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Comparative study of low cost adsorbents prepared indigenously from locally available bio-waste for the removal of methylene blue dye

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The removal of Methylene blue (MB) dye from aqueous solutions using *Fagopyrum esculentum* Moench (Buckwheat) and *Bambusa vulgaris* (common bamboo) as adsorbents was investigated. Spectroscopic data of the different adsorbents under study indicates the presence of carbonyls, alcohols and ethers as the most abundant carbon-oxygen functional groups on the activated carbons. The effects of various experimental parameters such as effect of initial concentration, contact time and pH have been studied using batch adsorption technique. Adsorption data fitted well with all the three adsorption isotherm models. However, Freundlich isotherm displayed a better fitting model than the other two isotherms because of the higher correlation coefficient of R^2 (0.8799–0.9962) this indicates the applicability of multilayer coverage of the Methylene blue (MB) dye on the surface of adsorbent. The adsorption kinetics was studied using three simplified models and it was found to follow the pseudo-second-order kinetic model with a high correlation value of 0.9991–0.9999.

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1. Introduction

Dyeing industry effluents constitute one of the most problematic wastewaters to be treated due to their high chemical and biological oxygen demands, suspended solids, content in toxic compounds and also for colour, which are the first contaminant to be recognized by the human eye [1]. About 15% of the total world production of dyes is lost during the dyeing process and is released as liquid Effluents [2]. The treatment of dyes in industrial wastewater presents several problems since dyes usually have a synthetic origin and complex aromatic molecular structures which make them very stable and generally difficult to be biodegraded and

photodegraded [3,4]. Methylene blue is a thiazine (cationic) dye, which is most commonly used for coloring among all other dyes of its category. It is present in noticeable amount in industrial wastewater, which imparts blue colour. The dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. If swallowed, the dye causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. It may also cause methemoglobinemia, cyanosis, convulsions, tachycardia and dyspnea, if inhaled. It is likely to cause irritation to the skin [5]. Many treatment techniques have been applied to a broad range of water and wastewater contaminated with dyes including physical or chemical treatment processes [6]. These include chemical coagulation, flocculation [7, 8], ozonation,

oxidation, photodegradation [9], ion exchange, irradiation, precipitation [10]. However, these methods are not widely used due to their high cost which requires various tools and are generally not feasible on large scale industries. In contrast, an adsorption technique is by far the most versatile and widely used. The most common adsorbent materials are: alumina silica [11], metal hydroxides [12] and activated carbon [13]. It has been reported that the adsorption onto activated carbon, have proven to be the most efficient and reliable method for the removal many pollutants, including different dyes [7]. Although commercial activated carbon is very effective adsorbent, its high cost requires the search for alternatives and low cost adsorbents [14]. Several low cost adsorbents have been tested for removing dyes [15] including carbon from palm-tree cobs [16], plum kernels [17], cassava peel [18], bagasse [19], jute fiber [20], rice husks [21], olive stones [22], date pits [23], fruit stones and nutshells [24]. The advantage of using agricultural by-products as raw materials for manufacturing activated carbon is that these raw materials are renewable and potentially less expensive to manufacture. Plant biomass is a natural renewable resource that can be converted into useful materials and energy [25]. The present study is an attempt to use *Fagopyrum esculentum* Moench (FEMC) (common Buckwheat), and *Bambusa vulgaris* (common Bamboo), as non conventional low-cost adsorbent for removal of MB dye from aqueous solution. The capacity of adsorbent for adsorbate is obtained by adsorption isotherm model, which is the equilibrium relationship between adsorbent/adsorbate systems. In this study, three models (Langmuir, Freundlich and Temkin) [26, 27] have been used to describe the sorption process of methylene blue (MB) onto these adsorbents. To determine the rate-limiting step for the adsorption process, which governs the overall removal rate and mechanisms of sorption three simplified kinetic models namely pseudo first-order, pseudo second-order and intraparticle diffusion model was studied.

2. Materials and Methods

2.1. Reagents and Apparatus

All the chemicals used are of analytical reagent grade. A stock solution of methylene blue was prepared by dissolving 1gm of methylene blue (MB) in 1000 ml of double distilled water and subsequently diluted with deionised water to the required concentration. The resultant solution contains 1000 mg/ L of methylene blue (MB). This solution is said to be stock solution of methylene blue. The pH of the working solution was adjusted to the desired value with 0.1M HCl and 0.1M NaOH. All chemicals used were of analytical reagent grade.

The apparatus used are

- 1) UV-Visible Spectrophotometer (PerkinElmer, lamda-25)
- 2) Elico-pH Meter

2.2 Preparation, activation and surface characterization of different carbons

2.2.1 Preparation of activated carbon by indigenous method

For this study, the initial carbonization is done at bamboo mission Dimapur, Nagaland, India. In the bamboo mission, indigenous method of preparation of bamboo charcoal (taken from *Bamusa vulgaris*/BVC) is done for commercial purpose. In this process, the whole bamboo culms are cut into a uniform size of 1 m each so that it fits into the kiln and stacking is easier. The bamboo is placed through the door at the bottom and is stacked horizontally in the kiln. The door is then closed with bricks and plastered with mud on the outside for better insulation and to prevent leakage. The feed is fired through the opening at the top of the kiln and once the feed is ignited, the opening is closed. During the initial stages of firing, the openings in the wall of the kiln are kept open to create the required draft. Initially black smoke will be emitted from the opening at upper end after which it will change to dense white fumes. Once the black smoke changes, openings are closed one by one starting from the top to bottom. Carbonization is achieved by maintaining the temperature at 400-500°C by regulating the openings both in horizontal and vertical directions. All the openings are closed after 2 days so that air is not allowed to enter the kiln to prevent the charcoal from catching fire. Cooling is done for a day to reduce the temperature to 100°C. The biomass is removed from the opening at the bottom of the kiln and are washed, dried, and crushed and further subjected to chemical activation with 0.1N HNO₃ and 0.1N H₃PO₄. And for which the carbons were washed with double-distilled water to remove the excess acid and dried at 150°C for 12 hours. All the activated carbons are chemically activated with 0.1N solution HNO₃ and 0.1 N H₃PO₄.

