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Characterization and equilibrium studies for the removal of methylene blue from aqueous solution using activated bone char

Edu J. Inam[1,2*], John B. Edet[1,2], Patrick E. Akpan[3], Kufre E. Ite[1,2]

[1] *Department of Chemistry, University of Uyo, Uyo-520001, Nigeria.*
[2] *International Centre for Energy and Environmental Sustainability Research (ICEESR),University of Uyo, Uyo-520001, Nigeria.*
[3] *Department of Science and Technology, Akwa Ibom State Polytechnic, Ikot Osurua, Nigeria.*

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eduinam@uniuyo.edu.ng ;
Phone: +2347082494480;

Abstract
The surface characteristics as well as adsorption potential of activated cow bone char for the removal of methylene blue (MB) from aqueous solution were investigated. Physical characteristics of the adsorbent revealed a large surface area, low pore volume, reduced ash and moisture contents, which have been identified as good adsorption characteristics. The surface of the adsorbent was predominated by mesopores with a few microporous structures as well as the presence of carbonates, phosphates, silicates and hydroxyl groups which are characteristic of the apatite phase. Adsorption efficiency for the removal of MB was observed to be influenced by pH, adsorbent dosage as well as initial dye concentrations. Equilibrium adsorption data was best described by the Freundlich isotherm with a good correlation coefficient suggesting multilayer adsorption of the dye molecules on the surface of the adsorbent. Based on the drive for reduced cost, removal efficiency and availability, activated carbon from cow bone could be a promising adsorbent for methylene blue-laden effluent that could be utilized in small and large industrial applications

1. Introduction
The quest for cost effective, readily available and highly efficient adsorbents has led to the search for materials of biological and chemical origin, for the removal of organic and inorganic contaminants from aqueous solution. This is an effort made to overcome the hurdles of high energy requirement and other limitations posed by routine methods like precipitation, reverse osmosis, coagulation, chemical oxidation and so on, which have been employed in the treatment of effluents [1, 2].

Dyes have an array of industrial applications and methylene blue is a thiazine cationic dye used as a redox indicator and has wide applications as paper and temporary hair colourant as well as dyeing of fabrics and coatings for paper stock [3]. Challenges of removing residual dye from effluents have been the major setback particularly in small scale textile industries which are prevalent in most developing countries. Within these regions, unavailability of sophisticated treatment facilities due to high cost have often been the reason for the direct discharge of dye effluents into the environment, which is not only aesthetically displeasing, but also hinders the penetration of light which interferes with photosynthetic processes in aquatic matrices [4]. Other health concerns including mutagenic and carcinogenic effects, jaundice, cyanosis quadriplegia, damage to the liver, reproductive systems and kidneys have been reported [5, 4, 6]. It is therefore necessary to develop readily available and cost effective materials that have excellent adsorption potentials and can be utilized for the removal of chromophoric organic contaminants from influents before disposal.

Among the various available solid substances known to possess this remediating activity, activated carbon has been reported to possess the highest adsorption potential due to their high specific surface and controlled chemical affinity [7]. It can be derived from organic based materials like coconut shells, animal bones, rice husks, banana pith and wheat straw, among others. In a study to investigate the adsorption efficiency of different animal bones for the bleaching of palm oil, activated carbons prepared from cow bone was reported to possess the highest decolourising effect over other animal sources due to its wide surface area, low pore volume, reduced moisture and ash contents as well as high yield of charcoal [8]. N'daye described recently the modelling of adsorption isotherms of dyes from aqueous solutions by various adsorbents. The objective is not an exhaustive review of all the types of adsorbents used, but to focus onto agricultural solid wastes and activated carbons [9]. Sequel to these excellent properties as reported, the focus of this research was to investigate the surface chemistry of activated carbon from cow bone using relevant spectroscopic techniques to give insight to the chemical characteristics as well as the porous nature of the adsorbent. Also, to evaluate the efficiency of the adsorbent for the removal of methylene blue from aqueous solution in order to assess its suitability for use in designing sorption beds for the removal of methylene blue from industrial effluents, which could serve as excellent treatment alternative especially to small scale textile industries.

