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Removal of methylene blue from aqueous solution by adsorption onto activated carbon prepared from animal bone and corncob – an agricultural waste

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ABSTRACT

Synthetic dyes are widely used in the rubber, textiles, plastics, paper and cosmetics industries to color their products. The effectiveness of adsorption for dye removal from wastewater has made it an ideal alternative to other expensive treatment methods. This study investigates the physicochemical properties of animal-bone- (AB) and corncob- (CC) derived activated carbon on the removal of methylene blue dye. The effects of condition variables such as initial dye concentration, adsorbent dose, pH and contact time were studied. The results show that animal-bone-derived activated carbon has better potential for dye removal than does the corn cob-derived equivalent. AB revealed a higher adsorption capacity of intensity (2.40) and is of higher surface area - 500 m^2g^{-1}, while CC has adsorptive capacity of 1.25, intensity of 2.80 and surface area of 420 m^2/g^{-1}. What is more, the removal efficiency increases as adsorbent dose increases. This makes it an interesting option for dye removal from aqueous solutions of dye.

***Keywords*:** Synthetic dye, Adsorption, Adsorbate, Adsorbent, adsorption isotherm, methylene blue

1. INTRODUCTION

The effluents from many textile plants contains large quantities of dyes which are easily visible when it enters a water way. The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons. Industries such as textile, leather, paper, plastics etc., are some of the sources for dye effluents [2]. The discharge of organic color containing

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effluent cause huge damage to environment. Hence their removal has recently become the subject of interest [3]. The removal of colour from waste water is often more important than the removal of the soluble colorless organic substances, which usually contribute the major fraction of the biochemical oxygen demand.

Many methods have been reported for removing textile dyes from waste water, among which are membrane filtration, coagulation/flocculation, precipitation, flotation, adsorption, ion exchange, ion pair extraction, ultrasonic, mineralization, electrolysis, advanced oxidation and chemical reduction. Biological techniques include bacterial and fungal biosorption and biodegradation in aerobic anaerobic or combined anaerobic/aerobic treatment processes [4].

Adsorption is one of the most effective methods and activated carbon is the preferred adsorbent widely employed to treat waste water containing different classes of dyes, recognizing the economic drawback of commercial activated carbon. Activated carbon has been widely used in waste water treatment to remove organic and inorganic pollutant [5].

Many investigations have studied the feasibility of using low cost plant materials (residues) like babul seed [6], barley husk [7], sun flower stalks [8], peel of cucumis sativa fruit [9], orange peel [10] and lemon peel as carbonaceous precursors for the removal of dyes from water and waste water. Previously the work on removal of textile dye from aqueous solution by adsorption technique using natural waste was investigated in the laboratory [11–13]. The present study was undertaken to evaluate the efficiency of carbon adsorbent prepared from Animal bone and Corncob an agricultural waste for removal of methylene blue dye in aqueous solution. The main aim of the current study has been to visualize the pattern of adsorption of this dye to various situations such as initial dye concentration, adsorption dose, PH and contact time. The effects of various operating parameters monitored and experimental conditions were decided. These fundamental data will be useful for further applications in the treatment of practical waste or process effluents.

2. MATERIALS AND METHOD

2. 1. Adsorbate

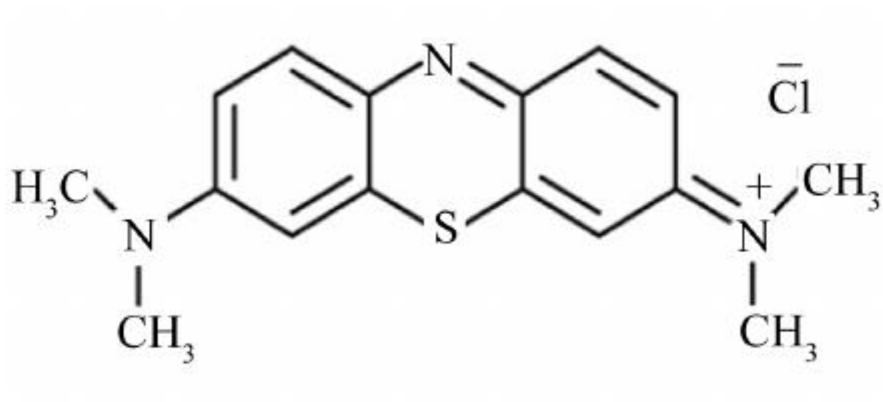
Table 1. Characteristics of Methylene Blue Dye

