The Removal of Methyl Red from Aqueous Solutions Using Banana Pseudostem Fibers

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Abstract: Problem statement: The aim of this study was to investigate the removal of methyl red, a mutagenic monoazo dye, from various aqueous solutions using banana pseudostem fibers of the size 212-350 micron. **Approach:** The parameters studied were the effect of pH, amount of adsorbent, contact time, concentration of adsorbate and agitation speed. **Results:** Equilibrium data were fitted to the Langmuir and Freundlich isotherm models. The data were best represented by the latter with an adsorption capacity and adsorption intensity of 0.351 and 0.302, respectively. **Conclusion/Recommendations:** Specific rate constants of the processes were calculated by kinetic measurements and a pseudo second order adsorption kinetics was obtained for all cases.

Key words: Sorption, methyl red, biotransformation, mutagenic, banana pseudostem fibers

INTRODUCTION

Rapid progress in industrial activities during recent years has led to the discharge of unprecedented amount of wastewater containing synthetic dyes, which pollutes the rivers and consequently causes harm to human and other living organisms. A majority of the used dyes are azo reactive dyes[1]. These are bright color dyes due to the presence of one or several azo (-N = N-) groups associated with substituted aromatic structures[2]. Effluents from textile, leather, food processing, cosmetics, paper and dye manufacturing industries are some examples of the sources of discharged azo dyes[3]. These dyes or their breakdown products are toxic to living organisms[4]. Furthermore, dyes in wastewater are difficult to remove because they are stable to light, heat and oxidizing agents. In short, they are not easily degradable[1,5]. In order to achieve a high degree of dye removal from wastewater systems, it is necessary to integrate biological, chemical and physical processes such as coagulation, ultra-filtration, electro-chemical adsorption and photo-oxidation[6]. Physical adsorption techniques are generally considered as the preferred means for removing and purifying organic substances due to their high efficiency and ability to separate a wide range of chemical compounds[7-11].

The above reasons have prompted enormous research interest in the use of agricultural waste as starting materials because of their low-cost and widespread availability. Some examples of agrowaste that have been used for the removal of dyes are palm kernel fibers[12], coir pith[13], sugarcane bagasse[14], banana peel[15], peanut hull[16], rice bran and wheat bran[17], rice husk[18], tea waste[19], waste apricot[20], rubber seed coat[21], coconut shell[22], apple pomace and wheat straw[23], halzelnut shell[24], plum kernel[25], corncob and barley husk[26], bamboo[27], grass waste[28], pumpkin seed hull[29] and garlic peel[30].

Methyl Red (MR) is a commonly used monoazo dye in laboratory assays, textiles and other commercial products; however, it may cause eye and skin sensitization[31] and pharyngeal or digestive tract irritation if inhaled or swallowed[32]. Furthermore, MR is mutagenic under aerobic conditions: it undergoes biotransformation into 2-aminobenzoic acid and N-N'-dimethyl-p-phenylene diamine[4,33-36]. Of late, there has been increasing interest to develop low-cost means[37] of reducing the amount of, if not completely remove, MR in wastewater before being discharged into receiving water body.

Banana plants are of the family Musacease and cultivated primarily for their fruit. As such, after harvesting the fruit, the matured pseudostems are generally disposed at a landfill or left to decompose slowly in a plantation field. In the present study, application of the agrowaste, ground banana pseudostem fibers of the size 212-350 micron, for the removal of methyl red from various aqueous solutions has been studied.

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MATERIALS AND METHODS

Sorbent: Banana pseudostems from the family of Musa acuminate × balbisiana Colla (ABB Group) cv 'Pisang Awak' were obtained locally. The pseudostems were chopped into cubes of average size of 2×2 cm. The cubes were boiled in distilled water for 1 h and then dried in an oven at 70°C until a constant weight was obtained. The resulting material was ground using a Warring Commercials high speed blender and sieved to isolate fibers of the size 212-350 micron.