2. Material and Methods

2.1. Pre-treatment, carbonization and activation

These stages were carried out according to the following procedure. Cow bone samples were collected from an abattoir and washed in distilled water to remove sand and dirt. Flesh attached to the bone samples was also removed and then sun dried for 3 h. The samples were thermally activated in a muffle furnace at 400 ^oC for 1 h in the absence of air. The carbonized material was crushed into powder in a clean plastic mortar and then placed in mug cubs. Chemical activation of the material was carried out by weighing 200 g of the powdered material into a clean beaker containing 250 mL of 2 M HCl solution and heated for 1 h. The sample was then filtered, washed with distilled water and dried in an oven at 80 ^oC for 24 h. The dried sample was sieved using a 1 mm pore size sieve to obtain a uniform sized adsorbent [9].

2.2. Characterization of the activated carbon

Surface characteristics including appearance, moisture content, ash, bulk density and particle size were investigated using standard procedures reported elsewhere [9]. Total surface area as well as the porous nature of the adsorbent was analysed using Brunnauer-Emmett-Teller (BET) and t-plot methods respectively, using micrometrics analyser (Tristar 3000). Surface functionalities of the adsorbent were evaluated using Fourier transform infra-red spectrophotometer (Fischer Thermoscientific, USA). X-ray diffraction patterns were obtained using X'Pert PRO MPD diffractometer at 40 mA and 40 kV, using Cu Kα radiation with a speed of 10 ^{o}/min.

2.3. Batch adsorption studies

1 g of MB was accurately weighed and dissolved in distilled water and made up to mark in a 1000 mL volumetric flask. Working solutions were obtained from the stock solution by dilution. Effect of pH on the adsorption of MB on the prepared activated carbon was investigated by the addition of 0.1 g of the adsorbent to 30 mL of 30 mg L^{-1} MB solution. The solution was adjusted using 0.1 M NaOH and 0.1 M HCl solutions within the pH range of 2-12 at room temperature (29 ± 1 ^oC) and shaken on a platform shaker at 180 rpm for 30 mins. [10]. Change in pH was noted at each instance and the point of zero charge was evaluated. The mixture was centrifuged and the supernatant was analysed using UV spectrophotometer (Jenway 73) at 661 nm. Effects of increasing dye concentration was investigated over the range of 2-30 mg L^{-1} using a fixed adsorbent dosage (0.05 g), while the effect of varying adsorbent dosage was investigated over the range of 0.02-0.30 g using a fixed dye concentration (30 mg L^{-1}). In each case, dye solutions were shaken at 180 rpm at room temperature, centrifuged and the supernatant analysed for residual dye.

3. Results and discussion

3.1 Textural characterization of activated carbon

The surface area, porous nature and other physical characteristics of the adsorbent are presented in Table 1, while the BET plot and the porosity distribution of the adsorbent is shown in Figure 1. Results revealed a surface area of 112 m^2/g predominated by mesopores, which covers about 80 % of the entire adsorbent surface. Porosity, in addition to surface area is a key parameter that determines the application direction of materials. In this study, the presence of bimodally distributed mesopores enhances accessibility to the active sites. In addition, the skewed distribution of pores across the micro and meso-regions is characteristic of hierarchically porous architectures, which may be applied to a wide range of liquid phase reactions. Further details of the pore characteristics is obtained from the nitrogen adsorption-desorption plot (Figure 1a) revealing a type IV isotherm with type H_3 hysteresis loop according to IUPAC classification, confirming the dominance of mesopores. These small mesopores and narrow distribution obtained from the N_2 adsorption plot may be attributed to the presence of small interstice on the surface of the adsorbent, which further suggests the possibility of capillary condensation within the mesoporous framework.

