



Preparation and characterisation of chitosan-*Hura crepitans* pod biochar and evaluation of its fuel properties and adsorption capacity for methylene blue remediation

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Abstract

Towards the beneficiation of agricultural waste for water treatment and energy, *Hura crepitans* pods (HC), pyrolysed at 500, 600 and 700 °C with holding times of 30 and 60 min, were modified with chitosan and used for the adsorption of methylene blue. The biochar was characterised using pH of point of zero charge (pHpzc), elemental analysis, BET, FTIR spectroscopy, XRD and SEM–EDX. The pHpzc of HC was 9.2 and elemental analysis showed that the % carbon of the biochar was higher than that of the feedstock. The higher heating value of HC biochar was greater than 20 MJ kg⁻¹; projecting it as alternative solid-fuel source. The biochar appeared in the region for anthracite on van Krevelen diagram. Modification of the biochar with chitosan decreased the BET surface area. The FTIR spectra showed distinctive functional groups responsible for adsorption, XRD depicted the amorphous nature of the biochar. The adsorption capacity of HC biochar increased as the pyrolytic temperature and holding time increased from 500 to 700 °C and 30 to 60 min, respectively. Langmuir isotherm and pseudo-second order kinetic models gave the best fit to the experimental data. The monolayer adsorption capacity of HC7B biochar was 48.78 mg g⁻¹. Thermodynamic parameters showed that the adsorption process was endothermic, disorderly and spontaneous. The mechanism of adsorption was mainly by non-electrostatic interaction such as π - π interaction. The highest percentage desorption was achieved with 0.1 M H₂SO₄ and HC biochar was successfully regenerated after 5 cycles. *Hura crepitans* pod biochar was effective in the adsorption of MB from aqueous solution and modification with chitosan improved its adsorption capacity.

Keywords Biochar · *Hura crepitans* · Pyrolysis · Adsorption · Methylene blue

1 Introduction

Proper management of wastewater is a herculean task in rural communities that incidentally, do not have access to potable water. Contamination of drinking water sources by organic contaminants such as dyes, pharmaceuticals, personal care products and endocrine disrupting compounds raises global health challenge. [1]. These contaminants have been implicated in several health problems such as kidney diseases, liver diseases, mutations, antibiotic-resistance, cancer and so on [2, 3]. Hence, there is a need to remove contaminants such as dyes from wastewater before discharge into water bodies.

Methylene blue is a cationic dye that is hugely utilised in textile and dye industries. As a result of the high demand for dyes in the afore-mentioned industries, proper treatment of their effluents should be done to avoid environmental

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pollution. Methylene blue (MB) is a skin, eye and nervous system irritant; it can affect the kidney, liver and other internal organs in the body; its presence in water can affect the oxygen level and photosynthesis which in turn, imparts the ecosystem of aquatic organisms negatively [2, 4]. Therefore, an effective technique that can eliminate MB in water should be sought.

Adsorption is one of the methods employed for the removal of pollutants from aqueous solution. Adsorption method is relatively simple and cheap because of the low cost and availability of some of the adsorbents used. Clay [5], industrial waste [6], agricultural waste [7] and municipal waste [8] are examples of low-cost adsorbents that have been used for water remediation. Agricultural wastes are abundant in nature and have been used extensively either in their pristine or modified form for adsorption of pollutants from aqueous solution. This is because they are composed of lignin, cellulose and hemicellulose which are essential for adsorption [9, 10]. The use and conversion of agricultural waste to products such as biochars can mitigate environmental pollution caused by dumping, decomposition and open burning of these waste.

Hura crepitans (HC), also known as sandbox, possum wood, or jabillo, is a perennial plant that belongs to the family Euphorbiaceae (spurge). The tree is found in the tropical regions of the world including Nigeria and is mainly planted for shade and as an ornamental plant. The tree is about 9 m tall and the tree bark is wholly covered with short spikes [11]. These spikes, together with long-stalked leaves which have distended, closely, parallel-pinnate nerves, make the tree highly recognisable [12]. On maturity, the fruit dries up and undergoes mechanical explosion and scatters seeds and pods all around the tree, leaving behind piles of waste around it. There is no known use of the pods but the seed contains a high level of non-edible oil which has been studied to proffer industrial applications [13]. Given the fact that the pods of *Hura crepitans* are ubiquitous, easy to access, and readily available, it forms the premise why we sought to process the pods into biochar and apply it as an adsorbent for the removal of methylene blue dye. It is noteworthy that Adewuyi et al., [14] determined the efficiency of *Hura crepitans* pod as a feedstock for biodiesel production and [15] evaluated the effect of pyrolysis parameters on biochar yield from *Hura crepitans*. However, to the best of our knowledge, neither *Hura crepitans* pod nor its biochar has been used for adsorption purposes.

Biochars are heterogeneous and carbon-rich materials which are formed through the pyrolysis of biomasses under low or no oxygen conditions [16]. The pyrolysis usually takes place in a muffle furnace at a temperature range of 350–800 °C for 30 min to few hours (slow pyrolysis) or a temperature range of 400–600 °C for few seconds (fast

pyrolysis) [17]. Apart from muffle furnace, other technologies that have been used for pyrolysis are tube furnace [4] and lindberg furnace [17]. Biochars have porous structure, high surface area, high cation exchange capacity, alkaline pH, active functional groups (such as C=C, C-H and Si-O-Si) and graphite-like aromatic structure [18]. These properties present the possibility of biochar as an effective adsorbent material. Biochars vary depending on the feedstock and pyrolytic conditions which are mainly temperature and heating time [19]. Biochars have been applied in different ways. For example, they have been used to improve soil fertility [20], served as a feedstock for renewable and alternative energy sources [21], and as an adsorbent for wastewater remediation [4]. Biochars that have been used for the adsorption of methylene blue from aqueous solution include soybean dreg [22]; lychee seed [23]; *Wodyetia bifurcata* endocarp [24]; cattle manure [25]; Casuarina seed [25]; weeds [26]; *Cedrela odorata* seed [27]; peanut shell [28]; bamboo stakes [29]; *Dacryodes edulis* leaf [2] and so on.

Although pristine biochars have been successfully used for the adsorption of contaminants from aqueous solutions, there is need to modify them in order to improve their adsorption capacities and efficiencies. Modification of biochar can change the specific surface area, surface functional groups, pore size, structure and pore volume [30]. Chemicals that have been employed for the modification of biochar include: chitosan and EDTA [32]; FeCl₃·6H₂O [33]; H₃PO₄ [31]; KOH [32]; NaOH [33]; H₂SO₄ [34] and so on.

Even though many biochars from agricultural wastes have been employed for remediation purposes, there are still some agricultural wastes that have not been explored. Therefore, in this work, a novel biochar derived from *Hura crepitans* pod (HC), which was pyrolysed at different temperatures and resident times, was used for the adsorption of methylene blue. The prepared biochar was modified with chitosan. The fuel properties of the prepared biochar, as well as, the influence of pyrolytic temperature, resident time, pH, contact time and other factors on its adsorption capacity were evaluated.

