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Equilibrium Adsorption Studies of Methylene Blue onto Blended Agricultural Wastes-Based Activated Carbon

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ABSTRACT

An effective adsorbent was prepared from *Caesalpinia Pulcherrima* and *Melaleuca Leucadendron* (Cajuput tree capsule) husk (BAC-PA) by Phosphoric acid activation method and its adsorption characteristic was studied for the removal of methylene blue from aqueous solution. Batch mode adsorption experiments were adopted. Maximum dye removal capacity was observed at a pH of 9. Equilibrium data were obtained at 303, 313, 323, 333 and 343K for the initial concentrations of 20, 40, 60, 80 and 100 mg/L. Adsorption isotherm models such as Langmuir, Freundlich, Temkin and Dubinin – Radus-Kevich isotherms were used to correlate the equilibrium data. Parameters obtained from the isotherm models were discussed in detail. This study will help in giving supporting evidence on the effective use of blended activated carbon from agricultural waste precursors in the adsorption of methylene blue.

Keywords: Methylene blue, activated carbon, Langmuir, Freundlich, Temkin, Dubinin–Radus-Kevich

INTRODUCTION

The problems of the ecosystem are increasing with increasing anthropogenic activities. Heavy metal pollution is one of the main problems affecting our ecosystem. Toxic metal compounds do not only contaminate the seas, lakes, ponds and reservoirs, but also contaminate underground water in trace amounts by leaching through the soil after rain and snow. Therefore, the earth's waters contain various toxic metals (Ihan and Fuat, 2000). Heavy metal contamination of water sources is of great concern because of its non-biodegradability and toxic effect to humans, other animals and plants even at very low concentrations (Khan *et al.,* 2006). Various chemical and physical methods have been used to remove metal ions from solutions in the past few decades. These methods include chemical precipitation, solvent extraction, ion exchange, evaporation, reverse osmosis, electrolysis and adsorption. Among these methods, chemical precipitation, solvent extraction, ion exchange and adsorption are more commonly used (Panida and Pisit, 2010) .Adsorption using activated carbon has been considered as, possibly, the most cost-effective method for heavy metal ion removal, especially at medium to low concentrations, because the process is simple and chemical consumption or waste generation is not a significant issue. Activated carbons form a large and important class of porous solids, which have found a wide range of technological applications (Lofty *et al.,* 2012). The characteristics and structural properties of activated carbon depend on the physical and chemical properties of the precursor, method of activation, oxidizing agent, time and temperature employed. Activated carbons are carbonaceous material that can be distinguished from elemental carbon by the oxidation of the carbon atoms found on the inner and outer layers of the molecular structure (Baker *et al.,* 1992). These materials are characterized by their large surface area, porous surface containing functional group. For this reason, activated carbons are widely used as adsorbents for the removal of organic chemicals and pollutant from air, gases, portable water and also in wastewater treatment (El-Hendway, 2003.). The surface oxygen functional groups can be easily introduced to the carbon by different activation methods including dry and wet oxidizing agents. Wet oxidation methods involve the reaction between the carbon surface and solutions of oxidizing agents such as phosphoric acid (H_3PO_4), Nitric acid (HNO_3), Zinc chloride ($ZnCl_2$), Potassium hydroxide (KOH), Potassium permanganate ($KMnO_4$), Calcium chloride ($CaCl_2$) etc. One of the fastest growing areas is the environmental application of activated carbon to treat effluent from textile industry. These effluent when discharged, defaces the look of natural water and highly toxic (Chu, 2001), also causes harm to mammalian cells by causing kidney tumors (Fermendes *et al.,* 1997). Many treatment methods have been employed to remove dyes from wastewater; using physical and chemical methods which are considered expensive in terms of energy and reagents consumption (Churhly, 1994).

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In recent years, the interest in the production of activated carbon from agricultural waste cannot be over emphasized; an added value to waste.

Several substances have been screened as alternative to conventional raw materials for the production of activated carbon which include; palm seed coat (Rengarag et al., 2002), coconut shells (Churhly, 1994), tridax procumbens (Raveenbra *et al.,* 2015), olive stones (Raveenbra *et al.,* 2015), cow bone (Gumus *et al.,* 2012), land snail shell (Gumus and Okpeku, 2015), orange waste (Perez-Martin *et al.,* 2007), terminalia arjuna nuts (Mohanty *et al.,* 2005), euphorbia antiquorum (Sivakumar *et al.,* 2009), periwinkle shell (Badmas *et al.,* 2007). Agriculture wastes such as coconut shells, banana peels, oil palm nut shells, rice husks, olive waste cakes, and guava seeds have be reportedly used (Fermendes *et al.,* 1997). The agricultural wastes are common in the Nigerian environment and grow to about 15 m in height and has dark, evergreen and produce husks in which lies a number of seeds. The husks litter our communities with corresponding negative environmental impact. This prompted the need to consider them in producing a blended activated carbon for the adsorption of a model solution of standard dye (Methylene blue).