Molecular formular	$C_{16}H_{18}ClN_3S$
Molecular weight	319.86
C1 Number	52015
Maximum Absorbance Max	664nm
Water Solubility	100g/L

Methylene blue (a cationic dye) was used for the adsorption studies. Methylene blue was manufactured by Gurr, BDH chemicals Ltd, Poole England. A stock solution of the dye with a concentration of 1000 mg per liter was prepared. This was done by weighing 1.0 g

(1000 mg) of dye and dissolving it in a 1000 ml volumetric flask. The working solution was prepared by diluting the stock solution with deionzed water to give the appropriate concentration of the working solutions. The concentration of the residual dye solution was measured using UV visible spectrophotometer at a wave length corresponding to the maximum absorbance for the dye solution. Batch adsorption studies were performed at room temperature (40 ±1 °C). Table 1. Enlists the properties of methylene blue dye used.

At room temperature MB appears as a solid, odorless, dark green powder that yields a blue solution in water. The hydrated form has 3 molecules of water per molecules of methylene blue. Solution in waters or alcohol has deep blue color. Methylene blue is a heterocyclic aromatic compound used as a dye for a number of different staining procedures



Scheme 1. Chemical structure of methylene blue

2. 2. Adsorbent Preparation

The animal bone and corncobs used were collected from local area of Eke Uke market in Uke town, Idemili North local Government Area, Anambra State of Nigeria in clean plastic bags. These waste materials were thoroughly washed with distilled water to remove the dirt and impurities. Size reduction of the bone was achieved by manual crushing using cutlass and hammer. It was later sundried for four days. The dried bone was carbonized for 4hrs to remove volatile compounds such as hydrocarbons at a temperature of 700–1100 °C using muffler furnace. The carbonization process was followed by steam activation at a temperature of 700 °C using muffler furnace to increase its surface area. 1000 g of the sample was measured, placed in a bucket.

This was followed by treatment with activating agent, tetraoxosulphate VI acid of 50% concentration until uniform mixture was obtained. The mixture was allowed to digest for 24 hours in order to increase the surface area of the adsorbent. After which excess acid was washed off the sample with sodium hydroxide and distilled water. The resulting black product was kept in an air–oven maintained at 105 °C for 12 hours followed by washing with $NaHCO_3$ and water until free from excess acid and at 120 ±5 °C to get activated carbon. The AB product obtained was screened through a mesh sieve with a particle size range of (180–300 µm) and the physical properties were analyzed by usual standard method

2. 3. Activated Carbon From Carbons

Carbon collected from the same source as animal bone was sundried. After which, the size reduction was achieved by crushing first with mortal daughter. This was followed by milling to smaller grain size. It is then screened through a mesh sieve with a particle size range of 180-300 µm. The carbon was prepared by chemical activation. 100 g of the dried sample was measured and treated with concentrated sulphuric acid in a weight ratio of 1:1 for 24 hours to increase the surface area of the sample. The sample was allowed to digest for 48 hours. After which the resulting black product was oven dried for 12 hours at 105 ±5 °C followed by washing of excess acid with sodium hydroxide and distilled water product obtained was ground to fine powder and physical properties analyzed by usual standard method.

2. 4. Batch adsorption studies

Adsorption experiments were performed at room temperature (40 ±1 °C), 1g of adsorbent was mixed with known initial dye concentrated (100–800 mgl^{-1}) 100 mgl^{-1} MB dye solution with 1g absorbed dose variation study. For pH variation, 100 mgl^{-1} MB solution was agitated with 1g of the sample for 4hours at 300 rpm. The aliquot was analyzed for residual methylene Blue concentration spectrophotometrically using UV-Visible spectrophotometer (spectrum, model 752s) at a wave length corresponding to the maximum absorbance for the dye solution (λ_{max} = 630 nm).

3. RESULTS AND DISCUSSION

3. 1. Characteristics of the Adsorbent

Table 2. Characteristics of activated carbons from Animal bone and corn cobs.