2 Materials and methods

2.1 Biochar preparation

Hura crepitans (HC) pods were picked under the trees in Fatilami Park, Abakaliki, Ebonyi State, Nigeria. The pods were washed thoroughly with distilled water to remove dirt and debris. After washing, they were air-dried for two weeks and then dried in an oven at 100 °C for 6 h to remove all moisture from the biomass. They were pyrolysed in a muffle furnace at 500, 600 and 700 °C, with heating rate of

10 °C min⁻¹ and at holding times of 30 and 60 min. After pyrolysis, the biochars were left to cool overnight in closed porcelain dishes; after which they were crushed and sieved through a 420 micron particle size mesh. The biochar samples were stored in air-tight containers and were labelled as HC5A, HC6A and HC7A for biochars that were pyrolysed at 500, 600 and 700 °C, respectively and resident time of 30 min. The biochars that were pyrolysed at 500, 600 and 700 °C for 60 min were labelled as HC5B, HC6B and HC7B, respectively.

2.2 Modification of HC biochar

Middle molecular weight chitosan was used for the modification of *Hura crepitans* pod biochar and 2.5 g of the chitosan was dissolved in 5 mL of acetic acid and added to 100 mL of deionised water. Then, 10 g of HC biochar was added to the solution and stirred at 300 rpm and 30 °C for 8 h. Thereafter, the solution was filtered and the residue was washed thoroughly with distilled water and dried in an oven at 90 °C for 24 h [35]. It was labelled as C-HC biochar and stored appropriately for future use.

2.3 Characterisation of biochar

The pH of biochar was determined by pouring 25 mL of deionised water into a beaker containing 1 g of biochar, the solution was stirred at 200 rpm and 25 °C for 1 h. After stirring, the solution was allowed to stand for 30 min and then the pH was measured using a pH meter [36]. The pH at point of zero charge (pH_{pzc}) of the biochar pyrolysed at 700 °C and holding time of 60 min was determined using the adjusted solid addition method where 50 mL each of 0.1 M KNO₃ solution was transferred to six different containers. The initial pH values (pH_i) of the KNO₃ solutions were adjusted to the desired pH (2, 4, 6, 8, 10 and 12) by adding either 0.1 M HCl or 0.1 M NaOH, after which 0.1 g of biochar was added to the solution, which was securely capped immediately. The solutions were then shaken intermittently for 48 h and after shaking, the final pH values of the solution (pH_f) were noted. The difference between the initial and final pH values (ΔpH=pH_i—pH_f) was plotted against the pH_i. The point of intersection of the resulting curve at which ΔpH=0 gave the pH_{pzc} of the biochar.

Elemental compositions (C, H, N, S) of HC biochar and raw HC pod were measured using a Flash 2000 Organic Analyzer, Thermofisher Scientific. Surface area and pore characteristics of biochars and modified biochars were assessed by nitrogen adsorption–desorption analysis using Micromeritics Tristar (II) instrument in a liquid nitrogen bath at 77 K. The functional groups present in the raw biomass, biochar, modified biochar and MB-loaded biochar

were gotten using a Fourier transform infrared (FT-IR) spectrophotometer (Bruker Alpha, Germany). The spectra were recorded at 400–4000 cm⁻¹ wave number range using KBr pellets. X-ray diffraction (XRD) measurements of raw HC pod, biochar, modified biochar and biochar loaded with MB were recorded by Rigaku Ultima IV, Japan. The surface morphology of HC biochar and modified-HC biochar was recorded by scanning electron microscopy coupled with electron dispersive x-ray spectroscopy (SEM–EDX) (TESCAN Vega TC instrument, VEGA 3 software, Czech Republic).

2.4 Batch adsorption experiments

Batch adsorption studies of MB removal using HC biochars were carried out by varying the factors that affect adsorption. The pH (3, 4, 5, 6, 7, 8, 9 and 10), adsorbent dose (0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8 and 1 g L⁻¹), initial concentration (10–150 mg L⁻¹), contact time (0.5–240 min) and temperature (25, 35 and 45 °C) were evaluated for the adsorption of MB using HC biochars. For the pH study, a drop-wise addition of 0.1 M HCl and 0.1 M NaOH was used to adjust the pH of MB solution and 100 mg of the adsorbent was contacted with 50 mL of 50 mg L⁻¹ MB dye solution in 200 mL plastic containers. The solution was agitated in a temperature-controlled shaker at 150 rpm for 60 min. After agitation, the solution was centrifuged at 5000 rpm for 5 min and the supernatant was removed using a syringe and filtered using a 0.45 μm syringe filter. The residual dye concentration was analysed using a UV/Visible Spectrophotometer at 664 nm. Adsorption capacity, q_e was calculated using Eq. 1, where C₀ is the initial MB concentration (mg L⁻¹), C_e is the equilibrium MB concentration (mg L⁻¹), V is the volume of MB solution (mL) and W is the weight of the adsorbent (mg).

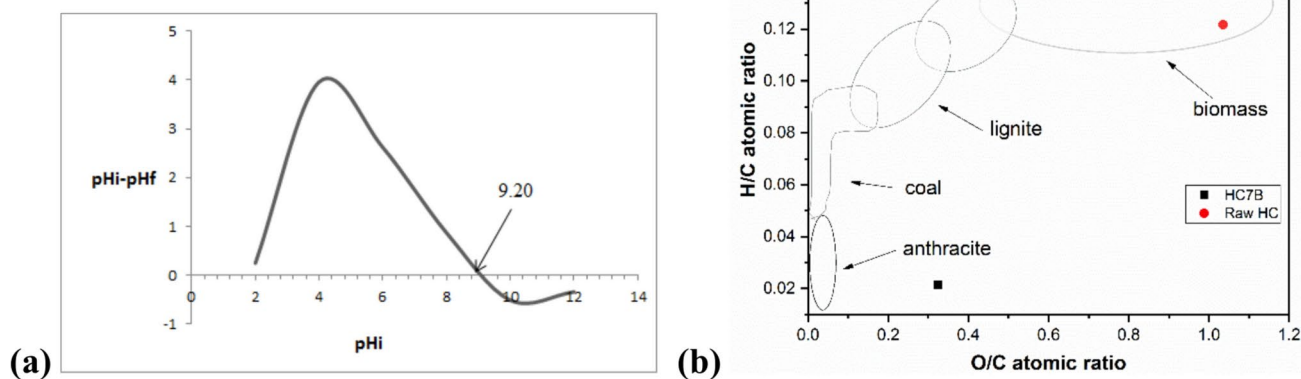
$$q_e = \frac{(C_0 - C_e) V}{W} \quad (1)$$

2.5 Desorption and regeneration study

Desorption study was carried out using 30 mL of 0.1 M HNO₃, H₂SO₄ and HCl and each of the acids was added to 0.2 g of HC7B biochar loaded with 50 mg L⁻¹ of MB solution. To load the HC7B biochar, 50 mL of 50 mg L⁻¹ MB solution was added to 100 mg of HC7B and the solution was agitated in a shaker for 3 h and filtered. The residue, which is the loaded HC7B biochar was dried in an oven at 100 °C. After the addition of the acid to the loaded HC7B biochar, the solution was agitated in a temperature-controlled shaker maintained at 25 °C for 1 h. Thereafter, the supernatant which was collected after centrifugation was filtered using a