The powdered activated carbon obtained after HNO₃ and H₃PO₄ treatment has a particle size in the range of 40-50 µm mesh. Another form of activated carbon in powder form are prepared by the pyrolysis of *Fagopyrum esculentum* Moench (FEMC) (common Buckwheat). The biomass were collected, washed, dried, and crushed before carbonizing in a Muffle furnace electrically heated at 600 °C for 4 hours. The activated carbon prepared was cooled to room temperature and washed with deionized water until the effluent was clear in colour. Finally the synthesized carbon was dried in oven at 110 °C for 12 hour. The synthesized carbon is chemically activated with 0.1N solution HNO₃ and H₃PO₄ respectively under similar conditions to modify the chemical structure. The surface modification of carbons was also done by subjecting to liquid phase oxidation.

2.2.2. Fourier transform infra-red spectroscopy (FT-IR)

FT-IR study was performed to understand the presence of different functional groups in the activated carbon [28-30]. The IR spectra were recorded using Perkin–Elmer SPECTRUM-2000 spectrometer. Carbon samples were dried in a drier, and then 2 mg of each sample was powdered and mixed with 300 mg of anhydrous KBr (Merck). The mixture was pressed under vacuum to obtain the pellets. The spectra were taken in the range between 4000 and 400 cm^{-1} (100 scans). The Background spectrum of air was subtracted from the spectra of the samples.

2.3 Adsorption Studies of methylene blue on activated carbons by Batch method

In order to understand the adsorption behavior of methylene blue (MB) dye, the effect of various experimental parameters has been investigated using batch adsorption experiments conducted at various pH values with different amounts of adsorbent. The effect of initial concentration is studied by varying methylene blue concentrations between 5- 45 mg/L. The effect of contact time was studied by varying the agitating time (range: 2-240 min) at fixed optimum initial concentration of methylene blue (20mg/L) with optimum dose of adsorbents (0.25 g/L) and also the effect of pH was studied ranging from 2-10. The percentage removal of the dye and the amount of dye adsorbed were calculated by the following equations.

$$\text{Percentage removal} = 100 \frac{(C_i - C_f)}{C_i}$$

$$\text{Amount adsorbed (q}_e\text{)} = \frac{(C_i - C_f)V}{M}$$

where C_i and C_f are the initial and final equilibrium solution concentrations of the dye (mg/ L), V is the volume of the solution (L) and M is the mass of the activated carbon (g). The data obtained have been analyzed for adsorption isotherms models.

3. Results and discussion

3.1 Surface characterization by (FTIR)

The FTIR spectra of all oxidized activated carbons are shown in Fig 1.1-1.4 and the observed characteristic band and their assignments are listed in table 1.1. The spectra for all the samples showed a broad band at around 3428-3100 cm^{-1} which is attributed to O-H/N-H stretching vibrations in hydrogen bonds. The bands observed at 2928-2428 cm^{-1} are due to alkane C-H stretching. This appears for all the carbon samples. The presence of methyl and methylene groups in all the samples is shown by the spectral appearance of C-H stretching absorption bands. Another band due to C-H deformation vibration is observed at 1428 cm^{-1} in one of the samples. A

peak centered at 2214, 2142 cm^{-1} may be attributed to $\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$ stretching [28, 29]. The band observed at 1828 and 1642 cm^{-1} are ascribed to the stretching vibrations of carboxyl groups present in lactone or conjugated carbonyl groups [30, 31]. The band absorption in the range 1142-1025 cm^{-1} can be assigned to C-O bonds, such as esters, phenols [32]. The band at wave number below 928 cm^{-1} may be related to out of the plane bending modes.

Table 1.1 FTIR spectrum band assignments

Wave number (cm^{-1})				Assignment
BVC (HNO_3)	BVC (H_3PO_4)	FEMC (HNO_3)	FEMC (H_3PO_4)	
3418	3420	3414	3385	O-H stretching in hydrogen bond.
2920,2820	2920,2816	2820,2607	2820,2450	Alkane (C-H Stretching)
2187	2185	2214	-----	$\text{C}\equiv\text{C}$ stretching
1687	1678	1816	----	C=O in carboxylic, aldehydes, ketones, esters and lactones
1510	--	----	----	C=C in aromatics or C=O stretch
1416	1447	1416	1419	C=O bonding in carbonyls
1125	----	1158	----	C-O stretch in phenols, ethers, lactones
1062	1068	1067	Alcoholic C-O stretch
875,780, 625	874,650	725,680,620	925,625	Plane deformation

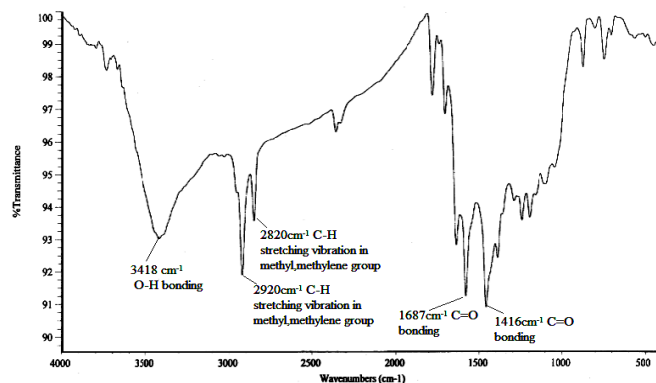


Fig 1.1: FTIR spectra for BVC (HNO_3)

