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Removal of Methylene Blue from Aqueous Solution Using *Artocarpus Integer* Agrowaste: Equilibrium, Kinetic and Thermodynamic Studies

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ABSTRACT

Presence of synthetic dyes in the industrial wastewater discharge is a serious threat for the environment. Present study was aimed to investigate the sorption of methylene blue (MB), from various aqueous solutions using Artocarpus integer peels (an agricultural waste). The study involved determination of effect of pH, contact time, concentration of adsorbate, amount of adsorbent, size of adsorbent, and temperature over sorption of methylene blue. Equilibrium data were fitted to the Langmuir, Freundlich and Temkin-Pyzhev isotherm models. The kinetic measurements were used to calculate specific rate constants of the processes and for all cases a pseudo second order adsorption kinetics was obtained. Various thermodynamic parameters such as standard enthalpy (H°), standard entropy (S°) and standard free energy (G°) were also evaluated.The AIP was subjected to modification by means of various known methods such as peroxide treatment,stearic acid treatment, mercerization, sulphuric acid treatment, acetylation, and formaldehyde treatment, and the adsorption capacity (q_e) of each modified AIP for MB was obtained. The present work shows that A. integer peel is an efficient sorbent for the removal of MB from aqueous solution and it may be an alternative to more costly adsorbents such as activated carbon.

Key words: *A. integer* peel, methylene blue, adsorption isotherm, equilibrium

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INTRODUCTION

Recent years witnessed the industrial wastewater discharge to possess synthetic dyes, such as: azo reactive dyes [1]. The dyes are generally discharged into wastewater from cosmetics, leather, textile, food processing, paper and dye manufacturing industries [2].As dye pollute the rivers, so declared as harmful for human and other living organisms [3]. The dyes are difficult to remove from wastewater due to their high stability against oxidizing agents, heat and light. Removal of dyes demands several chemical, biological, and physical treatment processes, such as: photo-oxidation, coagulation, ultra-filtration, and electro-chemical adsorption [4]. Butmajority of such technologies are expensive, when applied to treat large waste streams. The proven efficiency of adsorption techniques to remove organic and mineral pollutants and cost effectiveness support to their potential application in industrial wastewater treatment [5,6]. The high absorbent capacity, specific surface area and removal efficiency are the three important characteristics of activated carbon. Attributed to these properties, the activated carbon is claimed as wide used adsorbent for treatment of wastewater to removepollutants (organic and inorganic)[7]. Nevertheless, the high cost of activated carbon limits its application as an absorbent. The agrowastes such as: coir pith [8], sugarcane bagasse [9], banana peel [10], peanut hull [11], rice bran and wheat bran [12], rice husk [13], tea waste [14], waste apricot [15], rubber seed coat [16], pumpkin seed hull and garlic peel [16] coconut shell [17], apple pomace and wheat straw [5], halzelnut shell [18], plum kernel [19], corncob and barley husk [5], banana trunk fibers [20], bamboo [21], and grass wastes [22] are reported for their aaplication in the removal of dyes. *Artocarpus integer (A. integer)*,a tropical fruit that belong to *Moraceae* family is commonly called as cempedak. *A. integer* is reported to possess flavonoids, arylbenzofuransphenolic compounds, and stilbenoids[23]. Only one-third of *A. integer* is edible whereas the seeds and the rinds are generally thrown away and often considered as a waste. In the view of literary evidences, present study was aimed to establish the agricultural waste as low-cost biomaterialto remove of methylene blue from various aqueous solutions.

MATERIAL AND METHODS

Adsorbate

Methylene blue (MB) was procured from Fisher Scientific. The molecular formula of MB is $C_{16}H_{18}ClN_3S.2H_2O$ with formula weight 355.89 g/mol. The maximum wavelength of this MB dye was 610 nm. The structure of MB is shown in Figure 1. Preparation of stock solutions was done by dissolving accurately weighed dye samples into double distilled water to achieve a final concentration of 500 mg/L. Lastly, the mixture was diluted with double distilled water when necessary. To prevent exposure to direct light, the stock solution was covered with foil.