Table 1 Physical properties of raw HC pod and HC biochars

Adsorbent	% Yield	pH	% C	% H	% N	% O	H/C	O/C	HHV (MJ/kg)
Raw HC	—	—	46.26	5.63	0.21	47.90	0.122	1.035	17.827
HC5A	37.50	6.75	—	—	—	—	—	—	—
HC5B	35.00	7.16	—	—	—	—	—	—	—
HC6A	33.33	9.55	—	—	—	—	—	—	—
HC6B	31.00	9.70	—	—	—	—	—	—	—
HC7A	26.83	10.00	—	—	—	—	—	—	—
HC7B	23.33	10.05	74.08	1.58	0.34	24.00	0.021	0.324	25.236

**Fig. 1** (a) pHpzc of *Hura crepitans* pod biochar. (b) Van Krevelen diagram for raw HC and HC7B

syringe filter, and analysed by UV/ Visible Spectrophotometer at 664 nm. The entire process was repeated in 4 cycles. Since the amount desorbed and the amount adsorbed were known, percentage desorption was calculated using Eq. 2.

$$\% \text{ desorption} = \frac{\text{amount desorbed}}{\text{amount adsorbed}} \times 100 \quad (2)$$

3 Results and discussion

3.1 Percentage yield of HC biochars

The percentage yield of HC biochars decreased as the pyrolytic temperature and holding time increased from 500 to 700 °C and from 30 to 60 min, respectively as seen in Table 1. This decrease in yield with an increase in temperature and holding time can be attributed to intensified thermal decomposition of the structure of biomass. This trend was reported by other researchers [37]; who observed higher biochar yield at the lowest temperature from the pyrolysis of sewage sludge.

3.2 Characterisation of HC biochar

The pH of HC biochars is shown in Table 1 and there was an increase in pH as pyrolytic temperature and holding time increased. The lowest pH was observed at the least pyrolytic temperature (500 °C) and holding time (30 min) while the highest pH was observed for the biochar carbonised at 700 °C and holding time of 60 min. This is because the higher the pyrolytic temperature, the greater the loss of acidic functional groups such as carboxylic acid and phenols [18]. This trend was also reported by Shen et al., [18]; when wheat straw pellets and rice husk were pyrolysed at 550 and 700 °C, pH of the biochars increased from 9.94 to 10.03 for wheat straw pellets and from 9.71 to 9.81 for rice husk.

The pH of point of zero charge (pH_{pzc}) of an adsorbent is the pH at which the total negative charge equals the total positive charge on the adsorbent. Below the pH_{pzc} , the surface of the adsorbent is predominantly positively charged, while above it, the surface is predominantly negatively charged [38]. From Fig. 1a, it can be seen that pHpzc of HC7B was 9.20.

From CHNS elemental analysis, the percentage of carbon, nitrogen and hydrogen, as well as, the percentage of oxygen, obtained from subtraction of the total percentage

of other elements from 100, are shown in Table 1. From the result, carbon was the most abundant element in HC7B and the raw biomass; the % carbon for HC7B was higher than that of the raw HC biomass. Hydrogen and oxygen contents of the biochar were lower than those of the raw biomass; this shows that dehydration, decarboxylation and decarbonylation took place during the pyrolysis of HC pod feedstock [39]. The H/C and O/C ratios of the HC7B biochar were lower than those of the pristine biomass. Low H/C ratio indicates higher aromaticity while low O/C ratio indicates lower polarity and higher hydrophobicity of biochars [39, 40]. Increased aromaticity as a result of low H/C ratio promotes improved stability of biochars to withstand any form of degradation [40]. To investigate the suitability of the biochar as a fuel source, the Higher Heating Values (HHV) of the raw HC pod and its biochar were calculated using Eq. 3. As shown in Table 1, it can be seen that HC7B biochar possessed a higher HHV than the raw HC pod and this was as a result of its higher carbon content. Also, for any carbonised material to be suitable as an alternative solid fuel source, the HHV value must be greater than 20 MJ/Kg [41]. Interestingly, the HHV value obtained for HC7B in this work was found to be 25.236 MJ/kg. Thus, the HC7B presents itself as an alternative source of solid fuel. The data obtained from CHNS analysis of the adsorbents were used to plot van Krevelen diagram which is shown in Fig. 1b, where H/C ratios of the adsorbents were plotted against their O/C ratios. It can be seen that HC biochar appeared very close to the region designated for anthracite while the raw HC biomass appeared in the region designated for biomass on the diagram. This implies that pyrolysis of the chosen feedstock improved their fuel properties and placed them towards the region of anthracite on van Krevelen diagram; hence HC biochar can be used as a solid fuel alternative. It is also noteworthy that anthracite is the highest rank of coal [42].

$$\text{HHV} = 0.3491\text{C} + 1.1783\text{H} - 0.1034\text{O} - 0.015\text{N} \quad (3)$$

The N₂ adsorption–desorption isotherm of HC7B and chitosan-modified HC7B (C-HC7B) were obtained from BET analysis (Fig. 2a) with the result of the fittings inset. It can be seen from the figure that there was a relatively slight uptake of N₂ at low relative pressures but this improved as the values of P/P₀ tended to 1 which suggests minimal porosity associated with mesoporous adsorbents [43]. Hysteresis loops are observed in the curves showing that the adsorption and desorption curves do not coincide and hence, the two processes did not follow the same path. The N₂ adsorption isotherms of the biochars are type IV which are observed for mesoporous adsorbents [44]. The surface area and pore characteristics of the biochars are summarised in Table 2. Modification of HC7B with chitosan decreased

the surface area from 387.84 to 303.92 m² g^{−1} while its pore size increased slightly from 2.21 to 2.42 nm on modification. The same trend was observed when bamboo, sugarcane bagasse, hickory wood and peanut hull were modified with chitosan. The researchers attributed the decrease in the surface areas of these materials on modification with chitosan to be as a result of partial covering of the pores by chitosan [45].

FTIR spectra of all the HC biochars are represented in Fig. 2b while Fig. 2c shows those of HC7B, raw HC (R-HC), chitosan-modified HC7B (C-HC7B) and methylene blue-loaded HC7B (L-HC7B). All the HC biochars and the raw HC biomass showed the characteristic O–H, C–H, C=O and C–O which are indicative of polymeric hydroxyl, phenolic hydroxyl and carbonyl groups present in biomasses. These functional groups enhance the adsorption of pollutants on the adsorbent surfaces through different mechanisms such as hydrogen bonding, electrostatic interaction and surface complexation [46]. The spectra of all the individual biomasses prepared at different temperatures and times were similar, in that, there were no new or different peaks in these spectra. However, there were slight shifts in the wave numbers of some of the peaks. Modification of HC7B with chitosan did not add any new peak but slightly changed the wavenumbers of the peaks associated with O–H, C=O, C=C, C–O and C–Hstr; the intensities of the aforementioned peaks were reduced in the spectrum for MB-loaded HC. Raw HC sample had the most prominent C–Hstr peak showing that some of the basic components of the biomass might have been destroyed during its pyrolysis [39].

Figure 3a shows the XRD patterns of raw HC (R-HC), HC7B, chitosan-modified HC7B (C-HC7B) and methylene blue-loaded HC7B (L-HC7B). The peak associated with amorphous carbon was present in all the adsorbents and appeared at 24° except for R-HC where it appeared at 22° and whose intensity was the highest compared to the others. Graphitic peak was observed for all the adsorbents at 43° but this peak was very weak in R-HC. Loading the HC biochar with methylene blue did not change the appearance of the pattern as there was no marked difference between its pattern and the others.