Adsorbate: MR, 2-[4-(dimethylamino)phenylazo] benzoic acid, a dark red crystalline powder with a molecular weight of 269.30 and melting point 179-182°C, was received from Bendosen-Laboratory Chemicals and used without further purification. The molecular structure of MR is shown in Fig. 1. MR is red in aqueous solution of pH under 4.4, yellow in pH over 6.2 and orange in between. A stock solution of MR (500 mg L^{-1}) was prepared by dissolving 0.500 g of the dye in 1 L of distilled water and filtered via Whatman filter paper (No. 1). The prepared stock solution was then wrapped with aluminum foil and stored in a dark to prevent exposure to direct light.

pH study: The effect of pH was studied by agitating the fibers (0.20 g) in 50 mL of the stock solution using an orbital shaker at ambient temperature (25-27°C). The experiment was conducted at pH value range 2-7. Agitation speed was kept constant at 150 rpm for 120 min, which was sufficient to reach equilibrium. Since MR is a pH dependent dye, the dye concentrations were measured by a single beam UV/vis spectrophotometer (Genesys 20 Thermo Spectronic, Krackeler Scientific, USA) at various wavelengths. The pH was adjusted by adding appropriate amount of either 0.1 M NaOH or 0.1 M HCl solution before each experiment. The pH was measured by using a pH meter (Cyberscan 1500, EUTECH Instruments, India). When the equilibrium was established, the supernatant was carefully filtered through Whatman filter paper (No. 1) which was pre-saturated with distilled water. The maximum wavelength obtained for each desired pH value is shown in Table 1. It is worthwhile to note that no adsorption of MR occurred on the filter paper: A comparative study was done by measuring the concentration of the dye solution before and after filtering and the result showed no variation of concentration of the dye solution meaning that the amount of the dye adsorbed on the filter paper, if any, was negligible.
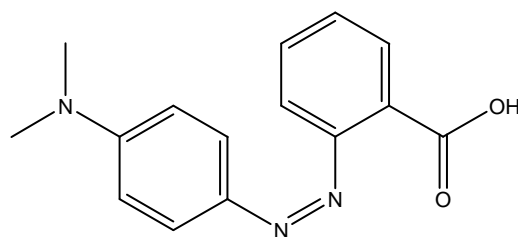

Fig. 1: Molecular structure of Methyl Red (MR)

Table 1: Optimal wavelength of MR solution at different pH

pH	Optimal wavelength (nm)
2	527
3	525
4	433
5	403
6	407
7	420

Contact time: Batch equilibrium studies were carried out by adding a fixed amount of the sorbent (0.20 g) into 250 mL Erlenmeyer flasks containing 50 mL of different initial concentrations (50-500 mg L^{-1}) of dye solution at pH 3. The flasks were agitated in an orbital shaker at 150 rpm at ambient temperature for 120 min. Aliquots (5 mL) were taken from the solutions and the concentrations were analyzed. The dye concentrations were measured at 525 nm at different contact times (0, 15, 30, 45, 60, 90 and 120 min). The adsorption at equilibrium, q_e (mg g^{-1}), was calculated using Eq. 1:

$$q_e = (C_o - C_e)\frac{V}{W} \tag{1}$$

Where:

C_o and C_e (mg L^{-1}) = The liquid-phase concentrations of dye at initial and equilibrium, respectively
V = The volume (L) of the solution
W = The weight (g) of dry sorbent used

Optimization of amount of adsorbent: For the purpose of optimizing the amount of the adsorbent, experiments were performed by adding different weights of the fibers into 50 mL of the stock solution of MR at pH 3 in a 250 mL Erlenmeyer flask and agitated for 120 min with a rotation speed of 150 rpm. The quantity of the fibers was varied between 0.1-0.3 g with an increment of 0.025 g to determine the optimum level of adsorption.

Concentration dependent study: The adsorption experiment related to the concentration of MR over a

range of 50-500 mg L^{-1} at pH 3 using 0.20 g of the fibers. This adsorption study was carried out in an orbital shaker agitated at 150 rpm with 50 mL of the dye solution in a 250 mL Erlenmeyer flask.

Agitation study: Agitation speed variation plays an important role in determining the efficiency of the adsorption at different rotation speeds. The effect of agitation speed at 50, 100, 150, 200 and 250 rpm on the adsorption was carried out. This study was carried using 50 mL of the MR stock solution at pH 3 with the sorbent dose of 0.20 g.

Spectroscopic study: Fourier Transform Infrared (FTIR) was used to identify the characteristic functional groups in the fibers. A known quantity (5 mg) of the fibers sample was powdered and then dispersed in dry potassium bromide (KBr). The mixture was thoroughly mixed in a mortar and pressed at pressure of 6 bars within 2 min to form a KBr thin disc. Then the disc was placed in a sample cup of a diffuse reflectance accessory. The IR spectrum was obtained using Perkin Elmer 2000 infrared spectrometer. The sample was scanned from 4000-400 cm^{-1} for 16 times to increase the signal to noise ratio.