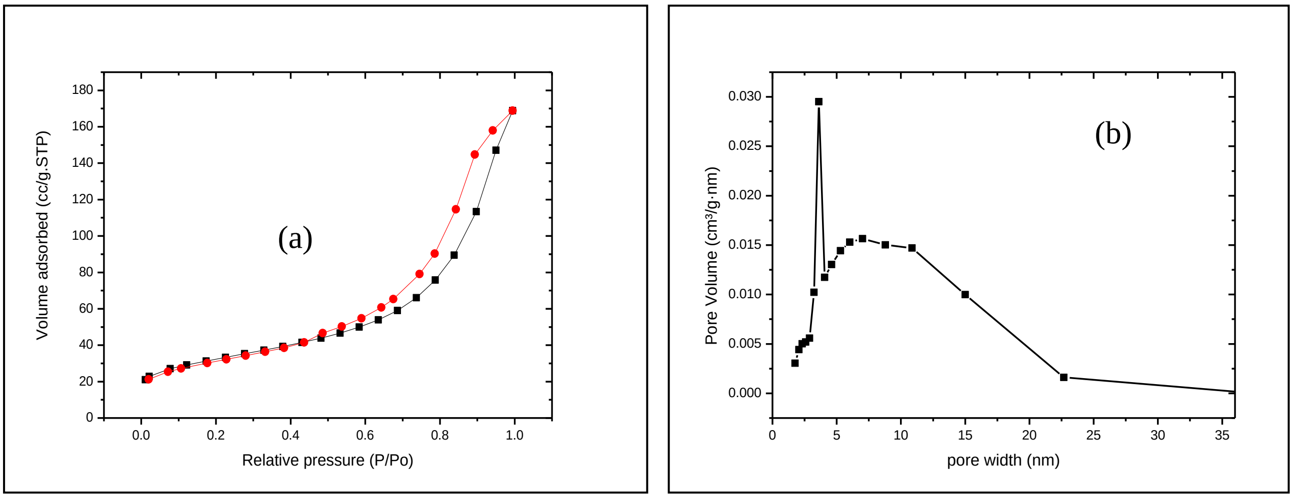

Figure 1: (a) Nitrogen adsorption-desorption isotherms of activated bone char and (b) Pore size distribution plot of activated bone char

Table1: Surface characteristics of the activated bone char.

Parameters	Result
Appearance	Black powdered solid
Bulk density (g/L)	1.05
Moisture content (%)	3.0
Ash content (%)	18.18
Particle size (µm)	300.0
BET surface area (m^2/g)	112.0
Micropore area (m^2/g)	20.0
Mesopore area (m^2/g)	92.0
Total pore volume (cm^3/g)	0.261
Micropore volume (cm^3/g)	0.01
Mesopore volume (cm^3/g)	0.251

The porosity plot (Figure 1b) indicates a bimodal pore size distribution, showing a sharp peak at about 3 nm and a broad peak between 5 nm and 10 nm. This skewed distribution of pores over the adsorbent surface creates an enhanced heterogeneous surface for the attraction and retention of dye molecules. Furthermore, the activated carbon has low ash and moisture contents which are characteristics of a good adsorbent [8].

3.2 Surface and crystalline characteristics of the activated carbon

Figure 2a shows the surface functionalities of the adsorbent. Results indicate the presence of hydroxyl groups (3435 cm^{-1}), which may be attributed to the presence of water molecules or hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) [11]. The bands observed at 607, 2202 and 2013 cm^{-1} may be attributed to the bending and stretching vibrations of phosphate groups derived from the naturally occurring calcium apatite. Peaks at 1472 cm^{-1} and 1672 cm^{-1} may be attributed to carbonates while silicon-oxygen peak is observed at 1034 cm^{-1}. X-ray diffractogram of the adsorbent confirms the presence of hydroxyapatite as shown by a sharp peak at about 33^o 2Θ. Also, the presence of well-defined peaks observed between 25^o and 60^o on the 2Θ axis are characteristic of the apatite phase [12]. Furthermore, the presence of carbonates and silicon groups on the surface of the adsorbent suggest possible ionic substitution which may further influence the crystalline nature of the apatite phase.