Figure 3b shows the surface morphology of HC7B which appeared irregular and uneven with flaky and rough surfaces. The irregular rough surfaces were observed in the SEM image of C-HC7B shown in Fig. 3c but in extension, a layered-structure was also seen in the image. The EDX spectra of HC7B and C-HC7B are shown in Figs. 3d and 3e, respectively where carbon was the prominent element in both spectra. Other elements found in both spectra were Si, K, P, Al, O, Ca and Mg while S and Cl were only seen in the spectrum for HC7B.

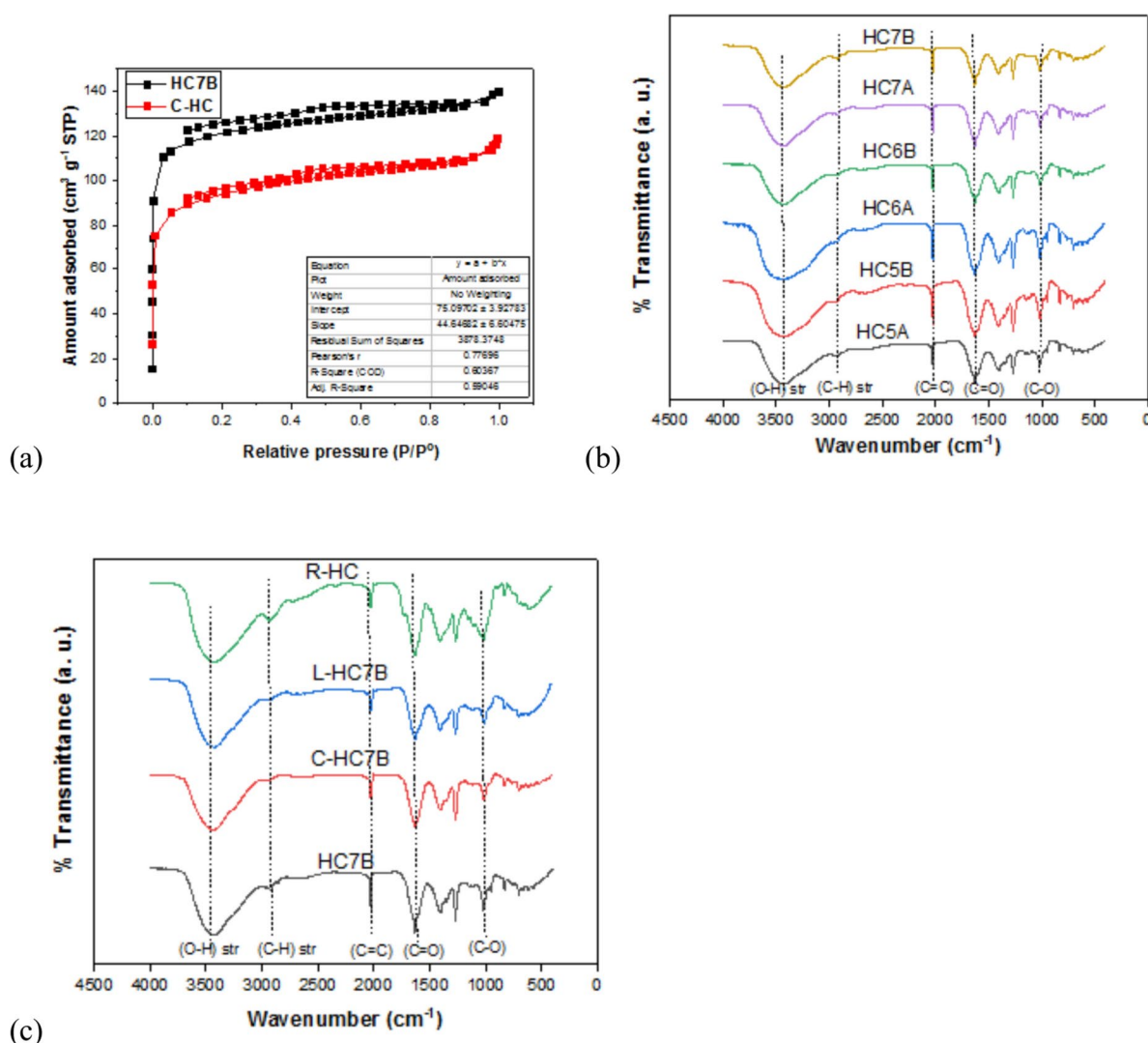


Fig. 2 (a) Adsorption/desorption isotherms of HC7B and C-HC7B. Inset: Pore diameter distribution of HC7B and C-HC7B. FTIR spectra of (b) HC prepared at different pyrolytic temperatures and holding time (c) HC7B, C-HC7B, MB-loaded HC (L-HC7B) and raw HC (R-HC)

Table 2 Surface and pore characteristics of HC7B and C-HC7B biochars

Biochar	S_{BET}^a (m ² g ⁻¹)	D_p^b (nm)	S_A^c (m ² g ⁻¹)	S_{ext}^d (m ² g ⁻¹)	V_{micro}^e (cm ³ g ⁻¹)	V_T^f (cm ³ g ⁻¹)
HC7B	387.84	2.21	287.62	100.22	0.132397	0.2141
C-HC7B	303.92	2.42	207.92	96.00	0.091662	0.1839

^a Specific surface area calculated from BET analysis

^b Pore size

^c t-plot micropore area

^d t-plot micropore external surface area

^e t-plot micropore volume

^f t-plot total pore volume

3.3 Effect of pH on the adsorption of MB

A plot of the adsorption capacities of HC biochars prepared at varying pyrolytic temperatures and holding times against pH is depicted in Fig. 4a. For most of the biochars, there

was an increase in the adsorption capacity with an increase in the pH of the dye solution from 3 to 8, after the pH of 8, the adsorption capacity reduced. All the biochars had their highest adsorption capacity at a pH of 8; hence, it was chosen as the optimum pH for the subsequent adsorption studies