S/No	Properties	Animal bone activated carbon	Corn cobs activated carbon
1	PH	5.9	5.9 ± 0.02
2	Moisture contents (%)	5	6 ± 0.00
3	Ash content (%)	22	24 ± 0.22
4	Porosity	0.823	0.810 ± 0.003
5	Apparent density	0.449	0.248 ± 0.056
6	Solubility in water (%)	0.36	0.44 ± 0.0.1
7	Volatile matter	38.32	37.33 ± 0.15
8	Surface ares (m^2g^{-1})	420 m^2/g	500 m^2/g ± 1.00

The data for proximate analysis, physical properties of the prepared activated carbon were determined by standard procedures. Surface area was determined by BET method. The physicochemical properties are listed in Table 2.

3. 2. Effect of Dye Concentration On Adsorption Behavior of Activated carbon

To study the effect of different initial concentration of methylene blue MB on adsorption behavior, six concentrations (100, 200, 300, 400, 500 and 600 mg/L) were used and the amounts adsorbed were calculated and given in Tables 3 and 4. The observed increase in the adsorption sites of adsorbent was as a result of increase in the surface area of the adsorbent. The amount of dye adsorbed (mg/g) increased with increase in time and the equilibrium for dye removal attainment was achieved after 240 mins. The initial dye concentration provides the necessary driving force to overcome the resistances to the mass transfer of MB between the aqueous and solid phase. The maximum adsorption obtained by Animal bone and corncobs are 93.01% and 91.11% respectively.

Table 3. Effect of different initial dye concentration on dye removal using Animal bone (Adsorbent dosage: 1 g/10 ml, initial pH: 5, Size: 180–300 μm, Agitation speed: 3000rpm, Time: 240 mins).

Initial dye concentration (mg/L)	**Percentage of methylene blue removal with time (min)**					
	40	**80**	**120**	**160**	**200**	**240**
100	23.15	38.56	50.61	66.22	80.74	84.30
200	24.34	40.67	52.73	68.26	82.86	86.26
300	22.40	37.50	58.74	72.24	84.90	87.20
400	25.53	45.92	58.24	71.24	85.92	87.25
500	28.64	50.82	57.98	76.64	87.84	90.78
600	38.49	54.86	61.50	75.52	89.91	93.01

Table 4. Effect of different initial dye concentration on dye removal using corncobs (Adsorbent dosage: 1 g/10 ml, initial pH: 5, Size: 180–300 μm, Agitation speed: 3000 rpm, Time: 240 mins)

Initial dye concentration (mg/L)	**Percentage of methylene blue removal with time (min)**					
	40	**80**	**120**	**160**	**200**	**240**
100	34.66	48.45	63.18	73.43	87.41	88.10

200	24.50	42.90	58.20	68.54	88.15	89.05
300	20.18	36.88	50.28	67.98	88.86	90.16
400	33.40	45.98	64.40	78.60	89.45	91.08
500	29.50	50.56	59.22	79.40	89.60	91.02
600	34.15	50.33	65.01	79.80	90.80	91.11

3. 3. Effect of Adsorbent Dose Variation

Table 5. Effect of different adsorbent dosage (Animal bone) on dye removal (initial concentration: 100 mg.lit, contact time: 240 min, pH of solution: 5, agitation speed: 300 rpm, temperature 40 °C, Size: 180–300 μm).

Adsorbent dose (g/100 ml)	Percentage of dye removal with time (min)					
	40	**80**	**120**	**160**	**200**	**240**
0.2	14.62	32.28	35.64	54.10	70.80	71.76
0.4	18.64	38.26	65.68	79.53	87.28	88.28
0.6	39.10	54.18	66.87	79.93	88.06	88.20
0.8	35.33	54.18	70.02	80.10	89.04	90.24
1.0	23.31	44.40	69.04	81.02	90.68	90.98
1.2	22.31	45.01	68.08	82.01	91.01	91.01

Table 6. Effect of different adsorbent dosage (corncobs) on dye removal (initial concentration: 100 mg/lit initial ph of solution: 5.0 contact time: 240 min, Agitation speed: 3000 rpm, Temperature: 40 °C, Size: 180-300 μm