Morphological analysis: The morphology of the fibers was observed using a Scanning Electron Microscopy (SEM) machine Model Leica Cambridge AS-360 at an accelerating voltage 15 kV. Prior to examination, the surface of the specimen was coated with a thin layer of gold approximately 30 nm using Sputter Coater Polaron SC 515.

RESULTS AND DISCUSSION

Effect of pH: The efficiency of sorption is dependent on the pH of the solution[37] because variation in pH leads to the variation in the degree of ionization and the surface properties of the sorbent[38]. In view of this, comparative experiments were performed over a pH range 2.0-8.0 to obtain the optimum pH for dye adsorption. The result shown in Fig. 2 shows that the sorption of MR increased from the initial pH 2 up to pH 3.0 and then decreased over the pH range of 4-8. Therefore, all subsequent studies were carried out at pH 3 as the optimum pH. Malik[39] and Mohamed[40] reported that at low pH region the surface of the fibers will be largely protonated. The positive ions (H^+) provide an electrostatic attraction between the fibers surface and the dye molecules leading to maximum adsorption. On the other hand,
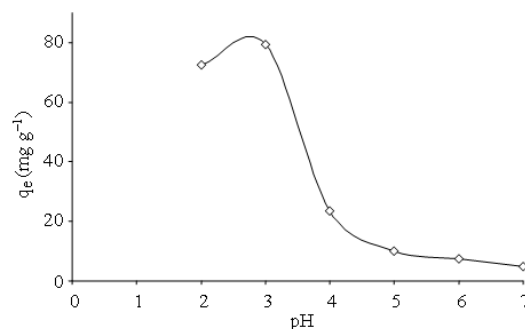

Fig. 2: Effect of pH on the adsorption of MR on banana pseudostem fibers (C_0 = 500 mg L^{-1}, temp. = 25-27°C, stirring rate 150 rpm, contact time 120 min and weight of fibers = 0.20 g
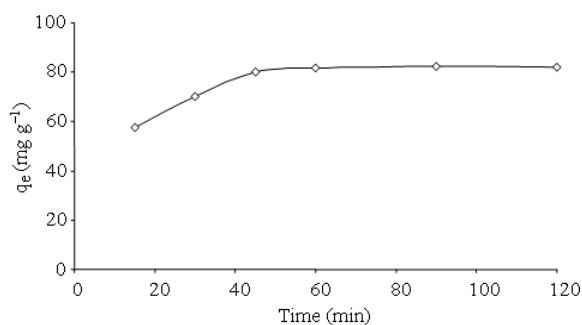

Fig. 3: Effect of contact time on the adsorption of MR on banana pseudostem fibers (C_0 = 500 mg L^{-1}, temp. = 25-27°C, stirring rate 150 rpm, pH 3 and weight of fibers = 0.20 g)

at pH above 3 (i.e., pH range of 4-8) the degree of protonation of the surface of the fibers will be less which result in the decrease in diffusion and adsorption thereby due to electrostatic repulsion[41,42]. Furthermore, lower adsorption of the direct dyes in alkaline medium can also be attributed to the competition from excess hydroxide ions (OH^-) with the anionic dye molecules for the adsorption sites. In this study, we found that the biosorption was slightly unfavorable at pH lower than pH 3. This is attributed to the increase in H^+ concentration leading to the formation of aqua complexes thereby retarding the dye sorption. Our finding agrees with that reported by Mohan *et al.*[43].

Contact time study: The effect of contact time on the amount of MR adsorbed on the fibers was investigated at initial concentration of 500 mg L^{-1}. The system was subjected to an agitation speed of 150 rpm for 120 min. Fig. 3 shows a rapid adsorption of the dye at the initial stages of the adsorption and equilibrium was attained

within 45 min. Such uptake indicates a high degree of affinity towards the MR molecules via chemisorption[44].

Optimization of amount of adsorbent: Results shown in Fig. 4 indicate that the adsorbent dosage increases proportionately to the availability of the adsorbent sites. The increase of adsorbent sites and surface area of contact with the dyes increases the amount of dye uptakes and consequently leads to a better adsorption[5]. This observed trend is mainly due to the increase in sorptive surface area and availability of more adsorption site[45].