MATERIALS AND METHOD

Materials

The carbonaceous precursor used for preparation of activated carbon (AC) are *Caesalpinia Pulcherrima* and *Melaleuca Leucadendron* (Cajuput tree capsule) husk and was collected from the premises of S.S Simon and Jude Seminary, Kuje, Abuja. Prior to use, samples were washed gently with water to remove mud and other impurities present on the surface and then sun dried for one week. All chemical reagents used in this work were procured from Merck chemicals, U.K, analytical grades. Other materials include Phosphoric acid H_3PO_4 laboratory standard reagent and distilled water.

Preparation of Activated Carbons

The adsorbents were prepared as described by (Hanafiah *et al.,* 2006). Husks from both wastes were collected after discarding the fruit pulps, sun dried, crushed and grinded in a ball mill individually before mixing in the ratio 1:1. The grinded samples were sieved to obtain the particles of uniform size, 1.0 mm. The ratio of acid to precursor was 2:1 i.e 200 mL of acid w/v for every 100g of the blended sample. The preparation of the activated carbon using phosphoric acid was carried out by using predefined conditions of carbonization temperature, concentration, and particle size and activation time suggested by the software (DOE) as shown in table 1. The precursor obtained were washed to remove surface bounded impurities and mud then dried. The adsorbents prepared were denoted BAC-PA throughout the work, where PA is Phosphoric acid.

Table 1: Optimized preparation conditions for preparing BAC-PA

AC type	Phosphoric acid Concentration (%)	Carbonization Temp. (^oC)	Activation time (hrs)	Particle size (mm)
BAC-PA	50	300	4.0	1.0

Batch equilibrium method

Experiments were carried out various temperatures such as 303, 313,323,333 and 343K in an orbital shaker at a constant speed of 130 rpm using 250 mL conical flasks containing predetermined dose of BAC-PA with 50 mL of methylene blue solution. Samples were agitated for pre-determined time and the adsorbent were separated from the solution by centrifugation at 1000 rpm for 10 min. The absorbance of the centrifugate was estimated to determine the residual dye concentration. The absorbance of the dye solution was measured at λ_{max} 590 nm using Systronics Double Beam UV-visible Spectrophotometer: 2202 (Igwe and Abia, 2003).

The percentage of removal dye was calculated using the following equation

$$q_t = (C_i - C_t)\frac{V}{W} \qquad (1)$$

$$(\%) of\ removal = \frac{C_i - C_t}{C_i}\ x\ 100 \qquad (2)$$

Where: C_i and C_t are the concentration of adsorbate (mg/L) at initial stage and at time‘t’ respectively

V is the volume of solution (L) W is the mass of adsorbent (g). Experimental result obtained from the effect of initial concentration and contact times were employed in testing the applicability of isotherm and kinetic models.

RESULTS

Table 2: Equilibrium parameters

	C_e (mg/L)				
	Temperatures				
Methylene Blue (mg/L)	303	313	323	333	343
20	1.176	0.980	0.784	0.588	0.392
40	2.156	1.764	1.564	1.176	0.784
60	2.941	2.540	2.156	1.764	1.176
80	3.921	3.529	2.352	2.352	1.764
100	4.901	4.313	3.137	3.137	2.549

Table 3: Equilibrium parameters

	q_e (mg/g)				
	Temperatures				
Methylene blue mg/L)	303	313	323	333	343
20	18.52	18.77	19.01	19.26	19.50
40	19.80	20.29	20.53	21.02	21.51
60	21.32	21.81	22.30	22.79	23.52
80	22.59	23.08	23.82	24.55	25.29
100	23.87	24.60	25.58	26.07	26.81

Table 4: Separation factor R_L indicating the nature of the adsorption process

R_L value	**Nature of the process**
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

Table 5 Langmuir isotherm constants for the adsorption of dye

T(K)	**q_m**	**b**	**R^2**
303	27.0	1.6086	0.995
313	27.0	1.9473	0.995
323	28.5	2.0582	0.990
333	29.4	2.6153	0.994
343	29.4	4.2500	0.997

Table 6: R_L values

	RL values				
	Temperatures ^oK				
MB (mg/L)	303	313	323	333	343
20	0.037	0.031	0.029	0.023	0.014
40	0.033	0.027	0.026	0.020	0.012
60	0.031	0.025	0.023	0.018	0.011
80	0.027	0.022	0.021	0.017	0.011
100	0.025	0.020	0.019	0.015	0.009

Table 7: Freundlich isotherm results

Temperature (K)	**n**	**K_f (mg/g)**	**R^2**
303	5.6	18.6	0.980
313	5.5	17.7	0.971
323	5.2	19.5	0.950
333	5.5	20.9	0.978
343	5.7	22.8	0.994