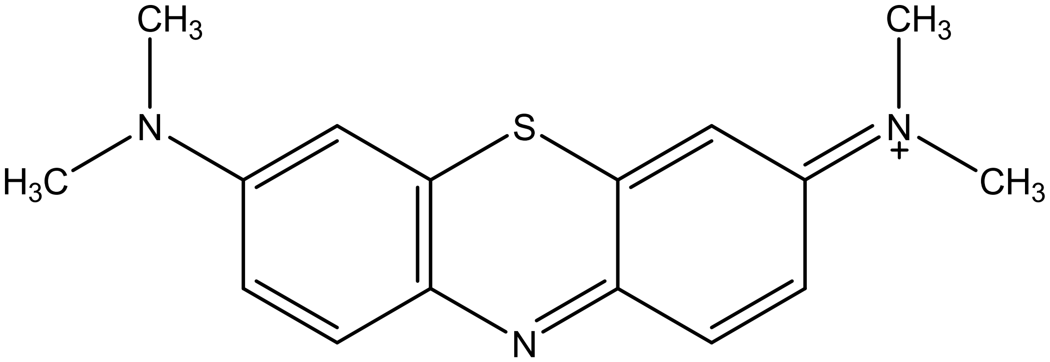

Figure 1: Chemical structure of methylene blue

Sorbent

A. integer peels were obtained locally. The peels were chopped into 2 x 2 cm of average piece size. The peels were boiled for 1 h in distilled water, and further drying was done in oven at 70 °C for constant weight. The resultant material was grounded using a Waring Commercials high speed blender and sieved to the size 212 -350 microns.

Equilibrium studies

In equilibrium studies, fixed amount of sorbent (0.2 g) was added to 250 mL Erlenmeyer flasks comprising 100 mL dye solution. The different initial concentrations (50–500 mg/L) of dye solution were taken. The solution mixtures were maintained at pH 7. Flasks of solution mixtures were agitated on isothermal water-bath shaker. The shaker was maintained with 150 rpm speed at 25 °C for 2 h, until equilibrium. From solutions, the aqueous samples were taken for concentrations analysis. Concentrations of dye were measured by UV/Vis spectrophotometer at 610 nm, at time $t = 0$ and equilibrium. Amount of equilibrium adsorption, qe (mg/g), was determined using following expression:

$$q_e = (C_o - C_e)\frac{V}{W} \qquad \text{...(1)}$$

Where, W is the mass of dry sorbent (g); C_o and C_e (mg/L) are concentrations of dye (in liquid-phase) at initial and equilibrium; and V is volume of solution (L).

Spectroscopic study

To ascertain the characteristic functional groups in fibers, the samples were subjected to Fourier transform infrared (FTIR) spectrometry. The potassium bromide (KBr) was mixed with powdered fibers sample (5 mg), and subjected to 6 bars pressure for 2 min to producea thin disc. Disc was kept in sample cup of diffuse reflectance accessory for IR spectrum recording by Perkin Elmer 2000 infrared spectrometer in a scanning range from 4000 cm^{-1}-400 cm^{-1}.

Treatments of *A. integer* Peel(AIP)

The AIP samples were modified as per the methods described in literature:

i. Mercerization (AIP1): In this method, 5% NaOH solution was used and the fibres were placed in the solution for 48 h at 25 ˚C [24].
ii. Acetylation (AIP2): This method involves soaking of mercerized fibers in glacial acetic acid for 1 h. Followed by decantation, and soaking of fibers for 2 minutes in acetic anhydride solution containing 2 drops of concentrated H_2SO_4 [25].
iii. Peroxide treatment (AIP3): This method involves immersion of mercerized fibers (30 g) into 1 L of a 6 % solution of benzoyl peroxide in acetone for 30 minutes [26].

iv. Stearic acid treatment (AIP4): This method involves refluxing of mixture of fibers (1 g), stearic acid (0.2 g), and solution of 100 mL of n-hexane containing 2 drops of concentrated H_2SO_4using Dean–Stark apparatus maintained at 65 °C for 6 h [26].

v. Sulphuric acid treatment (AIP5): In this method, mixture of fibres and concentrated H_2SO_4 in a ratio of 1:1was heated in muffle furnace maintained at 150 °C for 24 h [26].

In order to get a pH close to neutral, all resultant fibres were washed ample amount.

RESULTS AND DISCUSSION

Effect of pH

In adsorption process, dye solution pH performs an important role [27]. For MB toachieve optimum pH, various adsorption experiments were commenced in pH range from 2-8. The results depicted in Figure 2, indicated that dye adsorption was unfavorable at pH<4 and remained nearly constant over initial pH ranges 4-8. Hence, pH 7 was chosen for all subsequent studies. There may be two reasons for decrease in the adsorption at lower pH. Firstly,low pH caused decrease in number of negative charge adsorbent sites and increase in number of positive charge surface sites of system. Thiswould have assisted inmaking adsorption of positive chargedye cations unfavorable (as a result of electrostatic repulsion) [8]. Secondly, the surface charge became positive to make H^+ ions compete with dye cations resulting in the decrease in amount of dye adsorption. Similar behavior was observed for MB adsorption over other adsorbents also [28,29,30]