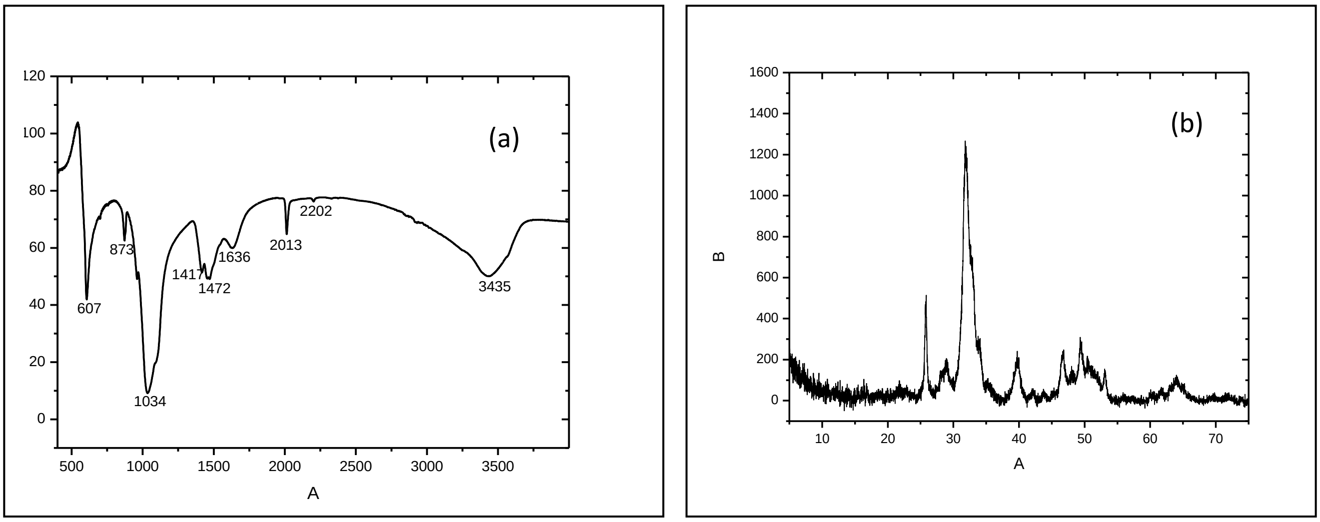

Figure 2: Spectroscopic characteristics of activated bone char consisting of (a) FTIR spectra and (b) XRD pattern

3.3 Batch adsorption studies of the activated carbon

Equilibrium studies including effects of solution pH, increasing adsorbent dosage and increasing dye concentration were conducted to evaluate the adsorption potential of the activated carbon. The results of the influence of varying pH on the adsorption efficiency as well as the estimated point of zero charge (pzc) are shown in Figures 3a and 3b respectively. Point of zero charge is an intrinsic property of a solid-water interface which describes the crystallinity as well as chemical nature of the adsorbent. The study revealed a rapid increase in adsorption as the pH was raised from 1.97 to 7.5 where maximum adsorption potential was obtained and the isoelectric point deduced from the plot (Figure 3b) was 6.8. It has been reported that cationic adsorption is highly favourable when $pH > pH_{pzc}$, while anionic dye adsorption is favoured at $pH < pH_{pzc}$, where the surface of the sorbent is positively charged [6]. Therefore, this implies that the adsorption process will best be favoured in alkaline medium, in which the hydrated surface of the adsorbent becomes deprotonated, thereby acquiring a negative charge which attracts the positively charged surface of the adsorbate. On the other hand, the reduced adsorption observed in acidic medium may be attributed to the competing effect of hydrogen ion to the surface of the adsorbent [13-16]. At high pH, the surface of the adsorbent was negatively charged, thereby enhancing the electrostatic attraction and retention of the cationic dye on the surface. This implies that the amount and nature of charged particles on the surface of the adsorbent plays an important role in the adsorption process. With a fixed dye concentration, gradual increase in adsorption with increasing adsorbent dosages was observed. The plot (Figure 4a) indicated rapid increase in adsorption due to fast accumulation of the cationic dye on the surface of the activated bone char.