Adsorbent dose (g/100 ml)	Percentage of dye removal with time (min)					
	40	**80**	**120**	**160**	**200**	**240**
0.2	13.34	30.54	37.01	45.63	62.35	63.17
0.4	22.65	46.16	58.81	72.44	86.05	86.25
0.6	44.40	60.43	78.40	78.80	85.55	84.24

0.8	44.40	60.43	78.40	78.80	85.55	84.24
1.0	50.10	60.01	77.01	85.04	87.06	88.08
1.2	52.62	63.45	77.07	86.01	88.09	89.04

The effect of adsorbent dose on removal of MB was studied by varying the dose of adsorbent (0.002, 0.004, 0.006, 0.008, 0.01 and 0.012 g/L) in the test solution while keeping the initial dye concentration 100 mg/L (Temperature 40 ±1 °C) at pH: 5. Experiments were carried out at different contact times for 240 mins. Table 5 & 6 show that of dye adsorption increased with increasing adsorbent doses. The increase in the removal of dye with large surface areas and greater active functional group was observed [14-16] The maximum adsorption of methylene blue by Animal bone AB and corncobs CC derived AC are and respectively.

3. 4. Effect of pH Variation

Adsorption is also affected by change in pH of the solution as shown in Fig 1. The hydrogen ion concentration (pH) initially affects the degree of ionization of the dye and the surface properties of the adsorbents. Experiments were carried out at 100 mg/L, initial dye concentration with 1g/L adsorbent mass at room temperature (39 ± 1 °C) for 3 hours equilibrium time. It is clear from the Fig 1. That for each initial concentration value of methylene blue, the percent removal increases as pH rises and after pH 5.0, the percent removal decreases with further increase in pH value. This clearly shows that the optimum pH for the present adsorbate – adsorbent system is 5.0 [17-20], reported similar result.

3. 5. Adsorption Isotherm

The distribution of dye between the adsorbent and dye solution when the system is at equilibrium, is important in order to obtain the adsorption capacity of Animal bone and corncob derived activated carbons. Table 3 summarized the Q and b (or K_L) values for the Langmuir isotherm, the kf and n values for the freundlich isotherm and the correlation coefficients for the two isotherms. The Langmuir isotherm is found to lie between 1 and 10 for beneficial adsorption. This is represented by the following equation

$$Ce/q_e = 1/Q_o^b + Ce/Q_o \qquad (1)$$

where: qe and Ce are defined as the amount of dye adsorbed (mg/g) and equilibrium liquid phase concentration (mg/L) respectively, K_L is a direct measure of the intensity of the sorption (1 mg/L), and Q_o is a constant related to the area occupied by a monolayer of adsorbate, reflecting the maximum adsorption capacity (mg/g). From the data of C_e/q_e Vs C_e, Q_o and K_L can be determined from m, the slope and intercept. The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor R_L which is defined by

McKay *et al.*, as $R_L = 1/1 + K_L C_o$ (2)

where: C_o is any adsorbate concentration at which the adsorption is carried out. Favorable adsorption is indicated by $0<R_L<1$. The Langmuir isotherm constants were presented in table 7 while the linear plots of C_e/q_e versus C_e suggest the applicability of the Langmuir isotherms, Fig. 2 and Fig. 4 for Animal bone and corncobs respectively.

Table 7. Langmuir and freundlich isotherm of activated carbon prepared from animal bone and corncob for MB.

Adsorbents	**Langmuir isotherm**				**Freundlich isotherm**		
	Q_o	**K_L**	**R^2**	**R_L**	**Intercept (K_f)**	**Slope (1/n)**	**R^2**
Animal Bone	28.038	0.050	0.94	0.246	0.486	0.667	0.95
Corncobs	26.004	0.032	0.86	0.346	0.85	0.357	0.90