Contact time study

The MB adsorption over*A. integer* dust was investigated as function of contact time to determine the equilibrium time for maximum adsorption. The influences of contact time on MB adsorption by *A. integer* dust are illustrated in Figure 3. The rate of MB adsorption was very rapid at the initial stage of sorption, caused by the fast diffusion and sorption of dye cation onto the external surface of sorbent. Later, the rate of MB adsorption declined gradually and reached to equilibrium within 100 minutes. This process was controlled by the pore diffusion velocity of dye cation into the intraparticle matrix of sorbent [31,32]. An equilibrium adsorption time of 135, 210 and 150 min was reported for the adsorption of MB onto wheat shells, banana trunk fibers and jute fibers [25].

Concentration dependent study

The amount of adsorption at equilibrium of MB on *A. integer* dust at various initial concentrations (50-500 mg/L) of MB results are shown in Figure 4. It is evident from Figure 4 that, uptake of dye was increased from 21.8 - 210.1 mg/g with increase in the initial dye concentration from 50-500 mg/L. Initial dye concentration supported in overcoming the resistance to mass transfer of MB between solid and aqueous phase [33].High initial MB concentration resulted in enhancement of adsorption process based on enhancement of number of collisions between MB molecules and *A. integer* dust. Similar phenomenon was witnessed for adsorption of dyes onto tea waste [33], pomelo peel [34], and castor seed shell [35].

Optimization of amount of adsorbent

Figure 5 exhibits influence of *A. integer* dust dosage variation (from 0.1-1.0 g) over percentage of MB adsorption. Results suggested that increment in adsorbent dosage reduced the adsorption capacity. A decrease in adsorbed amount at equilibrium with increase in dosage is attributed to increase in availability of sorptive surface area and more adsorption sites [36,37].

Study of size of the adsorbent

The effect of size of adsorbent on the dye adsorption percentage is shown in Figure 6. The graph indicates that the adsorption capacity was decreased from 43.77-39.68 as the size of the *A. integer* dust was increased from 63-500 μm. The decreasing trend of adsorption percentage with increase in size of adsorbent was due to decrease in adsorbent sites and surface area of MB uptakes which consequently lead to a lower adsorption.

Temperature study

There was a slight increase in the amount of MB adsorption from 42.5-44.3 mg/g as the temperature was increased from ambient temperature (25-27 ºC) to 60 ºC. It can be established that temperature variation from 25-27 ºC to 60 ºC temperature did not affected much of the adsorption capacity of the adsorbent.

Adsorption Isotherms

Langmuir adsorption isotherm model states that adsorbate is not transmigrated in the plane of surface and there is an occurrence of uniform energies of adsorption over surface [38]. The Langmuir isotherm is expressed in equation (2).

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} + C_e \qquad \ldots(2)$$

Where, C_e is adsorbate equilibrium concentration (mg/L); q_e is adsorbate amount adsorbed per unit adsorbent mass (mg/g); Q_o and b are Langmuir constants related to adsorption capacity and adsorption rate.

Plot of C_e/q_e values against C_e values, offered a straight line bearing slope of $1/Q_o$. From the Langmuir plot at the concentration (50 to 500 mg/L) (Figure 7) the value of Q_o was obtained and then the value for b was calculated and presented in Table 1.

Langmuir isotherm may be expressed as R_L, the constant separation factor with no dimension, as given in equation (3).

$$R_L = \frac{1}{1 + bC_o} \quad \text{...(3)}$$

The $R_L$values of 0.323indicated that the isotherm was favorable at the studied concentrations.

The Freundlich isothermmodel [39],considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption and can be represented by equation (4).

$$ln\ q_e = ln\ K_f + \frac{1}{n}(ln\ C_e) \quad \text{...(4)}$$

Where,C_e is adsorbate equilibrium concentration (mg/L); q_e is the adsorbate amount adsorbed per unit adsorbent mass (mg/g); K_f and n are Freundlich constants. The log q_e versus log $C_e$slopes and intercepts (Figure 8) determined the Freundlich constants (Table 1). $K_f$is adsorption capacity (that represents quantity of anionic dye ions adsorbed onto fibers for a unit equilibrium concentration) and value of $n >$ 1(that indicates adsorption process favorability [25]. Present study reports K_f value as 4.26. Adsorbent possess finite number of sites. Once all sites are occupied by adsorbed molecules then further adsorption is stopped. Considering the effect of indirect adsorbate/adsorbate interactions over adsorption isotherms, Temkin-Pyzhev [40] suggested that all molecules heat of adsorption in layer decreases in linearity with coverage. Temkin isotherm is expressed as equation (5).