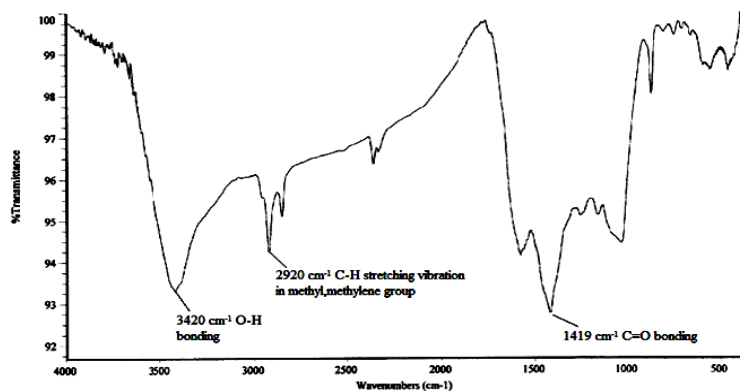


Fig 1.2: FTIR spectra for BVC (H_3PO_4)

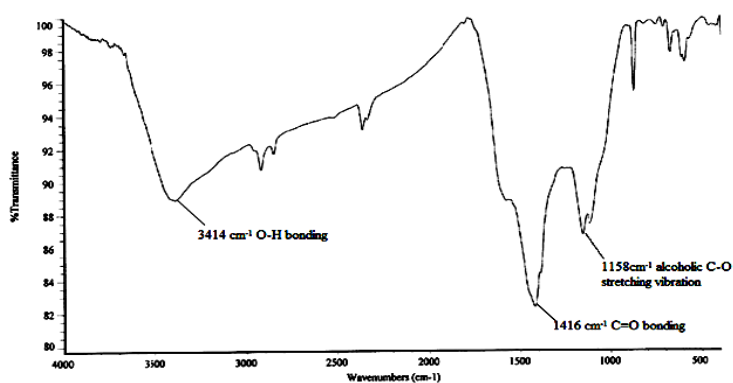


Fig 1.3: FTIR spectra for FEMC (HNO_3)

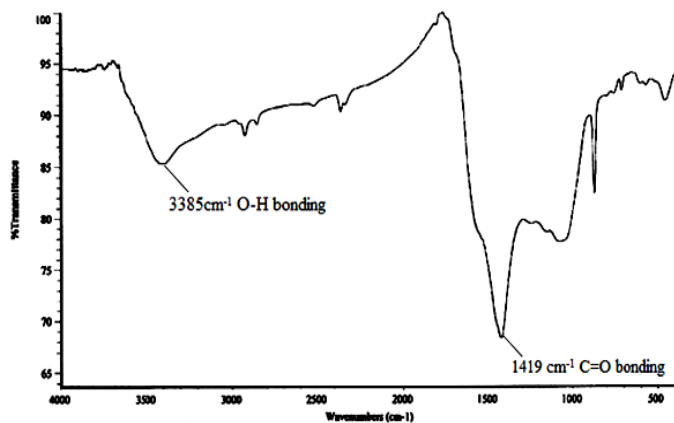


Fig 1.4: FTIR spectra for FEMC (H_3PO_4)

3.2 Effect of initial concentration

The effect of initial concentration on the adsorption of methylene blue (MB) was studied by varying the initial dye concentration between 5- 45 mg/L in 100 ml of methylene blue dye solution and adding 1 g of adsorbent and contact time of 120 mins. The effect of the initial dye concentration depends on the immediate relation between the dye concentration and the available binding sites on an adsorbent surface [33]. Fig.1.5. shows the effect of initial dye concentration with different adsorbents [BVC (HNO_3), BVC (H_3PO_4), FEMC (HNO_3) and FEMC (H_3PO_4)]. The relevant data shows that the amount adsorbed exponentially increases while the percentage removal exponentially decreases with the increase in initial concentration of the methylene blue. Generally the percentage of dye removal decreases with an increase in initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface [34]. At low concentration, there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will disappear [35]. However, the increase in the initial dye concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass at a high initial dye concentration [36]. In other words, the residual concentration of dye molecules will be higher for higher initial dye concentrations. The variation of percent removal of methylene blue with increasing Initial concentration is shown in Fig 1.5-1.6. The increase in the amount of methylene blue adsorbed with the initial concentration is shown in Fig 1.6.

3.3 Adsorption Isotherm

An adsorption isotherm gives the relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution [37]. Langmuir, Freundlich and Temkin adsorption isotherm models are

employed in this study to describe the experimental adsorption isotherm [38].

Langmuir adsorption is based on the fact that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir equation can be represented by:

$$\frac{C_e}{q_e} = \frac{1}{b} Q_{\max} + \frac{C_e}{Q_{\max}}$$

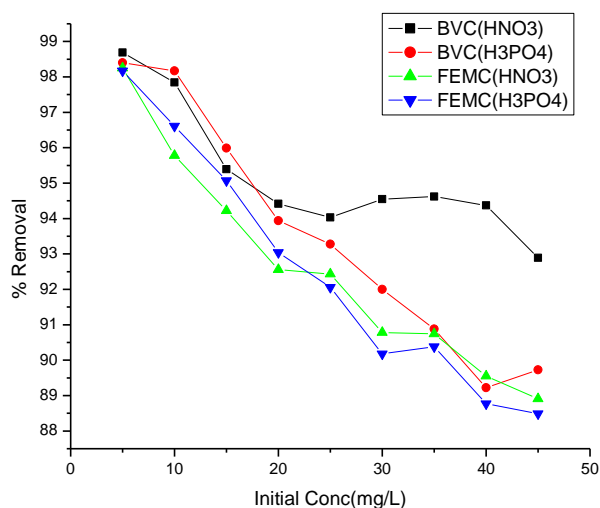


Fig 1.5: Variation of percent removal of MB dye with increasing Initial concentration