Concentration dependent study: The results shown in Fig. 5 show that an increase in initial concentration enhances the interaction between the dye molecules and the surface of the fibers. The dye molecules have to encounter the boundary layer effect before diffusing from boundary layer film onto the adsorbent surface followed by the diffusion of the dye into the porous structure of the adsorbent which eventually will take relatively longer contact time. The time profile of the dye uptake by the adsorbent is a single, smooth and continuous curve leading to a saturation point[41]. In addition, increasing the initial dye concentration increases the number of collisions between dye molecules and the adsorbent, which enhances the adsorption process.

Agitation Study: The effect of agitation speed on the dye adsorption at the adsorbent dosage of 0.20 g, initial dye concentration of 500 mg L^{-1}, pH 3 listed in Table 2. The data indicate that the adsorption capacity (q_e) increased as the agitation speed increased from 50-150 rpm. However, the q_e values at the agitation speeds of 150, 200 and 250 rpm are fairly the same suggesting that the effect of agitation has plateaued at about 150 rpm. This effect can be attributed to the increase in turbulence and the decrease in boundary layer thickness around the adsorbent particles as a result of increase in the degree of mixing[46]. This result is also in agreement with that reported by Al-Qodah[47] and Ho *et al.*[48], for the adsorption of dyes onto activated clay and shale oil ash, respectively.

Adsorption isotherms: An adsorption isotherm indicates how adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable
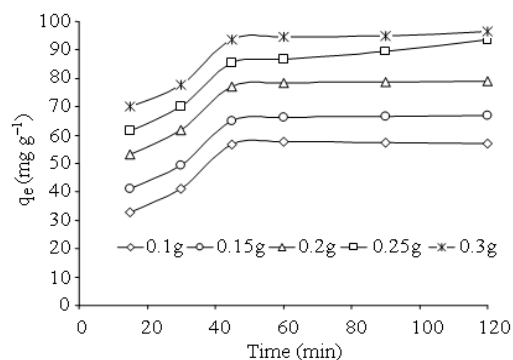

Fig. 4: Effect of adsorbent dose on the adsorption of MR on banana pseudostem fibers (C$_0$ = 500 mg L^{-1}, Temp. = 25-27°C, stirring rate 150 rpm and pH 3)
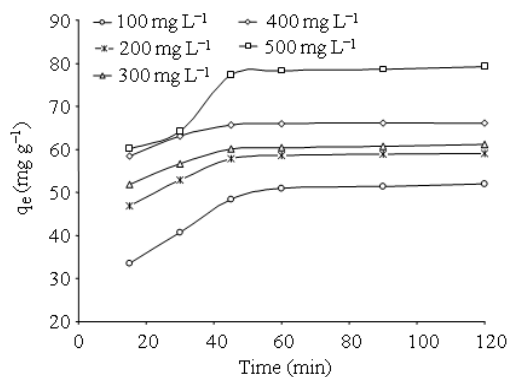

Fig. 5: Effect of MR concentration on the adsorption of MR on banana pseudostem fibers (weight of fibers = 0.20 g, Temp. = 25-27°C, stirring rate 150 rpm and pH 3)

Table 2: q_e and R^2 parameters for the adsorption of MR on banana pseudostem fibers (Weight = 0.20 g, ambient temperature, concentration 500 mg L^{-1} and pH 3)

Agitation rate (rpm)	q_e (mg g^{-1})
0	66.58
50	71.06
100	75.56
150	78.94
200	84.28
250	87.64

model that can be used for design purposes[49]. Adsorption isotherm is basically important to describe how solutes interact with adsorbents and is critical in optimizing the use of adsorbents. In this study, adsorption isotherm study was carried out on two isotherm models: Langmuir and Freundlich. The applicability of the isotherm models to the adsorption study done was compared by judging the correlation coefficients, R^2 values.