$$q_e = \frac{RT}{b} ln\ A + \frac{RT}{b} ln\ C_e \quad \text{...(5)}$$

Wherein B = $\frac{RT}{b}$

A plot of qe versus lnCe (Figure 9) enabled the determination of the constants A and B. The constant B was related to the heat of adsorption. The constant A and B along withR^2 values for the MB study are given in Table 1. As evident from the Table 1, a high regression correlation coefficient, R^2, is shown by the Freundlich model. This indicated that Freundlich model was suitable to explain the sorption equilibrium of the dye by modified AIP. When the linearity of the plots of the Langmuir, Freundlich and Temkin-Pyzhev T models was compared, it was found that the Freundlich model has a better fit. Hence, it is reasonable to establish that adsorption of colored substance on the fibers which contains heterogeneous adsorption sites that are similar to each other in relation to adsorption phenomenon. The study was supported by other research also [41].

Adsorption Kinetics

To examine the adsorption process mechanism, present study involved two simple kinetic models. The kinetics of adsorption was analyzed by the Langergren pseudo-first-order equation [40] as depicted in equation (6):

$$log\ (q_e - q_t) = log\ q_e - \frac{k_1 t}{2.303} \quad \text{...(6)}$$

Where, q_e and $q_t$are the amounts of metals adsorbed (mg/g) at equilibrium at time t (min) respectively; and k_1 (min^{-1}) is the rate constant adsorption. Values of k_1 at ambient temperature were calculated from the plots of log (q_e −q_t) versus t for an initial concentration of 5, 10 and 20 mg/L for the metals. The set of R^2 values obtained were poor. The experimental q_e values were not in agreement with calculated values determined from linear plots (Table 2). Model for pseudo-second-order was founded on equilibrium adsorption [41] is expressed in equation (7):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad \text{...(7)}$$

Where k_2 (g/mg min) is the rate constant of second-order adsorption. Linear plot fort/q_tversus t at ambient temperature yielded set of R^2 value that was greater than 0.990. This showed an agreement between experimental and calculated q_e value (Table 2).This indicates applicability of this model to describe the adsorption process of dye onto the fibers. The experimental data was also supported by other standard research [42].

Thermodynamics studies

The thermodynamic concept assumed that in isolated system the entropy change was the driving force, with no energy loss or gain [17]. The thermodynamic parameters considered to determine the processes were: change in enthalpy (ΔH°) which represents the enthalpic part of the driving force of growth, standard entropy (ΔS°) which represents the real driving force for the process, and standard free energy (ΔG°) which is the energy content of a system. The values of ΔH° and ΔS° were computed in Excel program using equation (8).

$$ln\ K_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad ...(8)$$

Where, T is the absolute solution temperature; R is universal gas constant (8.314 kJ mol^{-1}); and K_d is distribution coefficient which can be calculated using equation (9).

$$K_d = \frac{C_{Ae}}{C_e} \qquad ...(9)$$

Where C_{Ae}(mg/L) is the amount adsorbed on solid at equilibrium and C_e (mg/L) is the equilibrium concentration. The values of ΔH° and ΔS° were calculated from the slope and intercept of plot between lnK_d versus 1/T. ΔG° can be calculated using the equation (10). $\Delta G^o = -RT\ ln\ K_d$ ...(10)

The calculated values of ΔH°, ΔS° and ΔG° are listed in Table 4. The positive value of ΔH° indicates the endothermic the nature of the adsorption interaction. The maximum heterogeneous adsorption capacity (K_f) of MB onto AIP increased from 4.26 to 14.62 mg/g (1/mg)$^{1/n}$ with increase in solution temperature from 25 to 60 °C. The increase in randomness at solid-solution interface during adsorption process was confirmed by positive values of ΔS°. The ΔG° negative value is a clear indication of spontaneous nature and feasibility of adsorption process of MB onto AIP. The obtained data was in agreement with the conclusions of Deniz [42], Manju et al. [43] and Tseng [44].