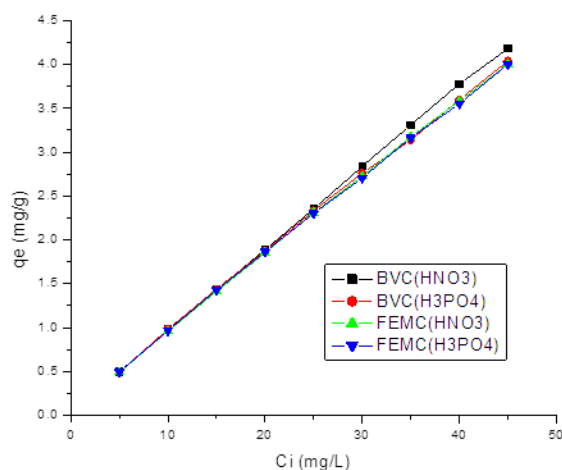


Fig 1.6: Variation of the amount of MB dye adsorbed with increasing initial concentration

Where q_e is the amount of methylene blue adsorbed (mg/ g) and C_e is the equilibrium concentration of methylene blue in the bulk solution (mg/ L) while Q_{\max} is the monolayer adsorption capacity (mg/ g) and b is the Langmuir constant related to energy adsorption capacity. The constants Q_{\max} and b can be calculated from slope and intercept of the plot C_e/q_e vs C_e [39]. Freundlich isotherm is an empirical equation describing the heterogeneous adsorption and assumes that different sites with several adsorption energies are involved [40]. The linear form of the Freundlich equation is shown below.

$$\log q_e = \log k + \frac{1}{n} \log C_e$$

The slope $1/n$ gives adsorption capacity and intercept $\log K$ gives adsorption intensity from straight portion of the linear plot obtained by plotting $\log q_e$ versus $\log C_e$. Temkin isotherm model predicts a uniform distribution of binding energies over the population of surface binding adsorption [41]. The Temkin isotherm is applied in the following form

$$q_e = \frac{RT}{b_T} \ln (A_T C_e)$$

The linear form of Temkin equation is

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e$$

$$q_e = \beta \ln \alpha + \beta \ln C_e$$

$$\text{Where, } \beta = \frac{RT}{b_T}; \alpha = A_T$$

T is the absolute temperature in Kelvin, R is the universal gas constant, 8.314 J/mol K , b_T is the Temkin constant related to 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 are calculated from the slopes and intercepts of q_e vs $\ln C_e$.

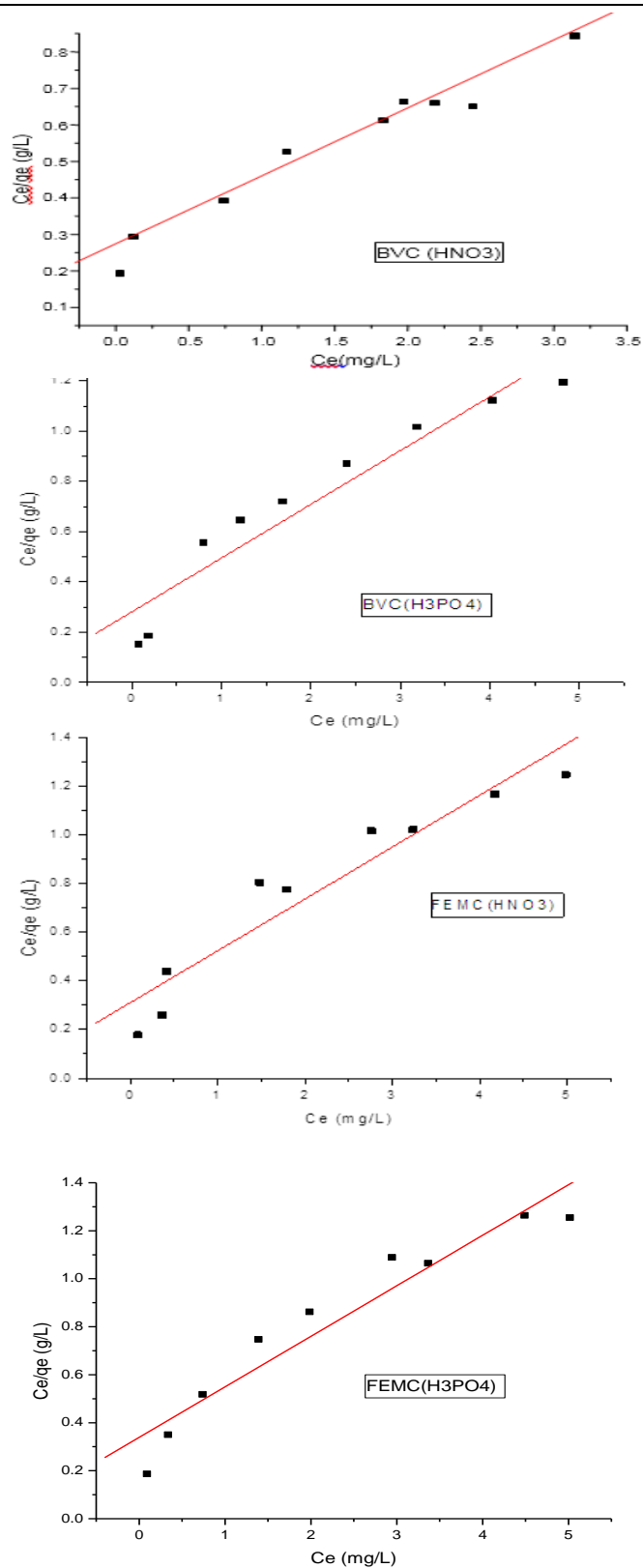


Fig 1.7: Langmuir adsorption isotherms for the removal MB dye by different adsorbents