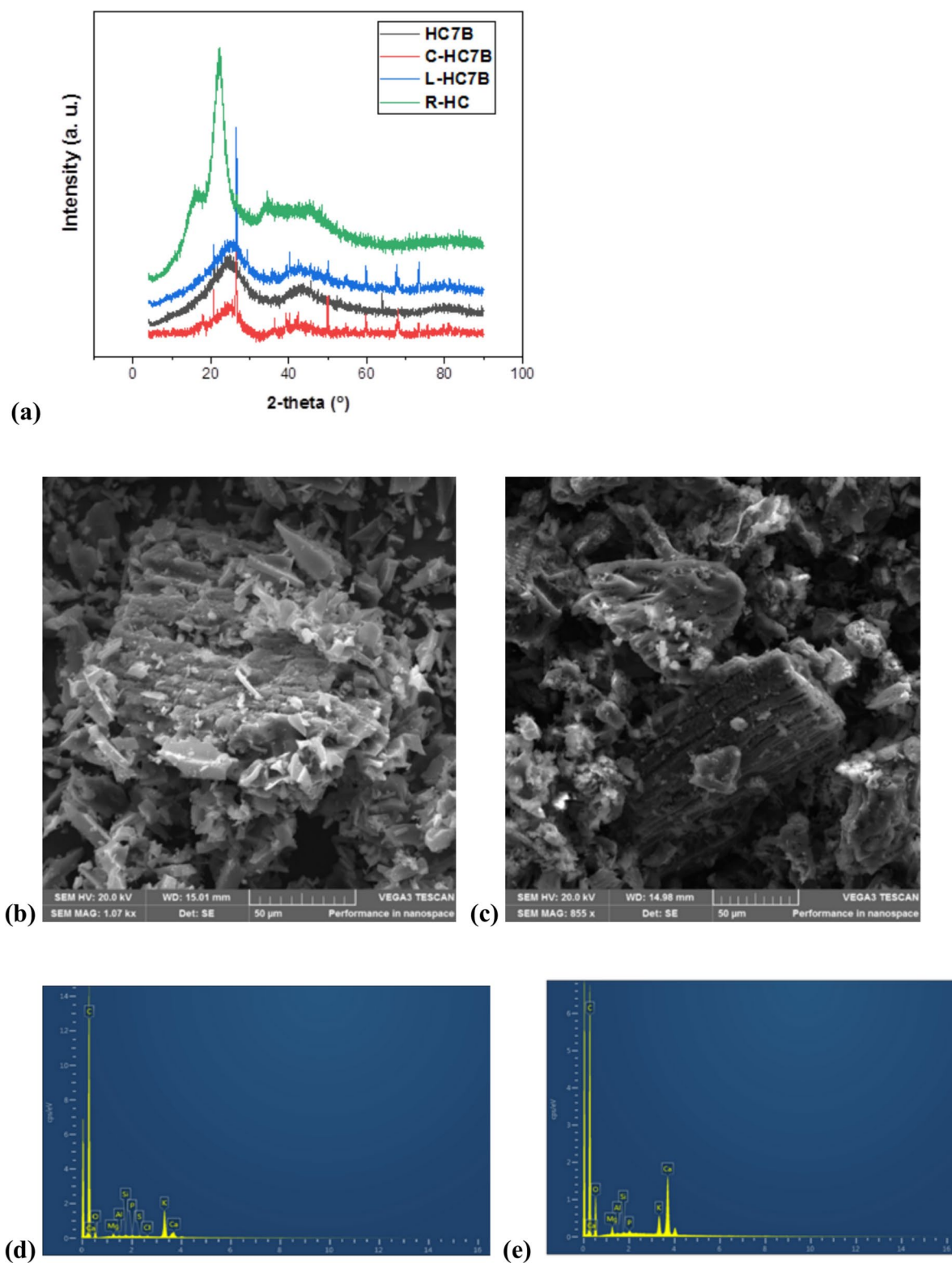


Fig. 3 (a) XRD patterns of HC7B, C-HC7B, methylene blue-loaded HC (L-HC7B) and raw HC (R-HC). SEM image of (b) HC7B (c) C-HC7B. EDX spectrum of (d) HC7B (e) C-HC7B

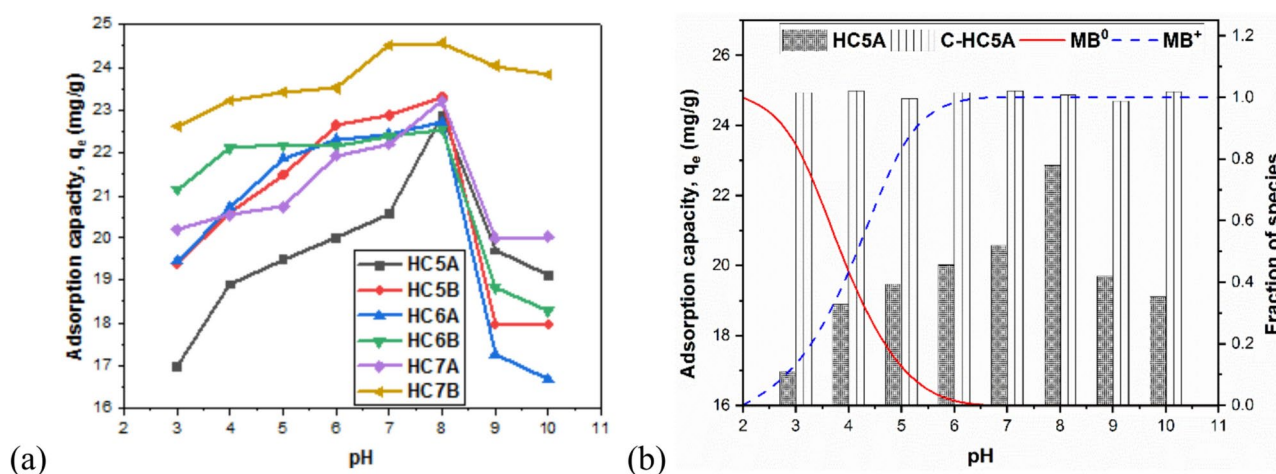


Fig. 4 (a) Effect of pH on the adsorption capacities of HC biochars. (b) Fraction of MB species and effect of pH on the adsorption capacities of HC5A and C-HC5A

using HC biochars. The least adsorption capacity observed at pH of 3 and 4 for each of the biochars was as a result of competition between MB positive ions and H^+ for limited adsorption sites at lower pH [47]. HC7B gave the highest adsorption capacity and percentage uptake of 98.29% at pH of 8 while HC5A gave the least; this prompted the modification of HC5A for this study. HC biochars pyrolysed at higher holding time had greater adsorption capacity and percentage uptake. For example, the adsorption capacity and percentage uptake of HC5A at pH of 8 were 22.87 mg g^{-1} and 91.46%, respectively while those of HC5B were 23.30 mg g^{-1} and 93.21%, respectively. The effect of chitosan modification on the adsorption capacity of HC5A biochar is shown in Fig. 4b. From the figure, modification with chitosan improved the adsorption capacity of the biochar at all the pH considered, including acidic pH where adsorption capacity was low for the pristine biochar. The optimum pH for the pristine HC5A biochar was 8 while that of the modified biochar was 7. Hence, other adsorption studies involving the modified biochar were done at pH of 7 since this was the optimum pH. There were two species of MB in solution and they are un-dissociated species, MB^0 and cationic species, MB^+ . The speciation of MB in solution is affected by the pH of the solution which can influence, in extension, the probability of having electrostatic attraction or repulsion between these species and surface charge distribution on the adsorbent [48]. Based on the speciation plot of MB species [48] as displayed in Fig. 4b, the distribution of MB species at different pH and the effect of pH on the adsorption capacities of HC5A and C-HC5A can be seen. The figure shows that at pH of 3 and 4, the species that dominated the solution was MB^0 , its concentration reduced drastically at pH of 5 and it disappeared totally at pH of 6. The concentration of cationic species, MB^+ at pH of 3 was very low; its concentration increased steadily from pH of 4

to 5 and it dominated the solution after pH of 6. Optimum pH for HC5A and C-HC5A was 8 and 7, respectively; at this pH, MB^+ dominated the solution. The pH_{pzc} of HC biochar shows that the surface of the biochar at this pH will be positively charged; hence there will be electrostatic repulsion between MB^+ and the adsorbent surface.