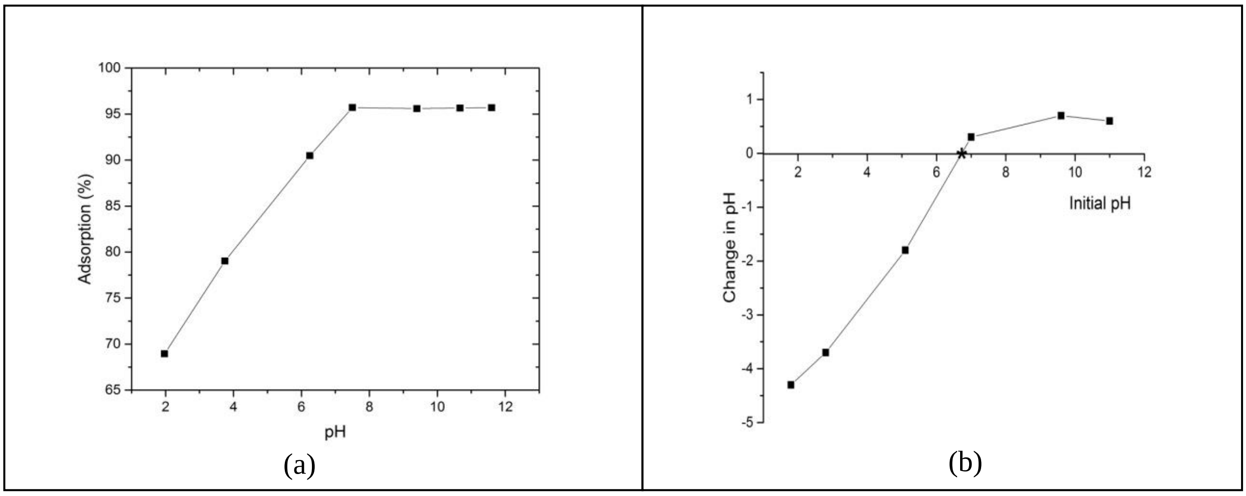

Figure 3: Effect of change in pH on the adsorption of MB on activated bone char (a) (MB concentration 30 mg/l; adsorbent dosage: 0.3g; agitation time 30 mins. at room temperature of 29 ± 1˚C) and (b) Plot showing the point of zero charge of the adsorbent.