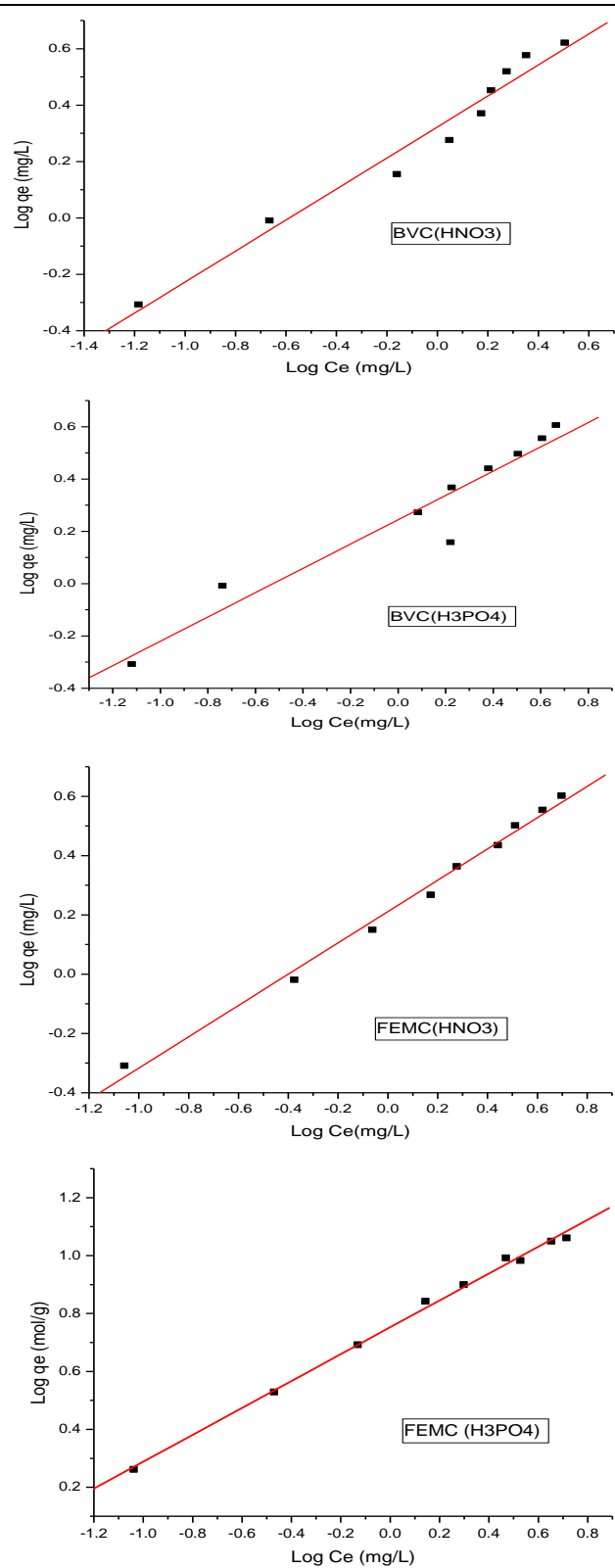


Fig 1.8: Freundlich adsorption isotherms for the removal of MB dye by different adsorbents

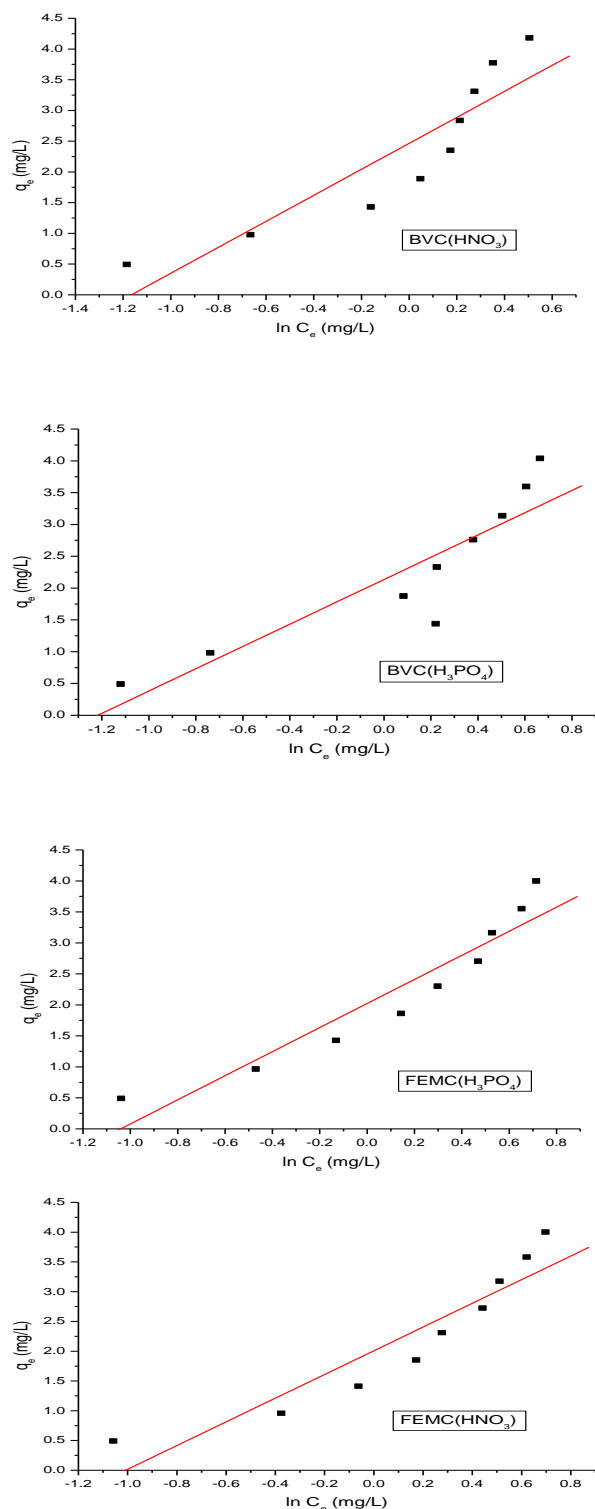


Fig 1.9: Temkin adsorption isotherms for the removal of MB dye by different adsorbents

3.3.1 Validity of Adsorption Isotherm models

Chi-square analysis

A chi-squared analysis, also referred to as χ^2 test, is any statistical hypothesis test in which the sampling distribution of the test statistic is a chi-squared distribution when the null hypothesis (when there is no relationship between two measured phenomena) is true [42].