Spectroscopic Study

The aim of using FTIR analysis in present study was to determine the existence of functional groups that are present on the fibers. The IR spectrum for *A. integer* peel fibers as KBr pallet is given in Figure 10. The absorption at 3338 cm^{-1}isrelated to stretching of hydroxyl groups of cellulose, hemicellulose and lignin that are present in the *A. integer* dust fibers. The medium band at 2918 cm^{-1} is related to the C-H stretching of saturated (sp3) carbon. The weak bands at 1734 and 1717 cm^{-1} correspond to the absorption of carbonyl group of carboxylic acids [40] of the hemicellulose which is a minor component of the fibers. The band at 1634 cm^{-1} corresponds to absorbed water the bending mode as fibers containing hemicellulose possess strong affinity with water [45]. Band at 1618 cm^{-1}is ascribed to C=C skeletal stretch of lignin aromatic ring contained in fibers [46]. The weak bands at 1423, 1375 and 1249 cm^{-1} are assigned to C-H bending, C-O stretching and O-H bending, respectively [45]. The bands at 1320 and 1158 cm^{-1} are ascribed to O-H bending and C-O skeletal vibrations, respectively. The bands at 1104 and 1036 cm^{-1} are assigned to C-O-H and C-O-C stretching, respectively. It is also worthwhile to note that the prominent bands at 2362 and 2324 cm^{-1} are attributed to the asymmetric and symmetric stretching of CO_2 [47].

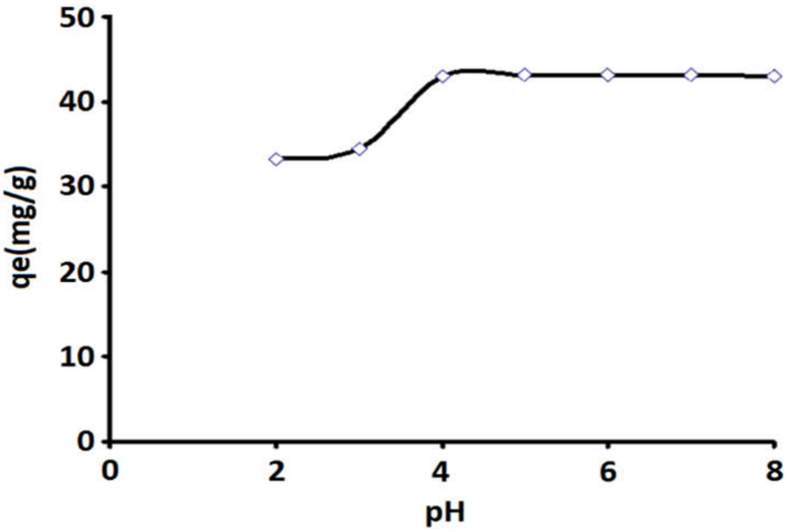

Figure 2: Effect of pH on the adsorption of MB on grounded *A. integer* peel (C_o = 100 mg/L, temperature = 25-27ºC, stirring rate = 150 rpm, contact time = 120 min, and weight of A. integer peel = 0.2 g)

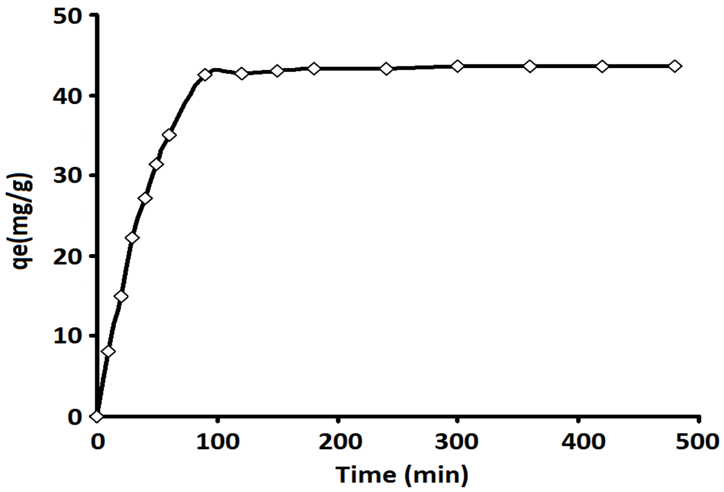

Figure 3: Effect of contact time on the adsorption of MB on grounded *A. integer* peel (C_0 = 100 mg/L, temperature = 25-27ºC, stirring rate = 150 rpm, weight of A. integer peel = 0.2 g and pH = 7)