Table 8 Temkin isotherm results

Temperature (K)	**b_T (Kj/mg)**	**a_T (L/g)**	**R^2**
303	6.721	1.238	0.959
313	6.807	1.229	0.968
323	6.357	1.242	0.931
333	6.776	1.215	0.965
343	7.154	1.189	0.990

Table 9 Dubinin – Radushkevich isotherm results

Temperature (K)	**q_D (mg/g)**	**E (Kj/mol)**	**R^2**
303	23.6	0.2357	0.805
313	23.6	0.2673	0.822
323	24.3	0.2887	0.731
333	25.0	0.3536	0.866
343	26.0	0.4082	0.894

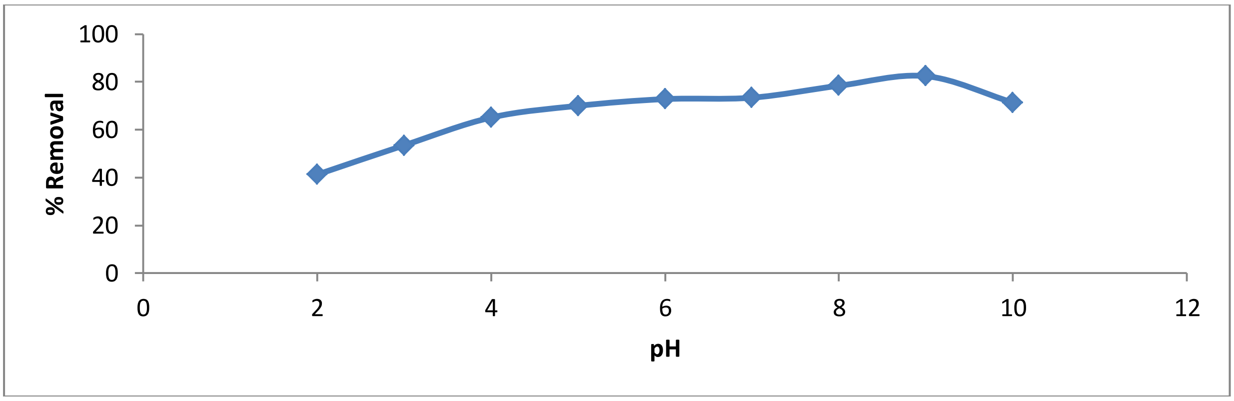
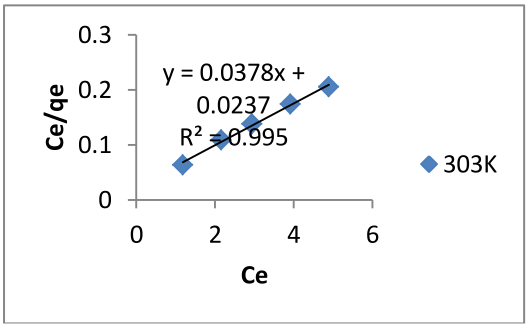
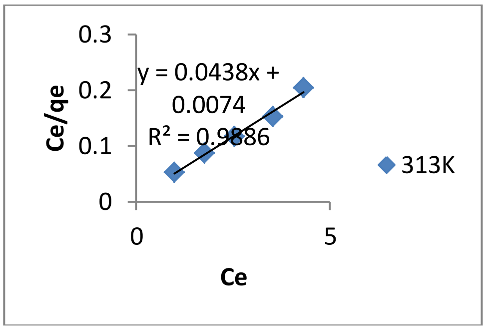


Figure 1 Effect of pH on methylene blue removal by BAC-PA

Langmuir Isotherms





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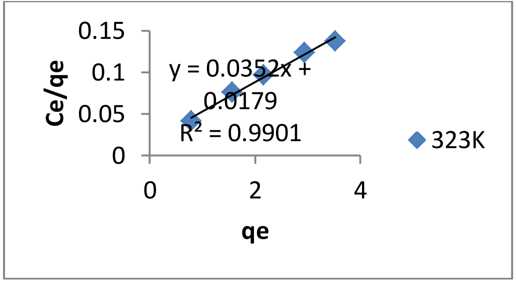

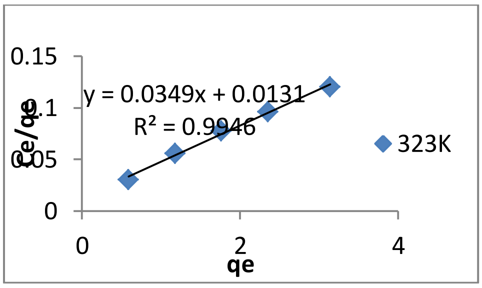

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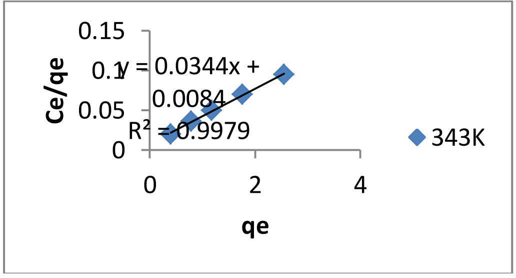