The chi-square test is used to determine whether there is a significant difference between the expected frequencies and the observed frequencies in one or more categories. To identify the suitable isotherm for sorption of Methylene blue ions onto carbon adsorbents, the chi-square analysis was carried out. The mathematical statement for chi-square analysis is [43].

$$\chi^2 = \sum \frac{(q_e(\text{expt.}) - q_e(\text{cal.}))^2}{q_e(\text{expt.})}$$

Where $q_e(\text{expt.})$ and $q_e(\text{cal.})$ are the experimental sorption capacity of Methylene blue (MB) ions (mg/g) at equilibrium time and the corresponding value that is obtained from the sorption model. If data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ; χ^2 will be a bigger number [42]. On comparing the various adsorption isotherm models from Table 1.2 we can clearly see that χ^2 values for Freundlich isotherm seems to be the lowest, as $q_e(\text{cal.})$ values are almost similar to $q_e(\text{expt.})$. This is also in accordance with their corresponding R^2 values.

3.4 Effect of contact time

The effect of contact time on the removal of methylene blue (MB) dye was studied by varying the agitating time (range: 2-240 min) at fixed optimum initial concentration of methylene blue (20mg/L) with a dose of adsorbents (0.25 g/L). The contact time plot shows the removal of methylene blue is rapid in early stages but it gradually slows down until it reaches the

equilibrium. The initial rate of adsorption was greater because the diffusion of dye molecules through the solution to the surface adsorbents is effected by the dye concentration. Once equilibrium was attained, the percentage sorption did not change with further increases of time. The equilibrium was attained after shaking for 240 min. The decrease in the extent of removal of methylene blue after 240 min of contact time in some cases may be due to the desorption process[44]. The relation between contact time and percent removal of methylene blue (MB) dye is shown in the Fig 1.10.

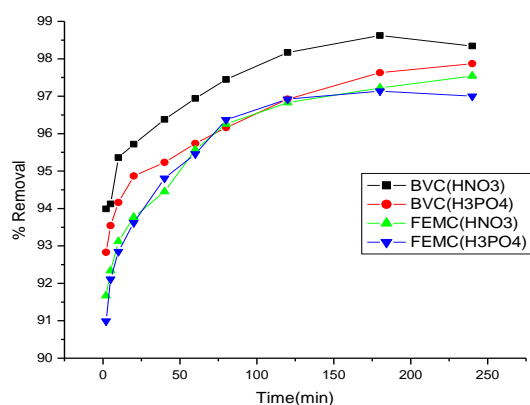


Fig 1.10: Effect of Contact time on percent removal of MB dye

Table 1.2 Comparison of Freundlich, Langmuir and Temkin adsorption isotherm models.

Freundlich Isotherm	R ²	LogK	1/n	q _{e(expt.)} (mg/g)	q _{e(cal)} (mg/g)	χ ²
BVC (HNO ₃)	0.9782	0.3517	0.5666	0.9784	0.9431	0.001273
BVC (H ₃ PO ₄)	0.9962	0.2456	0.4985	0.9717	0.9384	0.001141
FEMC(HNO ₃)	0.8799	0.1681	0.5323	0.9578	0.9296	0.000830
FEMC(H ₃ PO ₄)	0.9334	0.1471	0.5102	0.9561	0.9220	0.001216
Langmuir Isotherm	R ²	Q _{max}	b	q _{e(expt.)} (mg/g)	q _{e(cal)} (mg/g)	χ ²
BVC (HNO ₃)	0.9605	250.2	0.3388	0.9784	0.9459	0.001079
BVC (H ₃ PO ₄)	0.9591	248.75	0.3224	0.9717	0.9231	0.002430
FEMC(HNO ₃)	0.9397	215.7	0.2943	0.9578	0.9202	0.001476
FEMC(H ₃ PO ₄)	0.8592	198.5	0.2156	0.9561	0.9154	0.001732
Temkin Isotherm	R ²	B _T	A _T (L/g)	q _{e(expt.)} (mg/g)	q _{e(cal)} (mg/g)	χ ²
BVC (HNO ₃)	0.9075	0.3894	51.006	0.9784	0.9343	0.001987
BVC (H ₃ PO ₄)	0.8987	0.4610	25.754	0.9717	0.9156	0.003238

FEMC(HNO ₃)	0.9321	0.4369	19.003	0.9578	0.9087	0.002517
FEMC(H ₃ PO ₄)	0.9486	0.4633	16.224	0.9561	0.9096	0.002261

Table 1.3 Comparison of maximum biosorption capacity for the removal of MB on selected biosorbents.