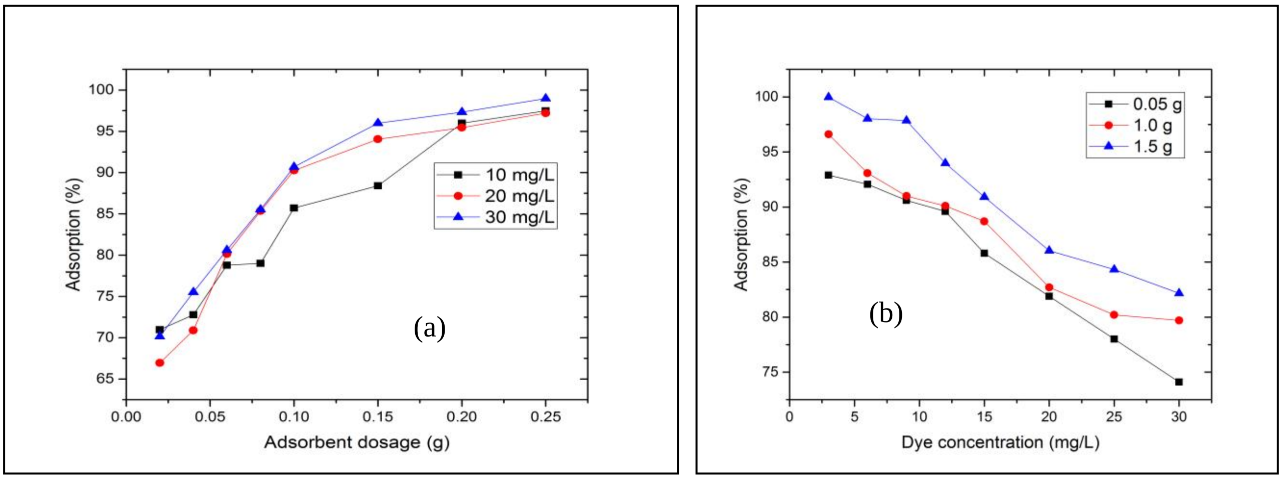

Figure 4: Equilibrium studies of the (a) Effect of increasing adsorbent dosage on the adsorption of MB on activated bone char (Concentration of MB: 30 mg/l; adsorbent dosage 0.02- 0.3 g; time: 30 mins. at room temperature of 29 ± 1˚C) and (b) Effect of increasing MB concentration on adsorption on to activated bone char (Concentration range of MB: 3-30 mg/L; adsorbent dosage 0.05 g; time: 30 mins. at room temperature of 29 ± 1 ˚C).

The activated carbon displayed a high adsorption potential with maximum adsorption at 0.3 g where almost all the dye molecules at the concentration under consideration were removed from the system. The corresponding increase in adsorption may be attributed to the availability of adsorption sites by which the dye molecules adhere. A gradual decrease in adsorption was observed as the concentration of the cationic dye was increased. This may be attributed to the gradual filling of the adsorption sites as the concentration of the dye increased. At 27 mg/L dye solution, saturation point is reached where the driving force of the dye started decreasing and the surface of the adsorbent might have been completely filled at this threshold. The significant differences in adsorption potentials at different adsorbate concentrations may be attributed to a shift in equilibrium, while increase in adsorption at different adsorbent dosages may be attributed to availability of sorption sites.

3.3 Equilibrium adsorption isotherms

Langmuir and Freundlich isotherm models (Figure 5) were used to study the mechanism of adsorption of MB on activated bone char. The parameters of each model are presented in Table 2. For Langmuir's model, the non-linear and linear mathematical expressions are given in equations 1 and 2 respectively, while the factor of separation of Langmuir (R_L) is calculated using equation 3. The nature of the plot at lower 1/Ce suggests that adsorption is mostly favoured by low dye concentration. The good correlation coefficient suggests that the maximum amount of MB that could be retained on the surface of the adsorbent corresponds to a monolayer adsorption where adsorbed dye molecules are localized at specific sites capable of accommodating a single species. Values of the adsorption capacities of other adsorbents for methylene blue from the literature are given in Table 3 for comparison. As listed in Table 3, the adsorption capacity of activated bone char is found to be substantially comparable with many reported adsorbents. This proves the viability of activated bone char as one of the most superior adsorbents for removal of methylene blue from aqueous solution. Comparing the monolayer capacities of activated bone char with other adsorbents utilized for the same purpose in the literature (Table 3), activated bone char had a higher monolayer capacity than class fly ash, raw beach sawdust, sheep bone and cotton stalk, but lower than pork bone and raw clay mineral.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (1)$$

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \qquad (2)$$

$$R_L = \frac{1}{(1 + k_L C_0)} \qquad (3)$$

where q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1}), k_L is the Langmuir constant related to the adsorption capacity (L g^{-1}), C_e is the concentration of adsorbate in the solution at equilibrium (mg L^{-1}), q_m is the maximum uptake per unit mass of adsorbent (mg g^{-1}), C_0 is the highest initial concentration of adsorbate .

On the other hand, the Freundlich isotherm model describes a multilayer adsorption where adsorbate molecules are retained at more than a single adsorption site on the surface of the adsorbent. The linear and non-linear mathematical expressions of this model are given in equations 4 and 5 respectively. The high correlation coefficient of the isotherm suggests that the mechanism of removal is more of a multilayer adsorption than adherence of dye molecules to a single adsorption site. The good correlation coefficient of both isotherms which suggest different mechanisms of adsorption is expected of materials with heterogeneous porosity as shown in Figure 3. The slope of the graph represented by the value of 1/n (Table 2) suggests a heterogeneous surface which favours multilayer adsorption confirmed by the dimensionless constant (R_L) [14].

$$q_e = K_F C_e^{1/n} \qquad (4)$$

$$\text{In}\, q_e = InK_F + \frac{1}{n} InC_e \qquad (5)$$

Where K_F (mg g^{-1}) (L mg^{-1}) ^{n} and 1/n are the Freundlich constants related to adsorption capacity and sorption intensity, respectively.