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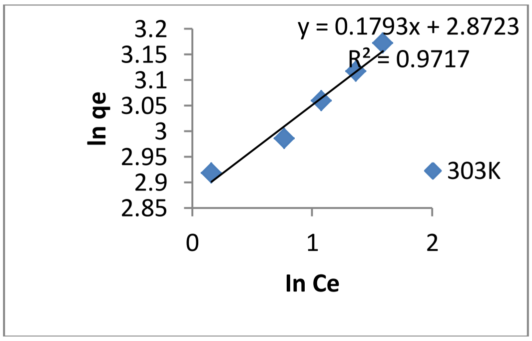
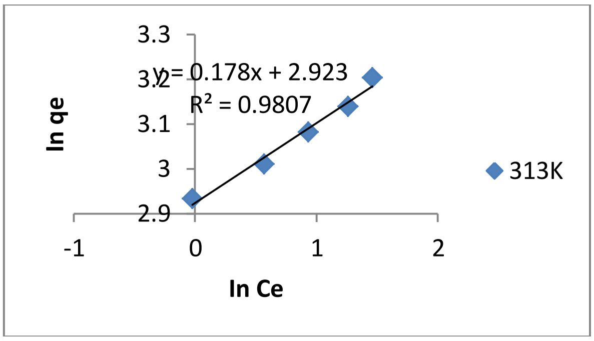
Figures 2 (a, b, c, d and e): Langmuir isotherms for methylene blue removal

Freundlich Isotherms





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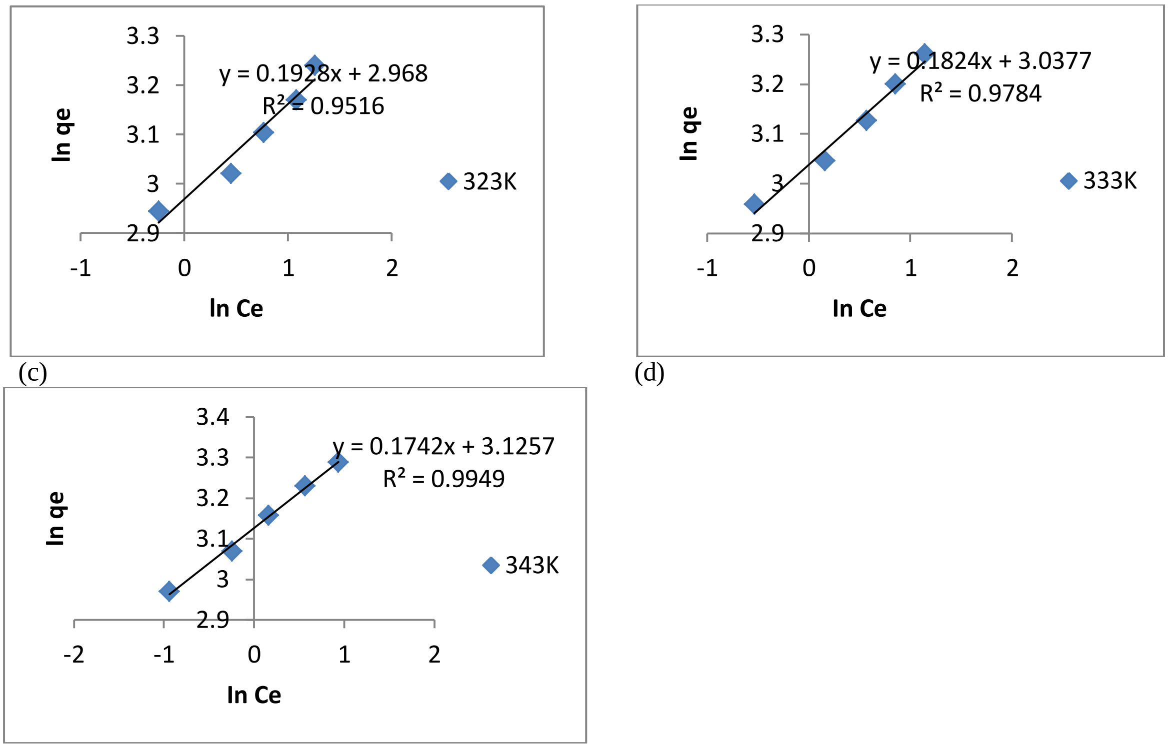