The value of R_L indicates the type of isotherm to be either favourable $O<R_L<1$, unfavourable $R_L>1$, linear $R_L = 1$ or irreversible $R = 0$. The value of R_L was found to lie between 0 and 1 for AB and CC suggesting the isotherm to be favourable at the concentration studied [21, 22]. The freundlich equation is also employed for the adsorption of methylene blue on the AB and CC adsorbent. The freundlich isotherm (Freundlich, 1906) is represented as:

$$\log q_e = \log K_f + (1/n) \log C_e \quad (3)$$

where: q_e is the amount of methylene blue dye adsorbed (mg/g, C_e is the equilibrium concentration of dye in the solution (mg/L) and K_f and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity respectively. Linear plot of log q_e versus log C_e showed that the adsorption of methylene followed also the freundlich isotherm (Figure 3 and 5 for AB and CC respectively). The values of K_f and n are given in Table 7. From the table, there was an increase in negative charges on the adsorbent surface that makes electrostatic forces like Vander Waals between the adsorbent surface and dye ion.

The molecular weight, size and radii either limit or increase the possibility of the adsorption of the dye onto adsorbent. However, the values clearly show the dominance in adsorption capacity. The intensity of the adsorption is an indicative of the bond energies between dye and adsorbent and the possibility of slight chemisorptions rather than physisorption. However, the multilayer adsorption of methylene blue through the percolation process may be possible. The “n” value for Animal bone activated carbon and corncob are evaluated as 1.5 and 2.8 respectively and lies between zero and unity indicating that the adsorption is much more favourable for a selected adsorbents [22].

