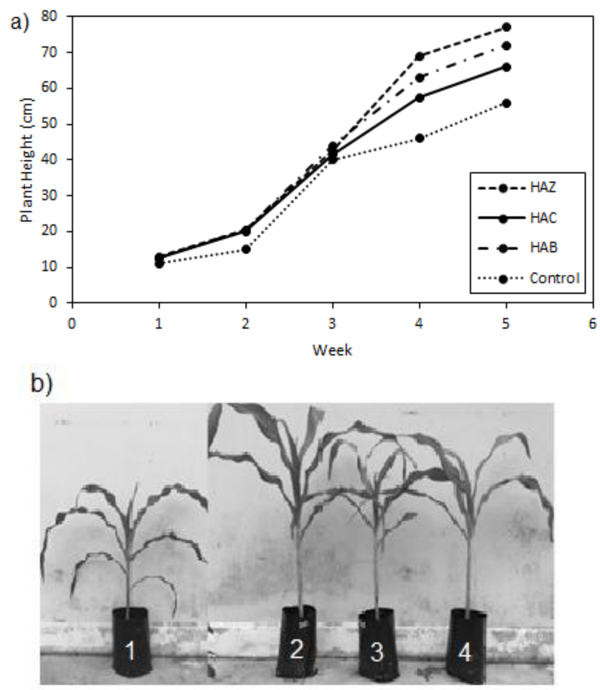

Fig. 3 - (a) Development of Plant Height in 5 Weeks; (b) Maize Plants after 5 Weeks (1: Control, 2: HAZ, 3: HAC, 4: HAB)

3.3 Comparison among Zeolite, Activated Carbon and Biochar

The effectiveness of zeolite, activated carbon, and biochar in removing HA from leachate and enhancing plant growth varied significantly, as summarized in Table 2. Activated carbon outshined the other adsorbents with a remarkable HA removal efficiency of 99.65% and the highest adsorption capacity (6.21 mg/g). This is primarily due to its extensive surface area and high porosity, which create numerous binding sites for HA molecules. Its functional groups also support strong chemical interactions, such as hydrogen bonding and π-π interactions, making it ideal for wastewater purification. However, its high cost (RM 20.00/kg) makes it less feasible for large-scale applications. Biochar, with a moderate removal efficiency of 79.90%, offers a practical balance between performance and cost. Its mesoporous structure facilitates effective electrostatic interactions with HA, and its affordability (RM 0.50/kg) makes it an attractive option for broader applications.

Table 1 - Effects of HAZ, HAC and HAB on Plant Growth after 5 Weeks

Parameters	HAZ	HAC	HAB	Control
Plant Diameter (cm)	2.050	1.690	1.785	1.650
Plant Height (cm)	77.0	66.0	72.0	56.0
Stem Fresh Weight (g)	145.03	84.50	97.52	90.27
Stem Dry Weight (g)	15.26	9.25	11.13	8.13
Root Fresh Weight (g)	56.45	18.32	37.42	12.63
Root Dry Weight (g)	7.51	2.97	4.60	1.27

Zeolite, while the least efficient in HA removal (52.77%), still plays a valuable role due to its ion-exchange capabilities. Its microporous framework, however, limits adsorption of larger HA molecules, explaining its lower performance compared to activated carbon and biochar. The HA-treated adsorbents also influenced plant growth differently. HAZ demonstrated the most significant growth after five weeks, reaching a height of 77.0 cm. This result can be attributed to zeolite's slow nutrient release, which sustains plant development over time. HAC was most effective during the early growth stage (10 days), likely due to its ability to retain nutrient-rich HA residuals. However, over five weeks, its plant height (66.0 cm) was lower than that of biochar and zeolite.

HAB supported consistent growth, with plants reaching 72.0 cm after five weeks. Its balanced performance, both in HA removal and plant growth enhancement, highlights its potential for integrated applications in wastewater treatment and agriculture. The results underscore the importance of selecting adsorbents based on specific goals. Activated carbon is ideal for wastewater treatment requiring high removal efficiency. Biochar, with its affordability and dual benefits, is well-suited for integrated systems. Zeolite, while less effective in HA adsorption, offers unparalleled benefits for long-term plant growth, making it a valuable tool in agriculture. Future research should explore hybrid systems combining these materials to optimize performance across both applications.

Table 2 - Comparison among Zeolite, Activated Carbon and Biochar

Parameters	Zeolite	Activated Carbon	Biochar
HA Removal Efficiency (%)	52.77	99.65	79.90
Adsorption Capacity (mg/g)	3.29	6.21	4.98
Plant Height in 10 Days (cm)	22.0	20.0	21.0
Plant Height in 5 Weeks (cm)	77.0	66.0	72.0
Purchase Price (RM/kg)*	0.72	20.0	0.50

4. Conclusion

The optimum conditions for HA adsorption are 60 min contact time, 50 g/L adsorbent dosage and solution pH of 3. The HA removal efficiency of zeolite, activated carbon and biochar were 52.77%, 99.65% and 79.90% respectively. On the other hand, all plants with application of HAZ, HAC and HAB performed higher growth than control. Plant with HAC had the highest growth in 10 days. In the study of 5 weeks, HAZ had shown the best performance in effects on plant growth. Biochar is suggested in this study as it possesses reasonable HA removal efficiency and acceptable effects on plant growth with low purchase price.

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