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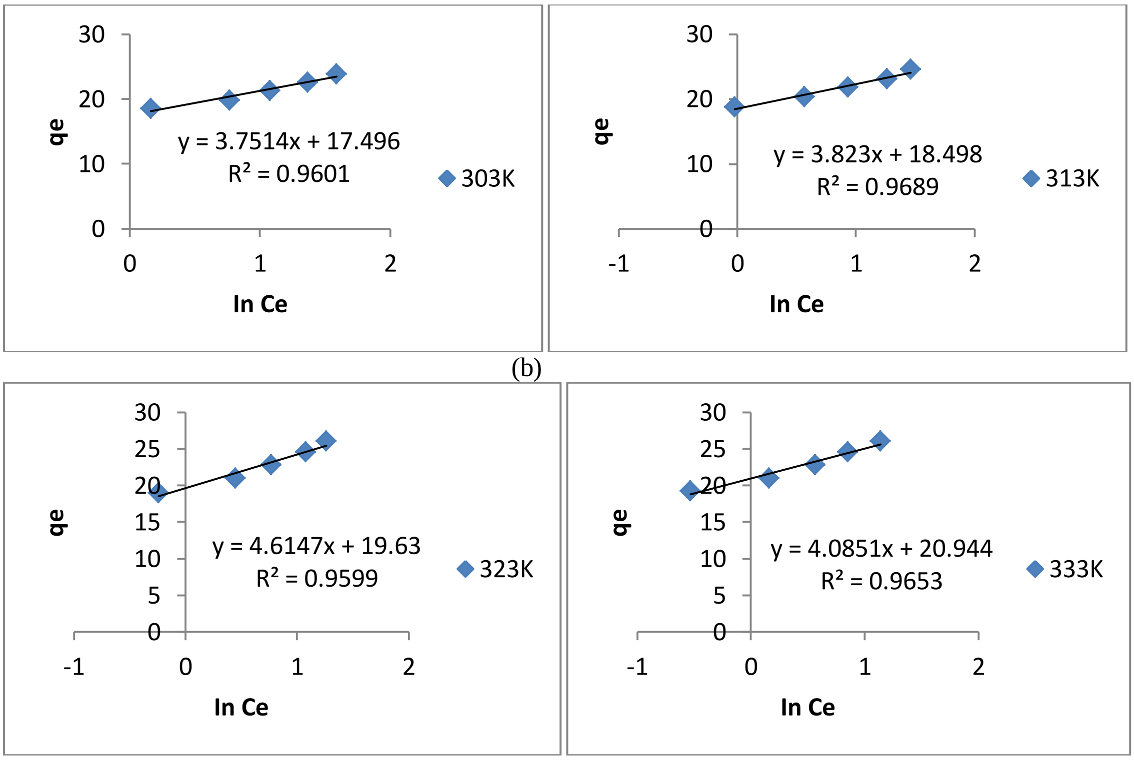
Figures 3 (a, b, c, d and e): Freundlich isotherms for methylene blue removal

Temkin Isotherms



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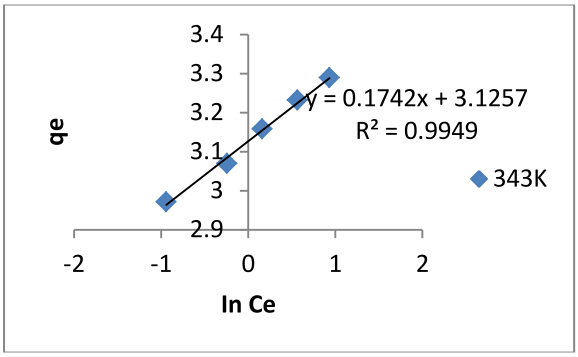