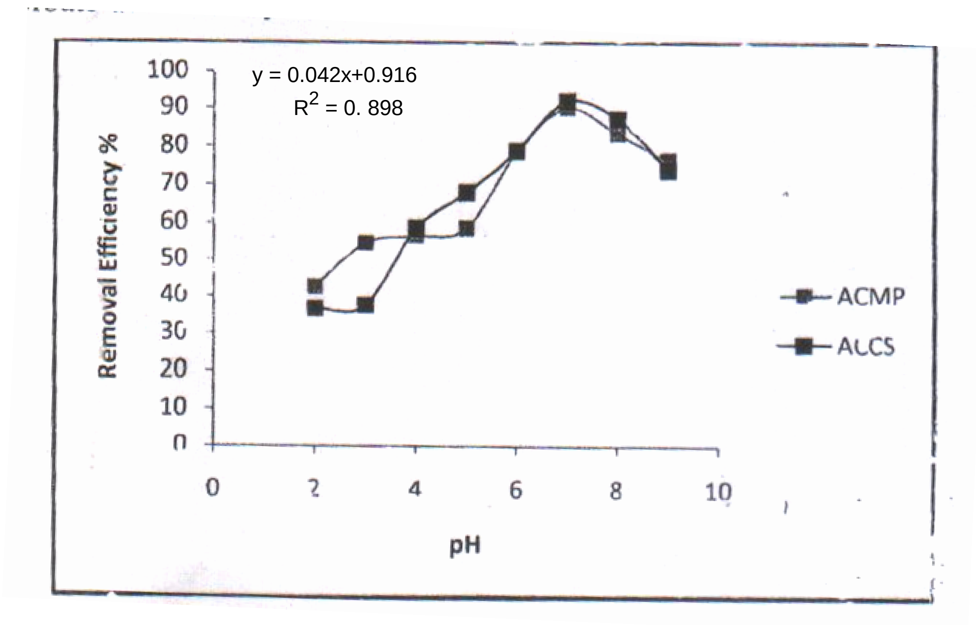


Fig. 1. Effect of pH on Methylene Blue removal

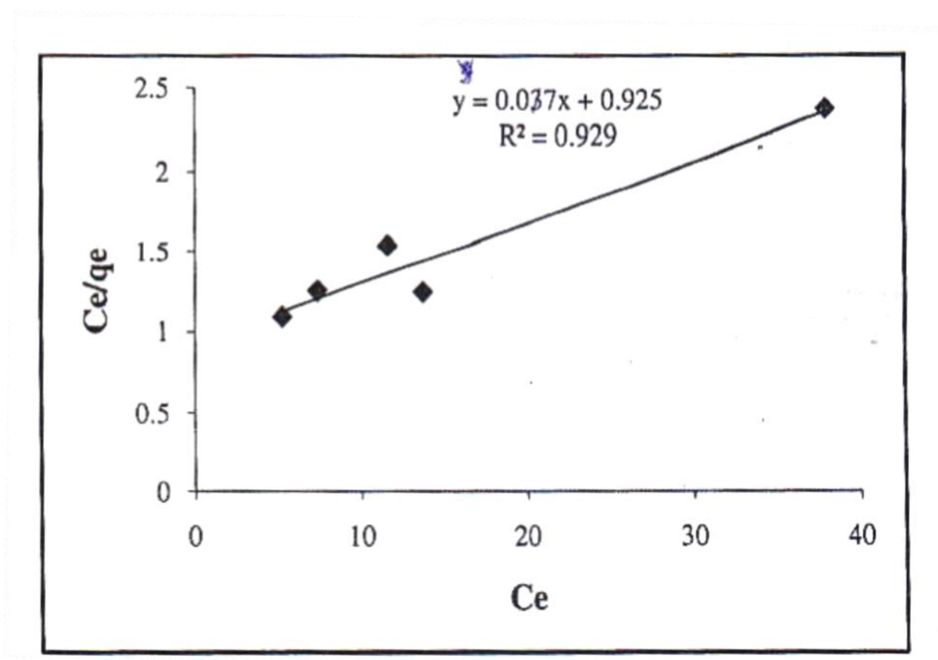


Fig. 2. Langmuir isotherm for the removal of methylene Blue by Animal bone

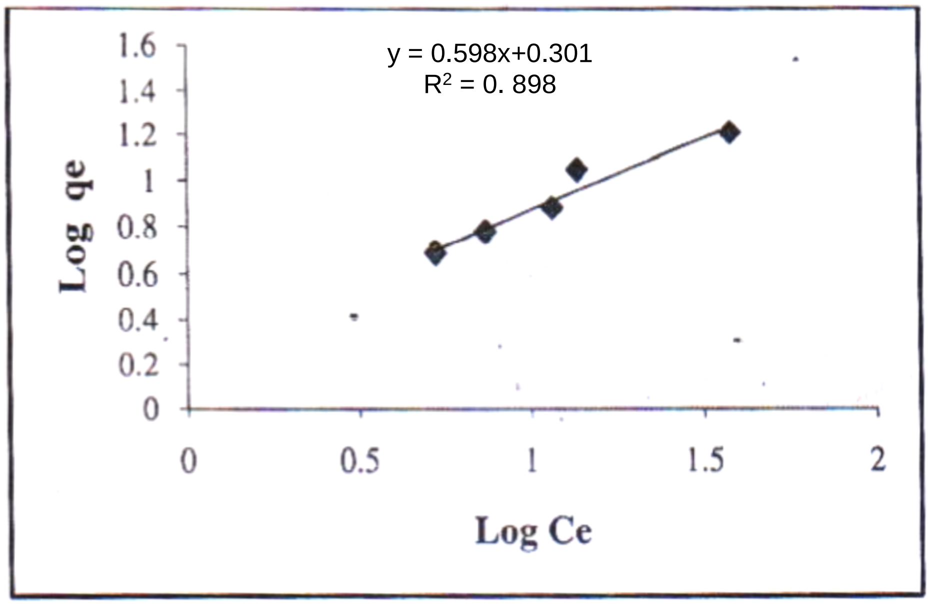


Fig. 3. Freundlich isotherm for the removal of methylene Blue by Animal bone

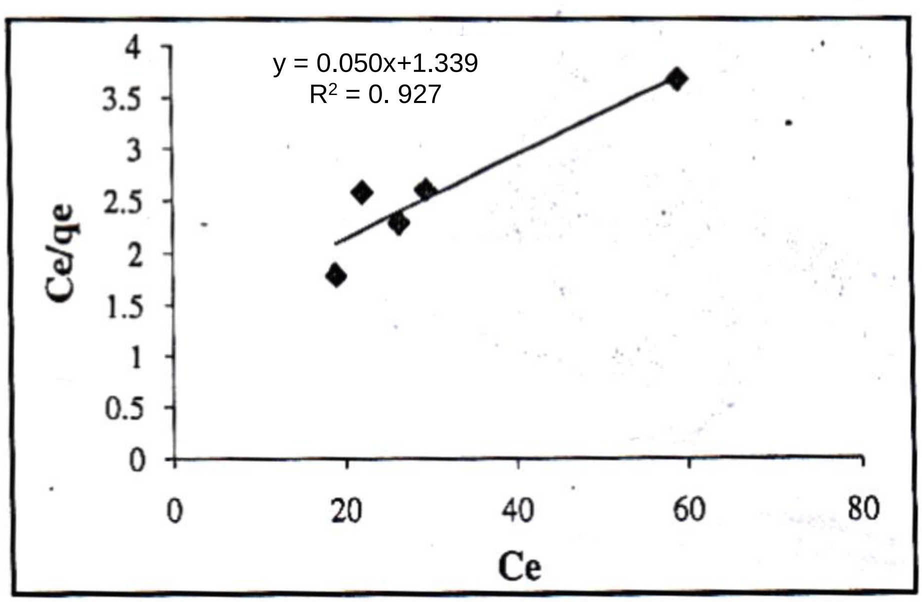


Fig. 4. Langmuir isotherm for the removal of methylene Blue by corn cobs

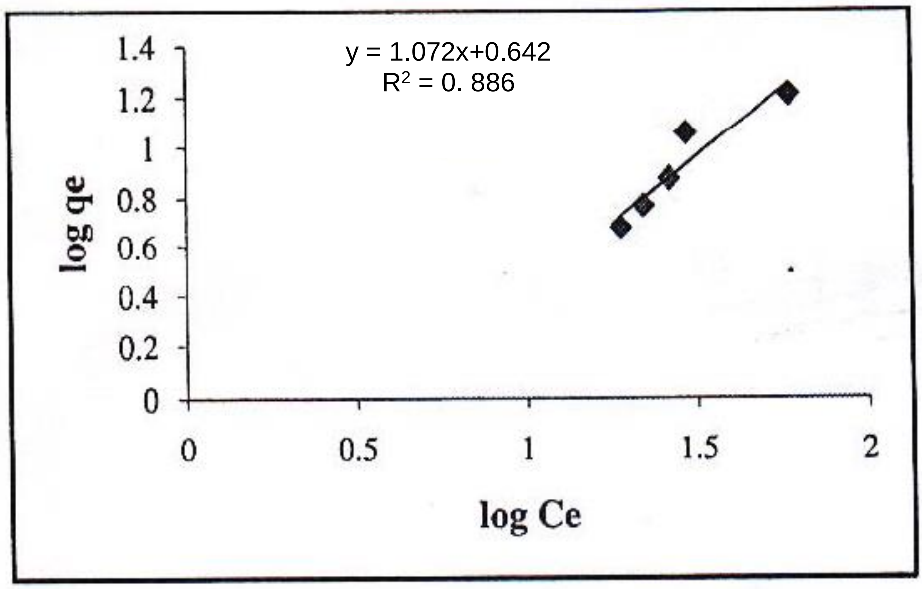


Fig. 5. Freundlish isotherm for the removal of methylene Blue by corn cobs

4. CONCLUSIONS

The results of the present investigation show that Animal bone and corncob derived activated carbon have considerable potentials for the removal of methylene blue from aqueous solution over a wide range of concentrations. The adsorbed amount of dye increased as the surface area increased with an increasing adsorbent mass. The adsorption capacities and intensities show that the activated carbon from animal bone is more efficient for the decolorization of an aqueous solution than that from corncob and it is of higher surface area. The surface charge on the adsorbent and the solution pH play a significant role in influencing the capacity of an adsorbent towards dye ions. A decrease in the pH of solution leads to a significant increase in the adsorption capacities of dye onto Animal bone based activated carbon and corncob derived activated carbon. The adsorbed amounts of dye increased with increase in contact time and reached the equilibrium in 180 mins. The equilibrium time is independent of initial dye concentration. The equilibrium data have been analyzed using Langmuir and freundlich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined from graphs of their linear equations. It was found that the freundlich isotherm appears to fit the isotherm data better than the Langmuir isotherm.

References

[1] Goddon McKay. Basic dye adsorption on activated carbon, water, air, and soil pollution. *J. App. Sci. Env. Sci.* 12 (1979) 307 – 317

[2] S.S. Azhar, Liew A.G., Suhardy, D., Hafiz, K.F., and Hafim M.D.I. Dye removal from aqueous solution by using adsorption on treated sugarcane bagasse, *AM Applied Sci* 2, 111 (2005) 499–1503.