3.4 Effect of adsorbent dose on the adsorption of MB

Figure 5a shows a graph of the adsorption capacities of HC biochars and C-HC5A against their adsorbent doses. For all the biochars, adsorption capacity decreased with an increase in adsorbent dose. The adsorption capacity of HC7B was slightly higher than those of the other biochars while HC5A gave the least. This trend is attributed to the fact that there is usually complete coverage and utilisation of active sites when the dose is low. When the adsorbent dosage is higher, it is more likely that a significant portion of the available active sites remain uncovered, leading to lower specific uptake. It can also be a result of an increase in diffusion path length because of the aggregation of adsorbent particles; this aggregation becomes increasingly significant as the weight of the adsorbent is increased [7]. The modified HC5A biochar followed the same trend exhibited by the pristine HC5A biochar. Modification slightly increased the adsorption capacity of HC5A when adsorbent doses of 50, 100 and 200 mg L^{-1} were used. There was no marked difference between the adsorption capacities of HC5A and its modified counterpart when the other adsorbent doses were compared.

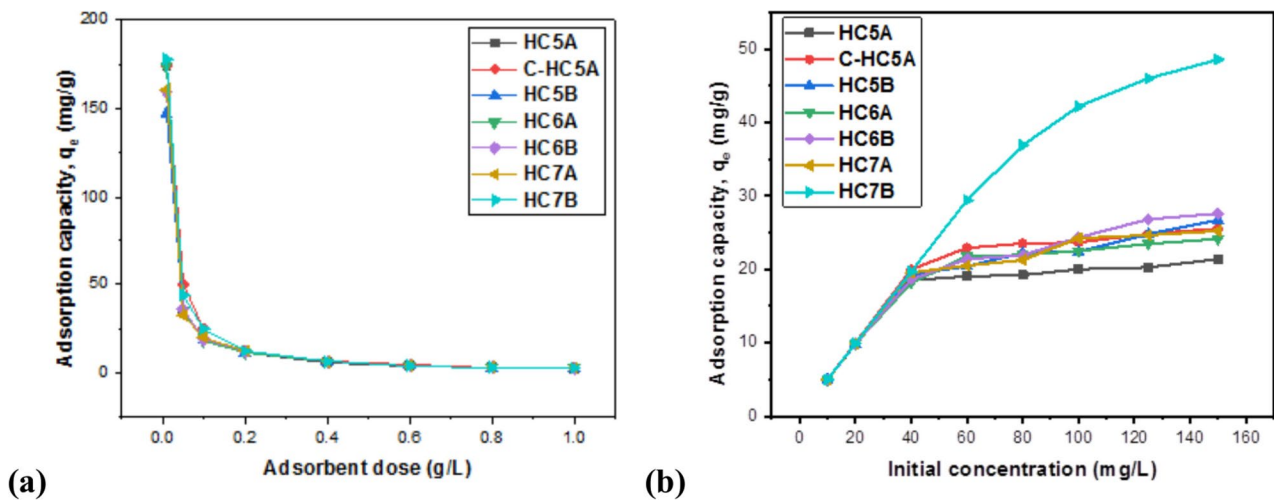


Fig. 5 (a) Effect of adsorbent dose on the adsorption capacities of HC biochars. (b) Effect of initial concentration on the adsorption capacities of HC biochars

3.5 Effect of initial MB concentration and adsorption isotherms

The adsorption capacities of HC biochars prepared at different pyrolytic temperatures and holding times increased with an increase in the initial concentration of MB solution as shown in Fig. 5b. The increase in the adsorption capacity of the biochars with an increase in the initial concentration is due to an increase in the driving force of the concentration gradient as the concentration of MB increases. Furthermore, the initial MB concentration provides an important driving force to overcome all mass transfer resistances. The adsorption capacity of C-HC5A was higher at all concentrations when compared to that of the pristine HC5A biochar. Improvement in the adsorption capacity of the modified biochar should have been as a result of an increase in the active adsorption sites on the adsorbent by chitosan [49].

Four Isotherm models—the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R)—were used to analyse the experimental data from this study. The linear equation for the Langmuir model is shown in Eq. 4 while the equation for the dimensionless factor, R_L is shown in Eq. 5. Langmuir model is based on monolayer coverage of an adsorbent by adsorbates [50]. Freundlich model proposes a multi-layer coverage of the adsorbent and its linear equation is shown in Eq. 6 [51]. Eq. 7 is the linear form of the Temkin model and the derivation of the Temkin isotherm is based on the assumption that the decline of the heat of sorption as a function of temperature is linear rather than logarithmic [52]. Linear representation of D-R isotherm model is given in Eq. 8 while Eqs. 9, 10 are for polanyi potential, ε and free energy of transfer, E , respectively [53].

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (4)$$

$$R_L = \frac{1}{1 + bC_o} \quad (5)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

$$q_e = B \ln K_T + B \ln C_e \quad (7)$$

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (8)$$

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (9)$$

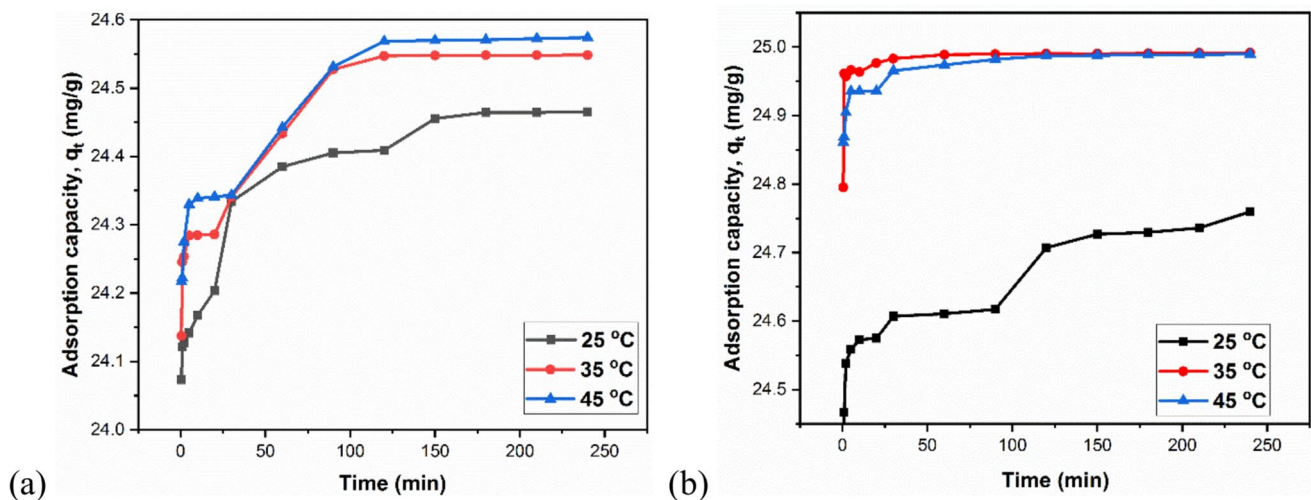
$$E = \frac{1}{\sqrt{2\beta}} \quad (10)$$

where b ($L \text{ mg}^{-1}$) is the Langmuir constant related to the energy of adsorption, q_m (mg g^{-1}) is the maximum adsorption capacity corresponding to complete monolayer coverage, q_e (mg g^{-1}) is the amount adsorbed per unit weight of the adsorbent and C_e (mg L^{-1}) is the equilibrium concentration of MB. K_F ($L \text{ g}^{-1}$) is the Freundlich constant and n is the adsorption intensity which varies with the heterogeneity of the material. The Temkin constant, B is related to heat of adsorption, K_T ($L \text{ mg}^{-1}$) is the equilibrium binding constant and β ($\text{mol}^2 \text{ J}^{-2}$) is the activity coefficient related to the mean free energy of sorption.