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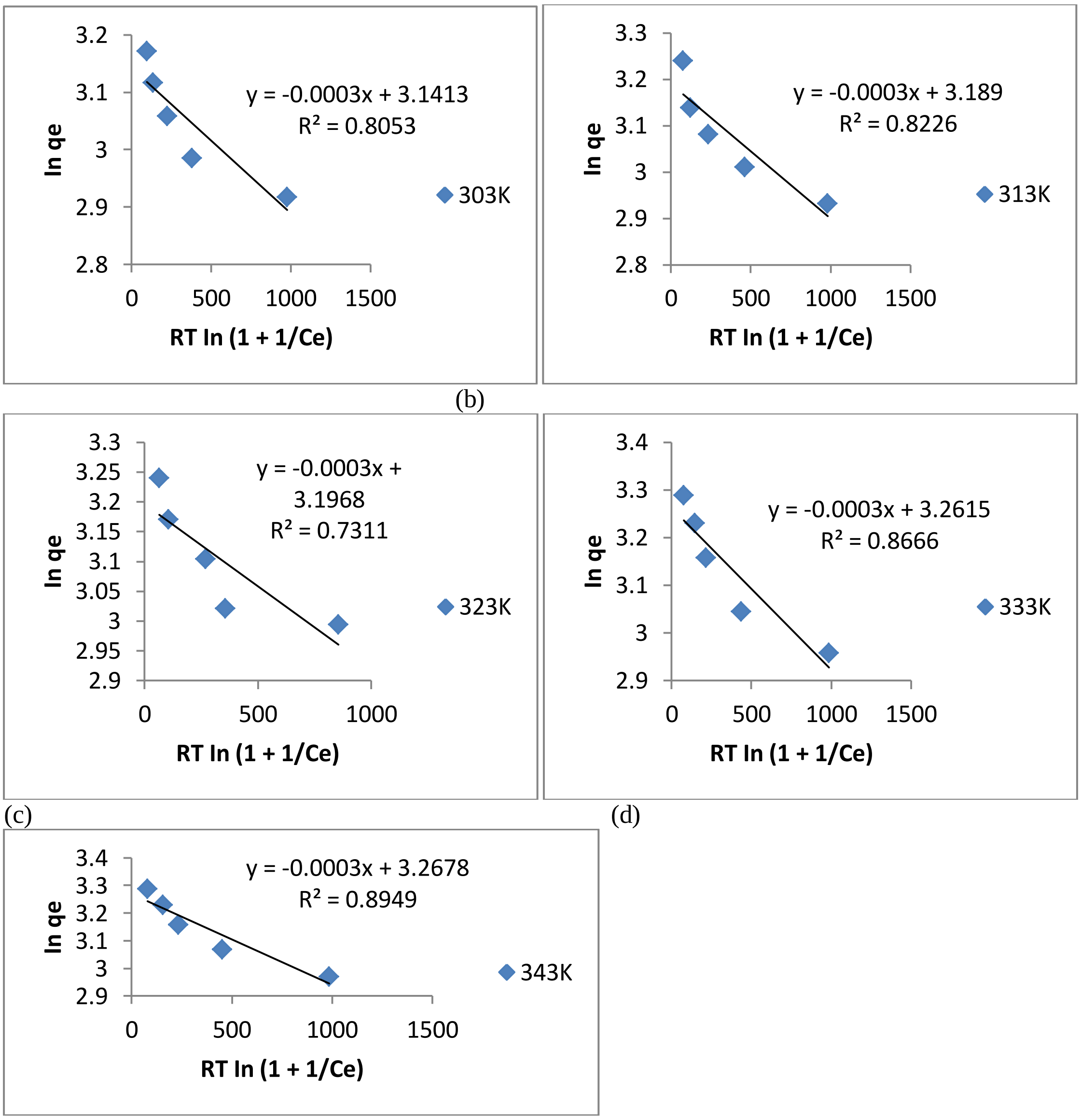
Figures 4 (a, b, c, d and e): Temkin isotherms for methylene blue removal

Dubinin – Radushkevich



(b)

(c)

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Figures 5 (a, b, c, d and e): Dubinin – Radus-Kevich isotherms for methylene blue removal

DISCUSSION

Effect of pH

pH is one of the most important factors controlling the adsorption of dye onto adsorbent particles, which affects the surface charge of the adsorbents as well as speciation of the solutes (Ramakrishna *et al.*, 1976). The hydrogen ion and hydroxyl ions are adsorbed quite strongly and therefore the adsorption of other ions is affected by the pH of the solution. It is usually expected that increase of cationic dye adsorption with the increase of pH due to the increase of the negative surface charge on the adsorbents (Minguang, 1998). The effect of solution pH was studied between initial pH range of 2 to 10, initial pH of the solution was maintained by the addition of 0.1M HCl and 0.1M NaOH solutions and agitated with 40 mg of adsorbent for 130 min at 303K. The results of effect of initial pH of dye solution on the adsorption of BAC-PA for initial dye concentration of 20 mg/L are presented in Figure 1. The lower adsorption at acidic pH is probably due to the presence of excess H^+ ions in the solution which compete with the cationic dye for adsorption sites (Minguang, 1998). As surface positive charge density decreases with an increase in the solution pH, the electrostatic repulsion between the positively charged dye and the surface of the adsorbent is lowered, which results in an increase in the extent of dye adsorption. Higher percentage removal (82.41%) occurred at pH 9.0 .But still at an alkaline medium. This might be due to the inter-ionic attraction between the OH^- ions which present in the solution in excess and dye cations. Hence the remaining experiments were conducted at pH 9 ± 0.5.

Equilibrium studies

Adsorption of methylene blue is considered to be a fast physical/chemical process; it is a collective term for a number of passive accumulation processes which include ion exchange, co-ordination, complexation, chelation, Vander Waal's attraction and micro precipitation. Proper analysis and design of adsorption separation processes require relevant adsorption equilibria as one of the vital information. In equilibrium, certain relationship prevails between solute concentration in solution and in adsorbed state. Equilibrium concentrations are the function of temperature. Therefore, the adsorption equilibrium relationship at a given temperature is referred to as adsorption isotherm. The concentration of dye solution at equilibrium (C_e) and the quantity adsorbed at equilibrium (q_e) at different temperatures are collected in Table 2 and 3.