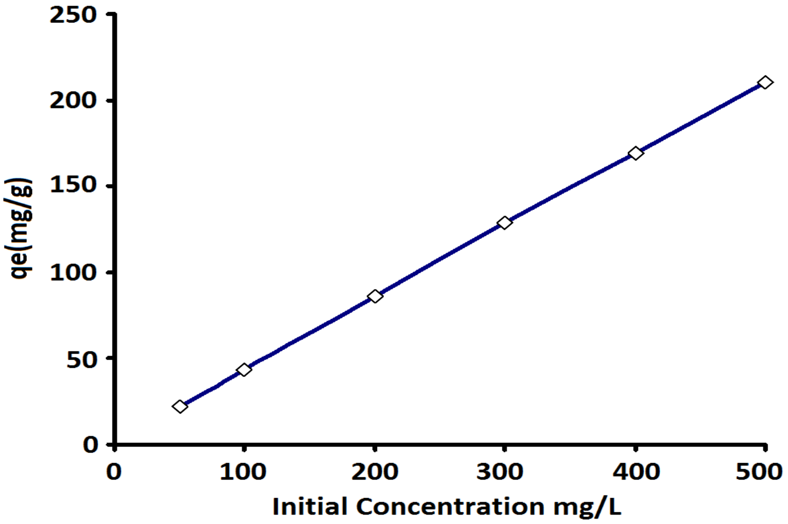

Figure 4: Effect of initial concentration of MB on the adsorption of MB on grounded *A. integer* peel (Temperature = 25-27ºC, stirring rate = 150 rpm, contact time = 180 min, weight of A. integer peel = 0.2 g and pH = 7)

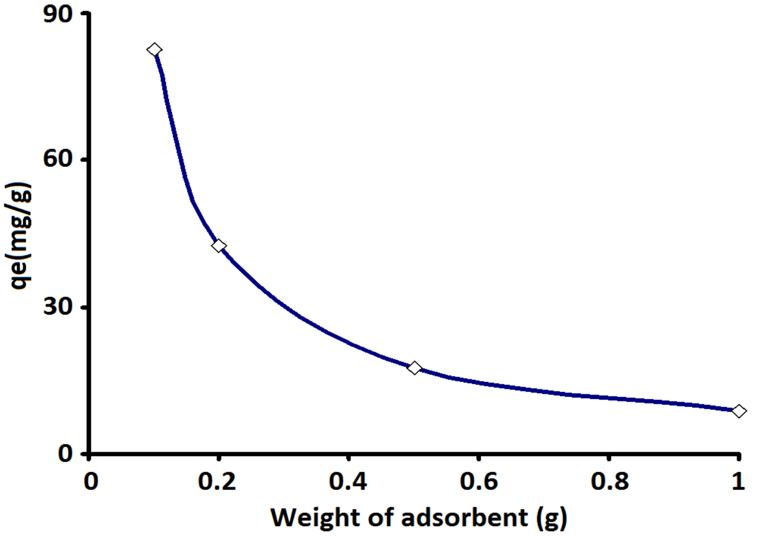

Figure 5: Effect of adsorbent dose on the adsorption percentage of MB on grounded *A. integer* peel (C_0 = 100 mg/L, temperature = 25-27ºC, stirring rate = 150 rpm, contact time = 3 h, and pH = 7)

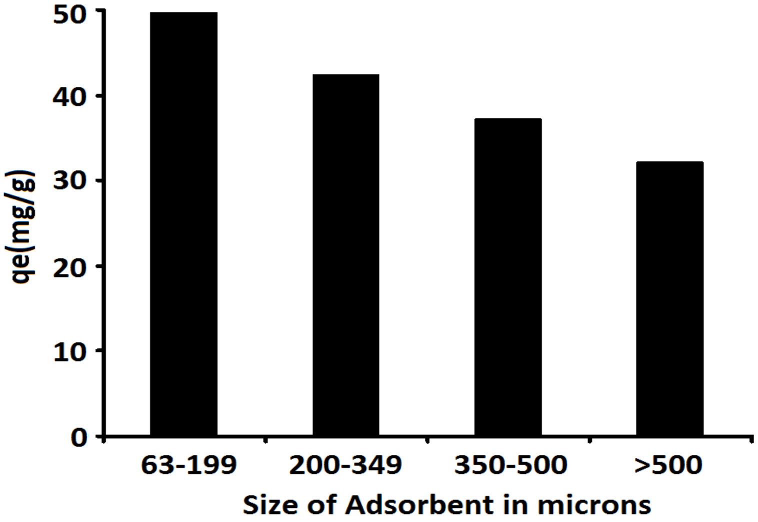

Figure 6: Effect of size of adsorbent on the adsorption percentage of MB on grounded *A. integer* peel (C_o = 100 mg/L, temperature = 25-27ºC, stirring rate = 150 rpm, contact time = 180 min, weight of A. integer peel = 0.2 g, and pH = 7)