Adsorbent	Q _{max} (mg.g ⁻¹)	References
BVC (HNO ₃)	250.2	This work
BVC (H ₃ PO ₄)	248.7	This work
FEMC(HNO ₃)	215.7	This work
FEMC(H ₃ PO ₄)	198.5	This work
Jackfruit peel:		
Oven dried	286	45
Microwave induced NaOH activation	400	46
Phosphoric acid activation	280	47
Jackfruit leaf powder	326	48
Pineapple stem	119	49
Coconut husk:		
Activated carbon	435	50
Microwave modified	418	51
Cedar sawdust	142	52
Peat	111	53
Oil palm fibre:		
Oven dried	223	54
KOH-CO ₂ activated carbon	204	55
Microwave activated	313	56
HCl activated	672	57
Spent tea leaves:		
Oven dried	147	58
NaOH modified	242	59
Tea waste	85.2	60
Bamboo charcoal:		
Thermal activation	26.5	61
Microwave	35.3	61
Base activated	454	38
Cotton stalk:		
Oven dried	147	62
Sulphuric acid treated	557	62
Phosphoric acid treated	222	62
Leaves of Solanum tuberosum	52.6	63
Stem of Solanum tuberosum	41.6	63
Activated banana peel	19.7	64
Pomelo skin:		
Oven dried	345	65
Activated	501	66

3.5 Effect of pH

The pH of a medium controls the magnitude of electrostatic charges which are imparted by the ionized dye molecules. As a result, the rate of adsorption will vary with the pH of an aqueous medium [67]. The effects of initial pH on dye solution were investigated by varying the pH from 2 to 10 and using initial dye concentration of 20 mg/L with contact time of 120 mins. At pH 2 the removal was minimum but it increased along with increasing initial pH of dye solution. The result in Fig. 1.11 shows that, the maximum adsorption was observed at pH 9 for BVC (HNO_3) and BVC (H_3PO_4). At pH 9 the dye removal percentage was 98.43% and 98.24% respectively. The maximum adsorption was observed for FEMC (HNO_3) when pH rises up to 10. However in case of FEMC (H_3PO_4) the adsorption capacity decreased when the pH was increased from 8. This can be attributed due to the negative charge on the surface that is very much reduced due to the excess protons in solution when compared to other adsorbents. The methylene blue (MB) adsorption usually increases as the pH is increased.

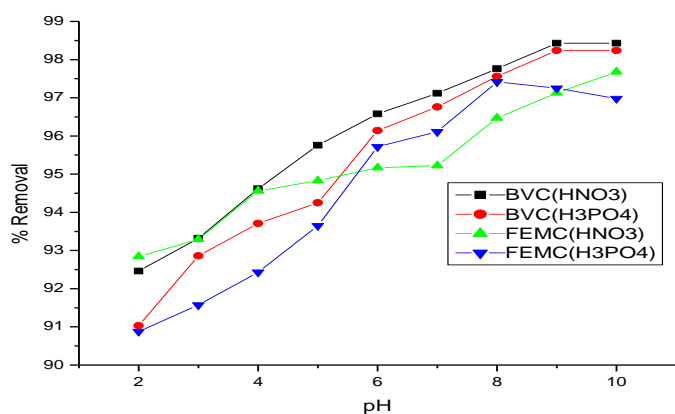


Fig 1.11: Effect of pH on percent removal of MB dye

Lower adsorption of MB at acidic pH is probably due to the presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites. At higher pH, the surface of activated carbon particles may get negatively charged, which enhances the adsorption of positively charged dye cations

through electrostatic forces of attraction [68,69]. Such observations were also reported by B.H. Hameed and S. Cengiz [70,71].

3.6 Study of adsorption kinetics

Kinetics is another important aspect in any evaluation of sorption as a unit operation [72]. One of the most important factors in designing an adsorption system is predicting the rate at which adsorption takes place, referred to the 'kinetics of sorption'. In adsorption processes, the selection of an adsorbent, its configuration, and attainment of equilibrium are related to the 'rate-limiting' process [73,74]. Thus, to estimate the time necessary to reach the sorption kinetic studies of Methylene blue (MB) dye, three simplified kinetic models namely pseudo first-order, pseudo second-order and intraparticle diffusion model have been discussed to identify the rate and kinetics of adsorption process.

1) Pseudo first-order model

Pseudo-first-order was suggested by Lagergren [75] for the adsorption of solid and liquid systems. The adsorption of MB dye from the solution to adsorbent can be considered as a reversible process with equilibrium being established between the liquid and solid phases. The linear form of Pseudo-first-order kinetic model [75] can be described as follows:

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \frac{k_1}{2.303} t$$

Where q_e and q_t (mg/ g) are the adsorption capacities of MB ions at equilibrium and at time t (min), respectively, and k_1 is the rate constant of pseudo first-order kinetics. The correlation coefficient (R^2) and pseudo-first order constant (k_1) for adsorbents are summarized in Table 1.4 the values of R^2 vary between 0.9744 - 0.9855. It was observed that the experimental q_e values did not agree with the calculated values.

2) Pseudo-second order model

Pseudo-second-order is based on the assumption that the adsorption rate is determined by the square of the number of vacant adsorption sites on the surface of adsorbent [76]. The mathematical expression of Pseudo-second-order kinetic model [76] is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where k_2 is the rate constant for pseudo second-order adsorption ($\text{g} / \text{mg} \cdot \text{1/min}$) and $k_2 q_e^2$ ($\text{mg} \cdot \text{g} / \text{1/min}$) is the initial adsorption rate. The linear plot of t/q_t versus t , yielded R^2 values that were greater than 0.999 for all adsorbents. It also showed a good agreement between the experimental and the calculated q_e values (Table 1.4).

Possible mechanism of adsorption

The mechanism for the removal of MB dye by adsorption may be assumed to involve the following four steps [77]:

- Migration of dye from bulk of the solution to the surface of the adsorbent.
- Diffusion of dye through the boundary layer to the surface of the adsorbent.
- Adsorption of dye at an active site on the surface of adsorbent.
- Sorption and desorption that take place within the particle and on the external surface.

Here the first and fourth steps do not belong to the rate controlling steps because in the first step there is no involvement of adsorbent and the fourth step is a very rapid process. Therefore, surface or pore-diffusion may be the rate controlling steps [78]. Weber and Morris' model is widely used to predict the rate controlling step [79]. They theorized that the rate of intraparticle diffusion varies proportionally with the half power of time and is expressed as

$$q_t = K_{id} (t^{1/2}) + C$$

where,

q_t = adsorbate uptake at time t (mg/g).