Table 3 depicts the isotherm model parameters and R^2 values of the four models evaluated for the adsorption of MB using HC biochars. Langmuir isotherm model gave the best fit for all the HC biochars. Its maximum adsorption values, q_m were higher than those of Dubinin-Radushkevich

Table 3 Equilibrium isotherm parameters for adsorption of MB using HC biochars at 25 °C

Isotherm models	HC5A	Modified HC5A	HC5B	HC6A	HC6B	HC7A	HC7B
Langmuir							
q_m (mg/g)	21.008	25.253	25.907	23.981	27.473	25.189	48.781
b (L/mg)	0.6733	1.0504	0.3712	0.6927	0.3333	0.5109	0.0246
R^2	0.9978	0.9984	0.9898	0.9985	0.9906	0.9957	0.9981
R_L	0.0098	0.0063	0.0177	0.0095	0.0196	0.0129	0.0079
Freundlich							
K_F	10.133	15.260	11.392	10.967	10.953	11.917	18.203
N	5.5648	8.5763	5.1467	5.1203	4.6083	5.5218	3.2765
R^2	0.8126	0.5695	0.8569	0.8975	0.9158	0.8251	0.9131
Temkin							
K_T (L/mg)	242.90	97.01	185.05	166.52	78.62	348.21	44.770
B	2.1485	1.6676	2.6085	2.5501	3.0154	2.4255	6.3668
b_T (J/mol)	1153.2	1485.7	949.8	971.6	821.6	1021.5	389.1
R^2	0.8848	0.6863	0.9147	0.9710	0.9719	0.8945	0.9784
Dubinin-Radushkevich							
q_m (mg/g)	19.5600	23.222	21.602	21.670	22.637	22.048	34.477
E (kJ/mol)	3.162	7.071	4.082	3.536	3.536	4.082	4.082
R^2	0.9865	0.4826	0.8929	0.9684	0.9226	0.9345	0.8192

**Fig. 6** (a) Effect of contact time on the adsorption capacity of HC7B. (b) Effect of contact time on the adsorption capacity of modified HC7B.

model for each of the HC biochars considered. For both models, q_m value increased with an increase in pyrolytic temperature and holding time while the reverse was the case for the Langmuir constant, b . Langmuir q_m for HC7B was 48.781 mg g^{-1} while that of the D-R model for the same biochar was 34.477 mg g^{-1} . Modification of HC5A with chitosan improved its maximum adsorption capacity as observed from both Langmuir and D-R models. The R_L values of all the HC biochars were far less than 1 suggesting that the adsorption processes of all the biochars were favourable. None of the free energy of transfer, E obtained from the D-R model was greater than 8 kJ mol^{-1} ; this shows that the adsorption type was physisorption. The values of n as obtained from the Freundlich model for all the HC biochars were between 1 and 10, further supporting that the adsorption processes

were favourable. The Freundlich constant, K_F increased with an increase in pyrolytic temperature and holding time, except for HC6A whose value was slightly higher than that of HC6B. Temkin equilibrium binding constant, K_T of HC biochars decreased with an increase in pyrolytic temperature and holding time; this implies that since the adsorption type is physical, desorption will most likely occur faster and better in biochars pyrolysed at higher temperature. Hence, HC7B was employed for desorption studies.

3.6 Effect of contact time and adsorption kinetics

The effect of contact time on the adsorption of MB by HC7B biochar is shown in Fig. 6a. At all the temperatures considered, adsorption was rapid within 60 min as a result

of the availability of more active sites on the adsorbent. After 60 min, adsorption slowed down and tended towards equilibrium because most of the sites were occupied by the adsorbate. The adsorption capacity of the pristine HC7B biochar increased with an increase in temperature given that the highest adsorption capacity was recorded at 45 °C while the least was at 25 °C. However, the difference in the adsorption capacity of the biochar at different temperatures was marginal; hence, the adsorption can be executed successfully at 25 °C. Figure 6b shows a plot of the adsorption capacity of chitosan-modified HC7B biochar against contact time at 25, 35 and 45 °C. For all the temperatures, adsorption was rapid within 10 min of contact time and then increased gradually with time until equilibrium was achieved.

Data from the study of the effect of contact time was analysed using pseudo-first order, pseudo-second order and intra-particle models. The linear equations of these models are shown in Eqs. 11 [38], 12 [53] and 13 [54] respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (11)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

$$q_t = k_{id} t^{1/2} + C \quad (13)$$

where q_t (mg g⁻¹) is the amount of solute adsorbed at time t (min), q_e (mg g⁻¹) is the amount of solute adsorbed at equilibrium and k_1 (min⁻¹) is the rate constant of pseudo-first order adsorption, k_2 (g mg⁻¹ min⁻¹) is the pseudo-second order rate constant, k_{id} is the intra-particle rate constant (mg g⁻¹ min^{0.5}) and C is the intercept.

Kinetic model parameters for HC7B and modified HC7B are shown in Table 4. Pseudo-second order model gave the best fit to the experimental data as its regression value (R^2) was higher and the q_e values calculated from the model were

in close proximity to the ones obtained from the kinetic experiments. The calculated q_e values increased with an increase in temperature and those of modified HC7B were higher than those of the pristine HC7B biochar. The boundary layer constant, C from intra-particle diffusion showed that it was not the only limiting step in the adsorption process and the values were also close to the q_e values calculated from pseudo-second order model.

3.7 Adsorption thermodynamics

Thermodynamic parameters of an adsorption process are necessary to conclude whether the process is spontaneous (ΔG), disorderly (ΔS), exothermic or endothermic (ΔH) [55]. The thermodynamic parameters are calculated from Eqs. 14, 15 and 16.

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (14)$$

$$K = \frac{q_e}{C_e} \quad (15)$$

$$\Delta G = \Delta H - T\Delta S \quad (16)$$

where K is equilibrium constant, R is universal gas constant, ΔH is change in enthalpy, ΔS is change in entropy, T is absolute temperature, q_e (mg g⁻¹) is the amount of solute adsorbed at equilibrium, C_e (mg L⁻¹) is the concentration of the solute at equilibrium, ΔG is Gibb's free energy. ΔH and ΔS can be obtained from the slope and intercept of a plot of $\ln K$ versus $1/T$, respectively.