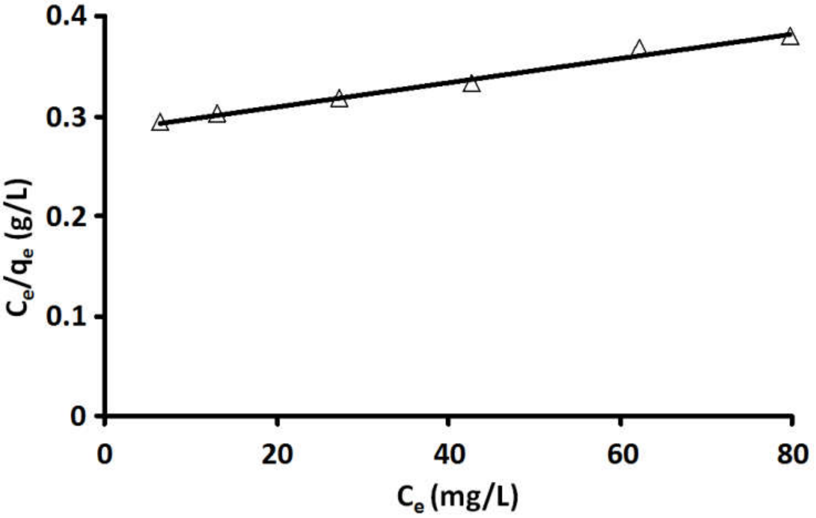

Figure 7: Langmuir isotherm for MB sorption onto grounded *A. integer* peel fibers at ambient temperature (25 - 27 ºC)

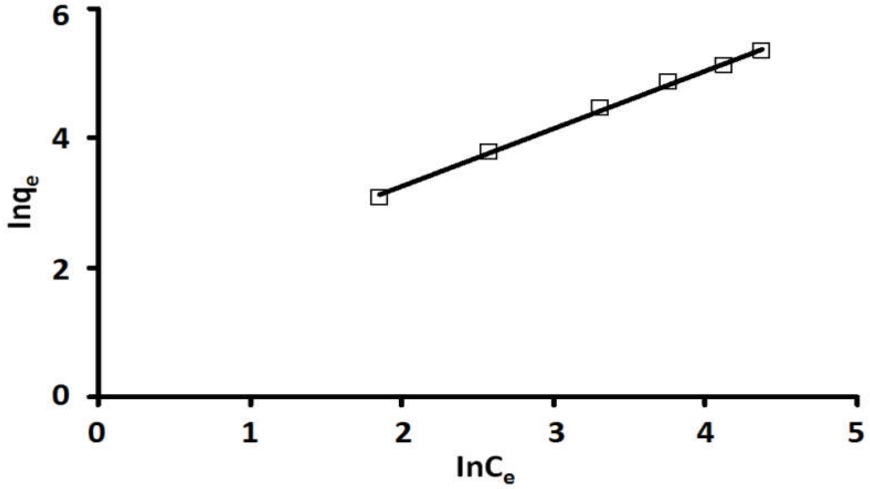

Figure 8:Freundlich isotherm for MB sorption onto grounded *A. integer* peel fibers at ambient temperature (25 - 27 ºC)

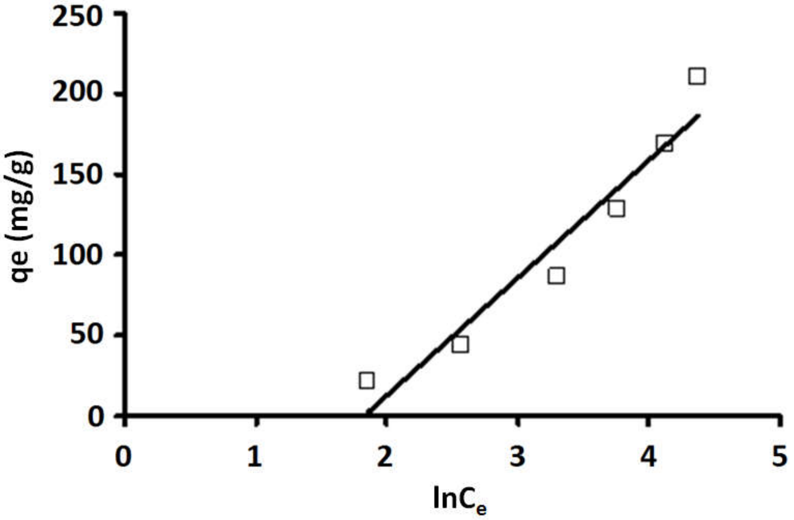

Figure 9.Temkin-Pyzhev isotherm for MB sorption onto grounded A. integer peel fibers at 25-27 °C temperature (25 - 27 ºC)

Table 1. Langmuir, Freundlich and Temkin-Pyzhev isotherm constants and correlation coefficients for sorption of methylene blue.