[3] M.M. Abd El – Lati F.I., Amal, M. Ibrahim2, M.F., EL – Kadyl, Adsorption Equilibrium, Kinetics and Thermodynamic of methylene blue from aqueous solutions using biopolymer oak saw dust composite. *Journal of American Science*. 6 (2010) 267–283.

[4] A. Kan delbauer, Bioremediation for the Decolorization of Textile Dyes – A Review, world. *Journal of Microbial Biotechnology*, 37 (2006) 474, 2011.

[5] R. Somasekhara, M.C. Removal of direct dye from aqueous solutions with an adsorbent made from tarrarind fruit shell, an agricultural solid water. *J ScI. Ind. Res* 65 (2006) 443–444.

[6] M. Sujatha, A. Geetha, P. Sivakumar, and P.N. Palanisamy. Orthophosphoric Acid activated Babul seed Cotton as an Adsorbent for the Removal of Methylene Blue, *EJ Chem.* 5 4 (2008) 742–753.

[7] T. Robinson, Chandran B, Sathya Naidu G and Nigam P. Studies on the removal of dyes from a synthetic textile effluent using barley hust in static – batch mode and in a continous flow, packed – bed reactor. *Biores Technol* 85 (2002) 43–49.

[8] Gang, Sun and Xu. Xiangjing. Sunflower Stalks as adsorbents for color removal from textile wastewater. *Ind Eng Chem Res* 6 (1997) 808–812.

[9] S. Thirumalisamys, and Subbaian, M. Removal of methylene blue from aqueous solution by activated carbon prepared from the peel of cucumis sativa fruit by adsorption. *Bioresources* 5 (2010) 419–437.

[10] N. Kanan, Meenakshisun daram M and Johnson R. Removal of Azure A from Aqueous solution by CAC and New Activated carbon from orange peel and lemon peel. *EJEAFche* 8 (2009) 574–583.

[11] U.V. Ladhe, S.K. Wankhede, V.T. Patil and P.R. Patil. Adsorption of Erichrome black I from aqueous solutions on activated carbon prepared from mosambi peel, *J. Appli Sci. Env. San.* 6 (2011) 149–154.

[12] U.V. Ladhe, S.K. Wankhede, V.T. Patil and P.R. Patil. Removal of Erichrome Black I from synthetic waste water by cotton waste. *E.J. chem..*, 8 (2011) 803 – 808.

[13] U.V. Ladhe, S.K. Wankhede, V.T. Patil and P.R. Patil. Removal of Erichrome Black I from synthetic waste water by activated Nilgiril leaves. *J. Chem and Pharm. Res.* 3 (2011) 760–675.

[14] G. Dursun and Ozer. Removal of Methylene Blue from Aqueous solution by dehydrated wheat brain carbon. *Journal of Hazardous Materials* 146 (2007) 262–269.

[15] F.A. Pavan, A.C. Mazzocato, Y. Gushikem. Removal of Methylene Blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent, *Bioresources Technology* 99 (2008) 3162–3165.

[16] S.D. Rhattri and Singh M.K. Colour removal from synthetic dye wastewater, using a bioadsorbent water, *Air and soil pollution.* 120 (2000) 283–294.

[17] H. Mas Rosemal. Mas Haris and Kathiresan Sathasivam. The removal of methyl red from aqueous solutions using banana pseudostem fibers, *Am J Applied Sci* 6 (2009) 1690–1700.

[18] Joseph N.O. Ezeugo. Development of Adsorbents from local Raw Materials, M. Eng Thesis. (2012) 23-31

[19] C. Namasivayam, Radhika, R., Suba, S. *Waste Manage.* 21 (2001) 381.

[20] McKay, G.J. *Chem, Tech. Biotechnol.* 32 (1982) 759.

[21] Arient, J. Prehled Barvivi, *SNTL Prague* 12 (1968) 24-69

[22] Agboinghale, F and Ugbesia, O.S. Adsorption of lead and nickel ion on orange peels. *J. Chem Soc.* Nigeria 12 (2005) 54–55.