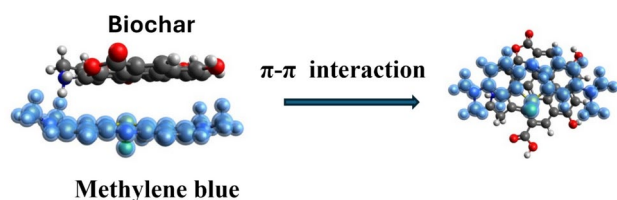
Table 5 shows the thermodynamic parameters of HC7B and C-HC7B. From the table, the heat of adsorption, ΔH for HC7B and chitosan-modified HC7B (C-HC7B) were positive, indicating that both adsorption processes were endothermic. The ΔH value for HC7B which was 9.169 kJ mol⁻¹

Table 4 Kinetic model parameters for adsorption of MB using HC biochars at 25 °C, 35 °C and 45 °C

Kinetic models	HC7B			Modified HC7B		
	25 °C	35 °C	45 °C	25 °C	35 °C	45 °C
q_e (exp) (mg g ⁻¹)	24.5103	24.5734	24.5812	24.7754	25.1902	25.2311
Pseudo-first order						
k_1 (min ⁻¹)	0.0111	0.0141	0.0254	0.0205	0.0083	0.0105
q_e (cal) (mg g ⁻¹)	3.0661	3.3368	3.1791	2.7511	26.6343	13.3364
R^2	0.9368	0.8861	0.9007	0.6937	0.5857	0.8317
Pseudo-second order						
k_2	0.3414	0.3619	0.3381	0.3200	0.5300	0.2000
q_e (cal) (mg g ⁻¹)	24.4499	24.5698	24.5720	24.7597	25.0000	25.0000
R^2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Intra-particle diffusion						
k_{id} (mg g ⁻¹ min ^{0.5})	0.0274	0.0265	0.0254	0.0202	0.0053	0.0074
C (mg g ⁻¹)	24.1010	24.2020	24.2360	24.4620	24.9280	24.8960
R^2	0.9244	0.9140	0.9353	0.8188	0.6091	0.7764

Table 5 Thermodynamic parameters for the adsorption of MB using HC biochars

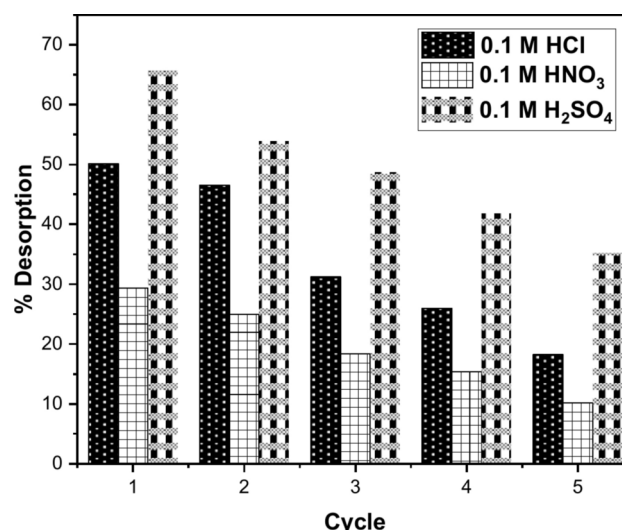
Biochar	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG (kJ mol ⁻¹)		
			25 °C	35 °C	45 °C
HC7B	9.169	56.933	-7.797	-8.367	-8.936
Modified HC7B	125.724	459.234	-11.169	-15.762	-20.356

**Fig. 7** Proposed adsorption mechanism of HC7B biochar

suggested physical adsorption [31] while that of chitosan-modified HC7B indicated chemical adsorption as its adsorption type which correlates with kinetic data that was mainly by pseudo-second order for HC7B. Both HC7B and C-HC7B showed disordered adsorption as their ΔS values were positive. Adsorption processes of both of them were spontaneous and their degree of spontaneity increased with an increase in temperature. The ΔS and ΔG values of C-HC7B were higher than those of HC7B. Adsorption of MB on citric acid-modified water hyacinth was endothermic, as indicated by the positive value of ΔH ; the spontaneity of the adsorption process, which was indicated by negative ΔG values increased as temperature increased from 30 to 60 °C [56].

3.8 Mechanism of adsorption

For HC biochars whose prototype, HC7B had pH_{pzc} of 9.20 and whose optimum pH for the adsorption of MB was 8; the proposed mechanism of adsorption is by non-electrostatic interaction such as π - π interaction between aromatic-rich MB (π -electron acceptor) and aromatic-rich biochar (π -electron donor) [57]. The mechanism was not by electrostatic interaction because the adsorption capacities of HC biochar were low at pH above 9 where the adsorbent surface was negative and the predominant MB species at that pH was MB⁺. From the kinetic results, adsorption followed pseudo-second order model which proposes chemisorption as the main adsorption mechanism [60]. The kinetic result correlates with proposed mechanism from pH study because π - π interaction is a chemical interaction [7]. The graphical representation of the mechanism of adsorption is shown in Fig. 7.

**Fig. 8** Desorption of MB from HC7B using three different acids

3.9 Desorption and regeneration

The percentage desorption of MB from HC7B biochar in five cycles is shown in Fig. 8. The figure shows that with each cycle, the percentage desorption decreased. In all the cycles, 0.1 M H₂SO₄ had the highest % desorption, followed by HCl and then HNO₃ which had the least. This shows that H₂SO₄ was a better desorbing solvent for HC7B. Ranges of % desorption for 0.1 M H₂SO₄, 0.1 M HCl and HNO₃ were 65.71–35.22%; 50.12–18.22% and 29.34–10.12%, respectively.

3.10 Comparison with other biochars

Table 6 shows the comparison of the Langmuir maximum adsorption capacities (q_m) of the prepared biochars in this study with q_m of some biochars from literature.

4 Conclusion

The adsorption capacity of *Hura crepitans* pod (HC) biochar increased with an increase in pyrolytic temperature and holding time. Modification of HC5A which was the least-performed biochar with chitosan increased its adsorption capacity; this shows that chitosan can improve the efficiency of a biochar if a lower pyrolytic temperature is desired. The HC biochar can be used as an alternative solid fuel source as its HHV was greater than 20 MJ kg⁻¹ and it had similar fuel characteristics with anthracite as seen on van Krevelen diagram. The optimum pH was achieved at 8 for the pristine biochar while it was at 7 for the modified biochar. Adsorption of MB using HC biochars followed the Langmuir isotherm model, indicating monolayer adsorption

Table 6 Comparison of monolayer adsorption capacities (q_m) of biochars prepared from different feedstock

Biochar	Pyrolytic temperature (°C)	q_m (mg/g)	Adsorbate	Reference
Anaerobic digestion residue	400	9.50	MB	[58]
Palm bark	400	2.66	MB	[58]
Eucalyptus	400	2.06	MB	[58]
Date seed	550	42.60	MB	[59]
<i>Dacryodes edulis</i> leaf	250	7.91	MB	[2]
Sewage sludge	550	24.10	MB	[60]
Wakame biochar nanocomposite	800	479.49	MB	[4]
<i>Hura crepitans</i> pod	500	25.91	MB	This study
<i>Hura crepitans</i> pod	600	27.47	MB	This study
<i>Hura crepitans</i> pod	700	48.78	MB	This study

and pseudo-second order kinetic model, indicating chemisorption. Thermodynamic analysis showed that adsorption was endothermic, disorderly and spontaneous. Adsorption occurred mainly by π - π interaction. The biochar was successfully regenerated after 5 cycles and supports its cost effectiveness. *Hura crepitans* pod biochar is a promising adsorbent for the removal of MB from wastewater and an alternative solid-fuel source.

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Author Contribution O.N: Conceptualization, Methodology, Investigation, Writing—Original Draft. J.B.: Methodology, Writing—Review & Editing, Supervision O.A.: Methodology, Writing—Review & Editing, Supervision, Funding acquisition, Resources.

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Data Availability No datasets were generated or analysed during the current study.

Declarations

Competing Interests The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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