Isotherms	
Langmuir	
Q_0 (mg/g)	833.33
b (mg/L)	0.004
R^2	0.986
R_L	0.323
Freundlich	
K_f(mg/g)	4.26
1/n	0.898
R^2	0.998
Temkin-Pyzhev	
A	0.160
B	73.08
R^2	0.936

Table 2. Comparison of pseudo-first-order, pseudo-second-order adsorption rate constants, and calculated and experimental q_e values at initial MB concentrations 100 mg/L

Initial concentrations (mg/L)	**$q_{e\ (Exp)}$**	**Pseudo First Order Kinetic Model**			**Pseudo Second Order Kinetic Model**		
		k_1	**$q_{e\ (Cal)}$**	**R^2**	***k_2***	**$q_{e\ (Cal)}$**	**R^2**
100	43.23	0.043	76.17	0.928	9.0×10^{-4}	47.17	0.991

Table 3. Thermodynamic parameter values of MB sorbed on grounded A. integer peel

Sorbent	**ΔH° (kJ/mol)**	**ΔS° (J/mol.K)**	**ΔG°(kJ/mol)**				
			298K	**303K**	**313K**	**323K**	**333K**
A. integer Peel Dust	- 6.71	4.48	- 4.28	- 4.63	-4.98	- 5.36	- 5.70

Table 4: Adsorption capacity (q_e) of the modified grounded *A. integer* peel.

Types of Treatment	**Untreated**	**AIP 1**	**AIP 2**	**AIP 3**	**AIP 4**	**AIP 5**
Adsorption Capacity, q_e (mg/g)	43.23	52.58	59.89	39.85	57.65	89.17

Adsorption capacity of the modified *A. integer* peel

The adsorption experiments for the modified *A. integer* peel were carried out at 100 mg/L at pH 7 using 0.2 g of the fibers with 150 rpm agitation speed. The amorphous waxy cuticle layer was leached out by mercerization and acetylation method. Peroxide treatment lead to fibrillation of fibers due to the leaching out of the waxes, gums and pectin substance [24]. Fiber moisture content was reduced, which enhanced its mechanical properties due to stearic acid treatment [43]. Acid treatment is generally increases the sorption capacity. It is observed in this study (Table 4) that all modified AIP except peroxide treated AIP showed a slight increase in sorption capacity. The order of the sorption capacity is sulphuric acid treated AIP 5>acetylated AIP 2 > stearic acid treated AIP 4> mercerized AIP 1> untreated AIP > peroxide treated AIP 3. The slight drop in sorption capacity of the peroxide treated AIP is attributed to delignification of the fibers [24]. The removal of hazardous material in the present study using biomaterial was supported by other studies also [48,49,50].

Present study successfully used *A. integer* peel fibers of 212 - 350 micronsize to remove the MB from aqueous solutions. The study successfully determined the effect of various parameters (namely pH, sorbent dose, contact time, dye concentration, sorbent size and temperature) on A*. integer* fibers. The kinetics of direct dye adsorption of MB on the *A. integer* peel fibers followed the pseudo-second-order model. The equilibrium data was fitted well in the Freundlich model of adsorption, which clearly suggested the heterogeneous coverage of the dye molecules over outer surface of the fibers. Reports suggest that activated carbon is currently having a major role in dye adsorption and currently available for approximately US 350 per tonne. The cost of activated carbon is considered high, even though the sorption capacity is reported to be at 55.56 mg/g [51]. In this work, *A. integer*, an agricultural waste demonstrated a slightly lower sorption capacity of 47.17 mg/g. Considering all other costs factors (transportation, labor, energy and chemicals), the production cost of *A. integer* peel waste would be USD 35 per tonne. The result of present study supports that development of this biomaterial needs attention due to its sorption capacity and cost effectiveness.

CONCLUSION

The experimental data of present study concludes that modified (especially sulphuric acid treated fibers) and optimized *A. integer* peel fibers possess high potential to successfully remove MB from aqueous solutions and follow pseudo-second-order model. The fitting of equilibrium data in Freundlich model of adsorption establishes heterogeneous coverage of dye molecules over outer surface of fibers. Hence, based on the cost comparison *A. integer* peel and activated carbon, the present study establishes that highly abundant *A. integer* peel (generally discarded as agricultural waste) can be utilized as a low-cost biomaterial for the removal of MB from aqueous solutions.

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