K_{id} = the rate constant of intra-particle transport ($\text{mg/g} \cdot \text{1/t}^{1/2}$)

From table 1.4, intraparticle diffusion can be evaluated with the help from the slope of the linear plot of q_t versus $t^{1/2}$. The values of intercept, C are related to the boundary layer thickness, i.e., the larger the value of the intercept, the greater is the boundary layer effect [80,81]. Fig 1.12 shows the multi-linearity in intra-particle diffusion plots for MB dye adsorption with different adsorbents. This indicates that intra-particle diffusion was not the only involved for MB dye adsorption, but there were some other processes involve in the rate controlling step. This suggests that adsorption occurred in three phases the initial steeper section represents surface or film diffusion, the second linear section represents a gradual adsorption stage where intra-particle diffusion is rate-limiting and the third section is final equilibrium stage. Thus, there were three processes controlling the adsorption rate.

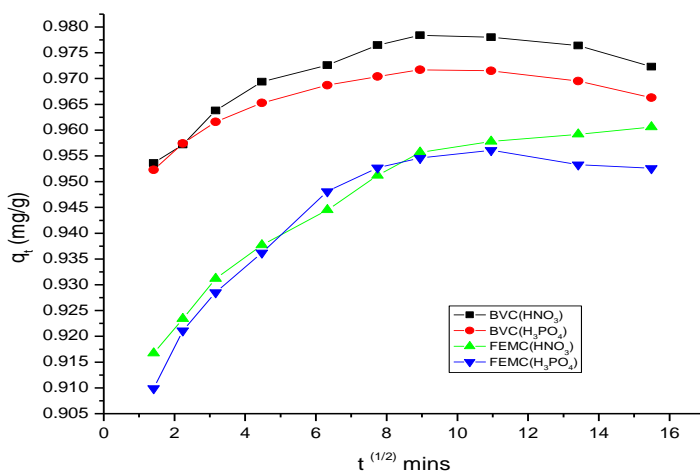


Fig 1.12 Intraparticle diffusion plots for the removal of MB dye on adsorbents

Table 1.4 Comparison of various kinetic models MB adsorbed by prepared adsorbents.

Kinetic models	Parameters	BVC (HNO ₃)	BVC (H ₃ PO ₄)	FEMC (HNO ₃)	FEMC (H ₃ PO ₄)
Pseudo-first-order	q _e (calculated) (mg/g)	0.0191	0.0217	0.0413	0.0479
	k ₁ (1/min)	0.0377	0.0561	0.0262	0.0396
	R ²	0.9855	0.9778	0.9744	0.9828
	q _e (experimental) (mg/g)	0.9940	0.9906	0.9823	0.9753
Pseudo-second-order	q _e (calculated) (mg/g)	0.9773	0.9712	0.9564	0.9560
	k ₂ (1/min)	0.0882	0.0998	0.2345	0.2776
	R ²	0.9999	0.9996	0.9991	0.9993
	q _e (experimental) (mg/g)	0.9940	0.9906	0.9823	0.9753
Intraparticle diffusion model	k _{id} (mg/g-1/min ^{1/2})	0.0012	0.0009	0.0029	0.0026
	C	0.9740	0.9794	0.9426	0.9386
	R ²	0.6913	0.6411	0.8472	0.7873
	q _e (experimental) (mg/g)	0.9940	0.9906	0.9823	0.9753

4. Conclusions

Spectroscopic data of the different adsorbents under study indicates the presence of carbonyls, alcohols and ethers as the most abundant carbon-oxygen functional groups on the activated carbons. A sharp peak at 1687 and 1678 cm⁻¹ for BVC (HNO₃) and BVC (H₃PO₄) was observed this corresponds to carbonyl functional group, thus indicating oxygen functional group on the surface of the adsorbents which enhances the adsorption property of Bamboo activated carbons. Adsorption studies of MB dye on activated carbons was studied where effect of initial concentration, effect of contact time and effect of pH were the parameters considered to determine the adsorption efficiency of the activated carbon samples. The results of the percentage removal of methylene blue dye increased with the increase of contact time and pH. On the contrary, the percentage of removal has decreased with the increase in initial concentration of the standard MB dye solution. The basic medium highly influences the maximum removal of methylene blue which may due to the preference of the dye cations for basic sites. The equilibrium data have been analyzed using Langmuir, Freundlich and Temkin isotherms. The adsorption data obeyed all the three isotherms up to some extent. However out of three isotherm models studied for this adsorbent-adsorbate system, Freundlich isotherm with high R² (0.8799–0.9962) was the most suitable equation to describe

the adsorption indicating a multilayer adsorption with heterogeneous distribution of active sites on the adsorbent.

Three adsorption kinetic models were studied, the pseudo second-order kinetic model accurately described the adsorption kinetics. The results show intra-particle diffusion was not the only rate limiting factor in adsorption of MB dye but there were three processes controlling the adsorption rate.

The adsorption mechanism was found to be chemisorption and the rate-limiting step was mainly surface adsorption. Thus these activated carbons can be effectively used for the removal of MB dye. Among the four low-cost adsorbents under consideration, the order of adsorption capacity of the various adsorbents is as follows: BVC (HNO₃) > BVC (H₃PO₄) > FEMC (HNO₃) > FEMC (H₃PO₄). This indicates the chemical activation by HNO₃ is more effective than H₃PO₄ activation for a given biowaste material. Among the adsorbents which were indigenously prepared BVC (HNO₃) possesses the highest or the maximum adsorption capacity. Hence it is the best and the most effective adsorbent in the removal of MB dye content in water. The suggested adsorbent materials are very cheap and are abundantly available. Because of their economic viability, these low cost adsorbents can be used in the process of eliminating the undesirable and unwanted ingredients in water.

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