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

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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.

Keywords: Bone char, Methylene blue, Adsorption, Activated carbon

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, 8]. 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 [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. Materials 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 °C 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 2M HCl solution and heated for 1 h. The sample was then filtered, washed with distilled water and dried in an oven at 80 °C 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 Brunauer-Emmett-Teller (BET) and t-plot methods respectively, using micrometrics analyser (Tristar 3000). Surface functionalities of the adsorbent were evaluated using Fourier transform infrared spectrophotometer (Fischer Thermoscientific, USA). X-ray diffraction patterns were obtained using X’Pert PRO MPD diffractometer at 40mA and 40kV, using Cu Kα radiation with a speed of 10°/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 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 °C) 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 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). 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. Figure 1 represents the BET plot and the porosity distribution of the adsorbent. 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 H3 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. 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 [9].

Table 1: 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 (m²/g)     | 112.0                   |
| Micropore area (m²/g)       | 20.0                    |
| Mesopore area (m²/g)        | 92.0                    |
| Total pore volume (cm³/g)   | 0.261                   |
| Micropore volume (cm³/g)    | 0.01                    |
| Mesopore volume (cm³/g)     | 0.251                   |
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$^\circ$ 2$\Theta$. Also, the presence of well-defined peaks observed between 25$^\circ$ and 60$^\circ$ on the 2$\Theta$ 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.
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, 14]. 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. 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.
Fig. 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.
Fig. 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).

3.4 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 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. 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.

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 high correlation coefficient of the isotherm suggest 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 ($R_L$) which is greater than unity [14].
Table 2: Isotherm parameters for the adsorption of MB onto HA

| 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 |

Fig. 5. Equilibrium Adsorption isotherms of (a) Langmuir and (b) Freundlich
Table 3: 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 |

4. Conclusions

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.

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Authors’ contributions

Author EJI designed and planned the experiments, JBE, PEA and KEI collected the samples and conducted the experiments. All authors read and approved the final manuscript.

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Availability of data and materials

The data used for this study is available from the corresponding author upon request.

Competing interests

All authors declare that they have no competing interest.

References

1. Šc´iban M, Radetic B, Kevrešan Z´, Klašnja M. Adsorption of heavy metals from electroplating wastewater by wood sawdust. *Biores. Technol.*, 2007;98:402–409.

2. Ofomaja AE, Unuabonah EI, Oladoja NA. Competitive modelling for the biosorptive removal of copper and lead ions from aqueous solution by Mansonia wood sawdust. *Biores. Technol.*, 2010;101:3844–3852.

3. Hu QH, Qiao SZ, Haghseresht F, Wilson MA, Lu GQ. Adsorption study for removal of basic red dye using bentonite. *Ind. Eng. Chem. Res.*, 2006;45:733–738.

4. Karaoglu MH, Dogan M, Alkan M. Removal of Reactive Blue 221 by Kaolinite from Aqueous Solutions. *Ind. Eng. Chem. Res.*, 2010;49:1534–1540.

5. Tumsek F, Avci O. Investigation of kinetics and isotherm models for the acid orange 95 adsorption from aqueous solution onto natural minerals. *J. Chem. Eng. Data*, 2013;58:551–559.

6. Salleh MA, Mahmoud DK, Karim WA, Idris A. Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review, *Desal.*, 2011, doi:10.1016/j.desal.2011.07.019

7. Liu QS, Zheng T, Wang P, Jiang JP, Li N. Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers, *Chem. Eng. J.*, 2010;157:348–356.

8. Djilani C, Zaghdoudi R, Modarressi A, Rogalski M, Djazi F, Lallam A. Elimination of organic micropollutants by adsorption on activated carbon prepared from agricultural waste. *Chem. Eng. J.*, 2012;189:203-212.

9. Mohammed A, Ahoje AA, Auta M and Jibril MA. Comparative analysis and characterization of animal bones as adsorbent. *Advances in applied science research*, 2012;3:3089-3096.
10. Pagnanelli F, Esposito A, Toro L, Veglio F. Metal speciation and pH effect on Pb, Cu, Zn and Cd biosorption onto Sphaerotilus natans: Langmuir-type empirical model, *Water Res.*, 2003;37:627-633.

11. Manalu JL, Seogijono B, Indrani DJ. Characterization of hydroxyapatite derived from bovine bone. *Asian Journal of Applied Sciences*, 2015;3:758-765.

12. Mendoza-Castillo DI, Bonilla-Petriciolet A, Jauregui-Rincon J. On the importance of surface chemistry and composition of bone char for the sorption of heavy metals from aqueous solution. *Desalination and Water Treatment*, 2015;54:1651-1662.

13. Hameed BH, Krishni RR, Sata SA. A Novel Agricultural Waste Adsorbent for the Removal of Cationic Dye from Aquous Solutions. *J. Hazard. Mater.*, 2009;162:305–311.

14. Markandeya, Singh A, Shukla SP, Mohan D, Singh NB, Bhargava DS, Shukla R, Pandey G, Yadav VP, and Kisku GC. Adsorptive capacity of saw dust for the adsorption of MB dye and designing of two- stage batch adsorber. *Cogent Environmental Science*, 2015; http://dx.doi.org/10.1080/23311843.2015.1075856.

15. Rudzinski W, Plazinski W. Theoretical description of the kinetics of solute adsorption at heterogeneous solid/solution interfaces: on the possibility of distinguishing between the diffusional and the surface reaction kinetics models, *Appl. Surf. Sci.*, 2007; 253: 5827–5840.

16. Hall KR, Eagleton LC, Acriros A, Vermeulen G. Adsorption process, *Ind. Eng. Chem.*, 1996;5: 212-219.

17. Oladoja NA, Raji IO, Olaseni SE, Onimisi TD. In situ hybridization of waste dyes into growing particles of calcium derivatives synthesized from a gastropod shell (*Achatina achatina*). *Chem. Eng. J.*, 2011;171:941-950.

18. Batzias FA, Sidiras DK. Dye adsorption by calcium chloride treated beach saw dust in batch and fixed bed systems. *J. Hazard. Mater.*, 2004;114:167-174.

19. Slimani R, Anouzla A, Abrouki Y, Ramli Y, Antri SE, Mamouni R, Lazar S, Haddad ME. Removal of a cationic dye-methylene-blue from aqueous media by the use of animal bone meal as a new low cost adsorbent. *Journal of Material and Environmental Science*, 2011;2: 77-87.

20. Ertas M, Acemioglu B, Alma MH, Usta M. Removal of methylene blue from aqueous solution using cotton stalk, cotton waste and cotton dust. *J. Hazard. Mater.*, 2010; 183:421-427.

21. Ghanizadeh G, Asgari G. Adsorption kinetics and isotherm of methylene blue and its removal from aqueous solution using bone charcoal. *Reaction kinetics, mechanism and catalysis*, 2011;102:127-142.

22. Velasco UI, Sierra I, Cepeda EA, Bravo R, Ayastuy JL. Methylene blue adsorption by chemically activated waste pork bones. *Col. Tech.*, 2015;131:322-332.

23. Feddal I, Ramdani A, Taleb S, Gaigneaux EM, Batis M, Gaffour N. Adsorption capacity of methylene blue, an organic pollutant, by montmorillonite clay. *Desalination and Water Treatment*, 2014;52:2654–2661.