Isotherm studies

The presence of equilibrium between two phases (liquid and solid phase) is rationalized by adsorption isotherm. The equilibrium data obtained from the experiments were processed with the following isotherm equations such as Langmuir, Freundlich, Temkin, and Dubinin- Raduskevich. Inference obtained from each isotherm is discussed in detail one by one.

Langmuir isotherm

It is a widespread-used model for describing dye sorption onto adsorbent. Langmuir equation relates to the coverage of molecules on a solid surface and the concentration of contacting solution at a fixed temperature. This isotherm is based on the following assumptions such as adsorption limited to monolayer coverage, all surface sites being a like; one site accommodates one species of the adsorbates and the ability of a molecule to be adsorbed on a given site independent of its neighbouring sites occupancy. Linear form of Langmuir equation is written in the following form (Do˘gan *et al.*, 2007)

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (3)$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e the equilibrium concentration of solute in the bulk solution (mg/L), q_m is the maximum monolayer adsorption capacity or saturation capacity (mg/g) and b is the adsorption energy, b is the reciprocal of the concentration at which half saturation of the adsorbent is reached. The essential characteristics of Langmuir isotherm can be described by a separation factor, R_L, which is defined by the following equation:

$$R_L = \frac{1}{1+bC_o} \quad (4)$$

Where C_0 is the initial concentration of the adsorbate solution. The separation factor R_L indicates the nature of the adsorption process as given in Table 4.

The results obtained from Langmuir isotherm model for the adsorption of dye are presented in Table 5. Concerned isotherm plots are shown in Figures 2 (a, b, c, d and e).

The regression coefficient (R^2) values are ranged from 0.990 to 0.997 for the five studied temperatures viz. 303, 313,323,333 and 343 K. These results show the best fitting of the equilibrium data in the Langmuir isotherms. The adsorption capacity is the most important characteristic of an adsorbent. It is defined as the amount of adsorbate taken up by adsorbent per unit mass of adsorbent. This variable is governed by a series of properties such as pore size and its size distribution, specific surface area, cation exchange capacity, pH, surface functional groups and also temperature. The mono layer adsorption capacity qm values (mg/g) for adsorption of methylene ranged from 27.0270 to 29.4117.

Further it is noticed that adsorption capacities are slightly increased with the increase of temperature. The dimensionless separation factor R_L values calculated for various initial concentrations at different temperatures are given in Table 6 for the adsorption of dye. These values are lie between 0 and 1 which indicate the favourable adsorption of methylene blue onto BAC-PA.

Freundlich Isotherm

Freundlich isotherm is an empirical equation. It is the most popular model for a single solute system based on the distribution of solute between the solid phase and aqueous phase at equilibrium. It suggests that sorption energy exponentially decreases on completion of the sorptional centers of an adsorbent. The Freundlich model describes the adsorption with in a restricted range only. It is capable of describing the adsorption of organic and inorganic compounds on a wide variety of adsorbents (Yanyan *et al.,* 2015). The linear form of the equation has the following form:

$$In\ q_e = In\ K_f + \frac{1}{n}\ In\ C_e \qquad (55)$$

where qe is the amount of adsorbate adsorbed (mg/g) at equilibrium, C_e is the equilibrium concentration of adsorbate in solution (mg/L) and Kf and n are the constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively As a robust equation, Freundlich isotherm has the ability to fit into nearly all experimental adsorption–desorption data and is especially excellent for fitting data from highly heterogeneous sorbent systems. 1/n is the heterogeneity factor and it is a measure of deviation from linearity of adsorption. A favourable adsorption tends to have n value between1 and 10. The larger value implies a stronger interaction between the adsorbent and adsorbate while 1/n equal to 1 indicates linear adsorption leading to identical adsorption energies for all sites. Sorption of solute on any sorbent can occur either by physical bonding, ion exchange, complexation, chelation or through a combination of these interactions. In the first case of physical bonding, as the solute is loosely bound, it can easily be desorbed using distilled water. Different mechanisms as mentioned can be involved as the interaction between sorbent and solute molecules depending upon the functional groups such as hydroxyl, carbonyl and carboxyl can present within the structure of adsorbent. The parameter 'n' value of Freundlich equation expresses these phenomena. The results obtained from Freundlich isotherm model are given in Table 7. The concerned isotherm plots are shown in Figures 3 (a, b, c, d and e). The regression coefficient (R^2) for Freundlich isotherms are ranged from 0.950 to 994 for all the studied temperatures viz. 303, 313, 323,333 and 343 K. It indicates that the experimental data fit well into Freundlich model. Freundlich constant adsorption capacity K_f (mg/g) values for adsorption of methylene blue ranged from 17.68 to 22.76 respectively. Further it is noticed that the adsorption capacity increased with the increase of temperature. The adsorption intensity constant 'n' values are ranged from 5.2 to 5.7 for all the studied temperatures, i.e., between 1 and 10, which indicate the favourable physical adsorption. In general Freundlich constant values infer a better performance of BAC-PA.