Table2: Isotherm parameters for the adsorption of MB onto activated bone char.

Isotherm	Parameters	Value
Langmuir	q_{max} (mg/g)	16.077
	K_L (L/mg)	2.059
	R_L	0.907
	R^2	0.9474
Freundlich	K_F ($mg^{1-1/n}$ $L^{1/n}$ g^{-1})	9.2627
	n	1.9558
	R^2	0.9936
	1/n	0.5113

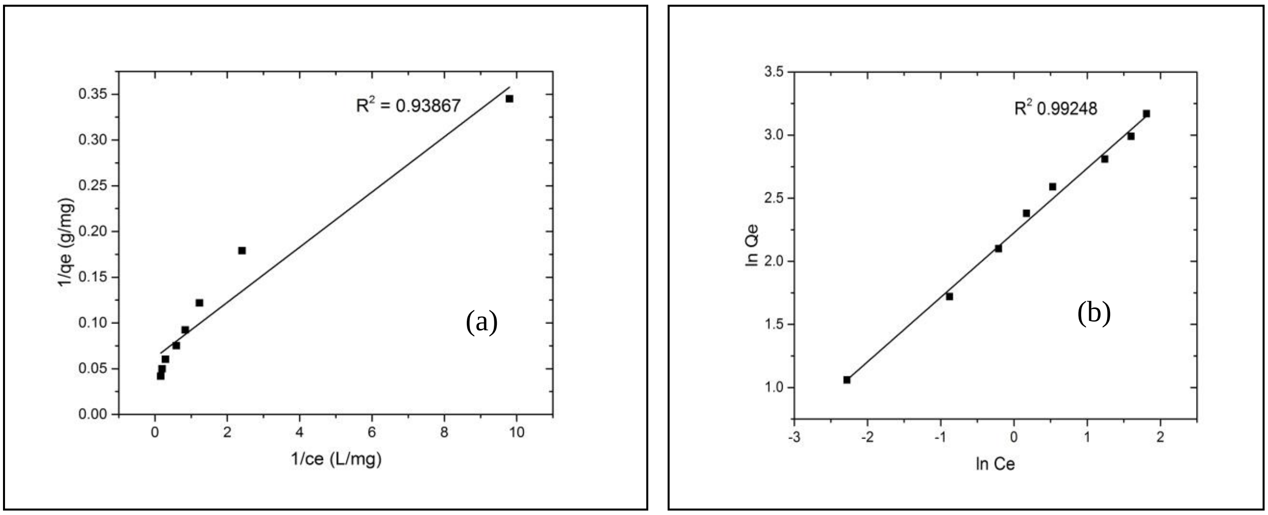

Figure 5: Equilibrium Adsorption isotherms of (a) Langmuir and (b) Freundlich

Table3: Comparison of monolayer capacities of adsorbents for the removal of MB from aqueous solution.

Adsorbents	Monolayer capacities (mg/g)	References
Class fly ash	4.92	[17]
Raw beach saw dust	9.78	[18]
Animal bone meal	22.72	[19]
Cotton stalk	11.60	[20]
Sheep bone	5.00	[21]
Pork bones	29.10	[22]
Raw clay mineral	33.0	[23]
Cow bone char	16.08	This study

Conclusion

The adsorption characteristics of activated carbon from cow bone char was investigated for its surface properties and adsorption efficiency for use in the treatment of a cationic dye-laden effluent. The surface characteristics indicated a heterogeneous surface predominated by mesoporous structure. Equilibrium adsorption studies indicated increasing adsorption potential at high pH due to the negatively charged surface of the adsorbent in this medium which enhances attraction of dye molecules to the surface of the adsorbent. Equilibrium adsorption data suggest a multilayer adsorption promoted by the heterogeneous surface of the adsorbent. This study revealed that activated carbon from cow bone has good adsorption properties and could be utilized for the treatment of methylene blue dye waste water before discharge into the environments. For future studies, the usability of activated bone char for dyes removal from real wastewater will be tested and as comparison, a fixed bed column will be employed to investigate the effect of reactor design.

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