Temkin isotherm

The Temkin isotherm assumes that the heat of sorption in the layer would decrease linearly with coverage due to sorbate-sorbent interactions. Further the fall in the heat of adsorption is not logarithmic as stated in Freundlich expression (Xiao-Yi Huang *et al.*, 2011). The linear form of Temkin equation is.

$$\boldsymbol{q_e = \frac{RT}{b_T}\ In\ a_T + \frac{RT}{b_T} In\ C_e} \qquad (6)$$

Where, b_T is the Temkin constant related to the heat of sorption (J/mg) and a_T the equilibrium binding constant corresponding to the maximum binding energy (L/g). The Temkin constants a_T and b_T were calculated from the slopes and intercepts of q_e versus ln C_e. The results obtained from Temkin model for the removal of methylene blue are represented in Table 8. Concerned isotherm plots are shown in Figures 4 (a, b, c, d and e). The regression coefficient (R^2) values are ranged from 0.959 to 0.990 for the five studied temperatures viz. 303,313, 323, 333 and 343 K. These results show the best fitting of the equilibrium data with Temkin isotherm.

Equilibrium binding constant 'a_T' values (L/g) for adsorption of methylene blue are ranged from 1.1897 to 1.2425.The Temkin constant related to heat of sorption, b_T values (kJ/mg)for adsorption of methylene blue are ranged from 6.3579 to 7.1547. Low values of heat of adsorption, supports he physisorption mechanism. Both the binding constant 'a_T' values and heat of sorption, b_T values found to increase with the increase of temperatures.

Dubinin – Radushkevich isotherm

The linear form of Dubinin – Radushkevich (DR) isotherm equation is presented as (Igwe and Abia, 2007):

$$\text{In qe} = \text{In}\ q_D - 2B_D RT\ In\ (1 + \frac{1}{C_e}) \qquad (7)$$

A plot of ln q_e against RT ln $(1+\frac{1}{C_e})$ shown in Figures 5 (a, b, c, d and e) yielded straight lines and indicates a good fit of the isotherm to the experimental data. The apparent energy (E) of adsorption from DR isotherm model can be estimated using the equation given below.

$$E = \frac{1}{\sqrt{2B_D}} \qquad (8)$$

The DR isotherm constants and mean free energy were presented in Table 9. It was found that the DR isotherm model gives a satisfactory fit for the metal ions adsorption data irrespective of type of AC with high regression coefficients as shown in Table 9. The magnitude of the activation energy can be used to determine the type of adsorption process. Although it is not well supported to determine the rate controlling step from activation energy, the simplicity makes it easy to have a general insight into the undergoing process. If the value of E < 8 kJ/mol, the adsorption type can be explained by physisorption, and if E is in the range of 8 – 18 kJ/mol then the adsorption type is ion exchange (Basar, 2006). And also the process is classified as film-diffusion-controlled when E < 16 kJ/mol, particle-diffusion-controlled when E is 21 – 38 kJ/mol, and chemical-reaction-controlled when E > 50 kJ/mol (Maji et al., 2007). The low values of apparent energies obtained for all the ACs confirms that the adsorption of adsorbates on prepared ACs is physical adsorption (Boyd and Soldano 1953).
The regression coefficient (R^2) values are ranged from 0.731 to 0.894 for the five studied temperatures viz. 303, 313,323,333 and 343 K. These values reveal that fitting of equilibrium data with D-R isotherm are not as good as other isotherms studied earlier. The mono layer adsorption capacity q_D values (mg/g) for adsorption of methylene blue are ranged from 25.0136 and 26.0342 respectively. Further it is noticed that adsorption capacity increased with an increase in temperature. Values of the mean free energy E (kJ/mol) for the adsorption of methylene blue are ranged from 0.2357 and 0.4082. The very low values of E infer the physisorption interaction.

CONCLUSION

This investigation has shown that Blended activated carbon from agricultural based waste precursors could be a good precursor for preparation of a low cost activated carbon for removal of dye from wastewater. The maximum adsorption of methylene blue was observed at the initial solution pH 9. Equlibrium data were well fitted into Langmuir, Freundlich, Temkin isotherms having regression coefficient values (R^2) around 0.9. The regression coefficient values (R^2) for Dubinin – Radus-Kevich isotherm ranged from 0.731 to 0.894 only. 'R_L' values obtained from Langmuir isotherm and 'n' values obtained from Freundlich isotherm reveal the favourability adsorption of methylene blue onto BAC-PA. Equilibrium binding constant 'a_T' values and the heat of sorption, b_T values obtained from the Temkin isotherm supports the physisorption mechanism and endothermic nature of adsorption. The very low mean free energy values 'E' obtained from the Dubinin – Radushkevich isotherm infer the physisorption interaction. The adsorption capacities obtained from the isotherms show the feasibility of BAC-PA as an effective adsorbent for the removal of methylene blue from aqueous solution.

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