Langmuir isotherm model: Langmuir isotherm model assumes the uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Langmuir sorption is a model based on the physical hypothesis that there are no interaction between adsorbed molecules and the adsorption energy over the entire coverage surface. Also there is no transmigration of the adsorbate in the plane of the surface of the adsorbent[50]. On the other hand in the Langmuir model, it is assumed that intermolecular forces decrease rapidly with distance and this lead to the prediction that coverage of the banana pseudostem fibers is of monolayer type. Once a particular site of the adsorbent is occupied by an adsorbate molecule, no further adsorption takes place at that site. The linear form of Langmuir isotherm equation is given in Eq. 2.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \qquad (2)$$

Where:
C_e = The equilibrium concentration of the adsorbate (mg L^{-1})
q_e = The amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1})
Q_o and b = Langmuir constants related to adsorption capacity and rate of adsorption, respectively

When C_e/q_e was plotted against C_e, a straight line with slope of $1/Q_o$ was obtained, as shown in Fig. 6. The value of Q_o was determined from the Langmuir plot at the concentration range 100-500 mg L^{-1} as 88.50 and then the b value was calculated to be 0.05. The correlation coefficient of Langmuir isotherm, R^2 is 0.983.

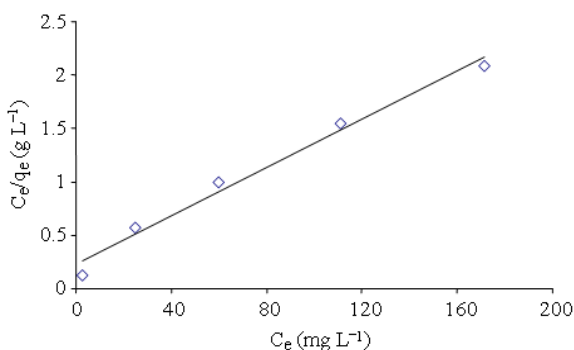Fig. 6: Langmuir isotherm for MR sorption onto banana pseudostem fibers at ambient temperature (25-27°C)

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given in Eq. 3:

$$R_L = \frac{1}{1 + bC_0} \qquad (3)$$

The value of R_L indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The value of R_L was found to be 0.0385 suggesting the isotherm to be favorable at the concentrations studied.

Freundlich isotherm model: This model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption[51] and can be represented by Eq. 4:

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

Where:
C_e = The equilibrium concentration of the adsorbate (mg L^{-1})
q_e = The amount of adsorbate adsorbed per unit mass of adsorbent (mg g^{-1})
K_f (mg g^{-1}) and n = Freundlich constants with n giving an indication of how favorable the adsorption process
K_f = The adsorption capacity of the adsorbent

K_f can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto the fibers for a unit equilibrium concentration. The slope of 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero[52]. Figure 7 clearly reveals that for the adsorbents log q_e versus log C_e plots are linear. The Freundlich constants were derived from the slopes and intercepts of log C_e versus log q_e and are shown in Table 3. By analyzing the Freundlich isotherm, it describes the heterogeneous system and reversible adsorption. However, the adsorption is not restricted to a monolayer formation but the model predicts that dye concentration in the adsorbent will increase with increase in dye concentration in the solution. Theoretically, adsorbent has finite number of sites and once all these sites are occupied by adsorbed molecules further adsorption cannot take place.

Table 3: Langmuir and Freundlich isotherm constants and correlation coefficients for adsorption of MR on banana pseudostem fibers at ambient temperature

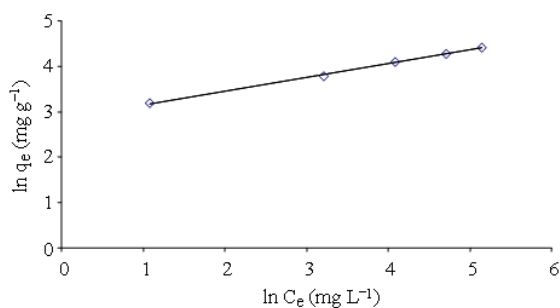| Isotherms	Parameters
Langmuir:	
Q_0 (mg g^{-1})	88.50
b (mg L^{-1})	0.050
R^2	0.983
Freundlich:	
K_f (mg g^{-1})	17.25
n	3.310
R^2	0.998

Fig. 7: Freundlich isotherm for MR sorption onto banana pseudostem fibers at ambient temperature (25-27°C)

As seen from the Table 3, a high regression correlation coefficient, R^2 (0.998) was shown by the Freundlich model. This indicates that the Freundlich model was suitable for describing the sorption equilibrium of MR by the banana pseudostem fibers. From the plot shown in Fig. 7, the K_f value and n value was recorded at 17.25 and 0.302, respectively. When the linearity of the plots of the Freundlich and Langmuir models was compared, it is found that the former has a better fit. Thus it is reasonable to conclude that the adsorption of MR on the fibers that consist of heterogeneous adsorption sites that are similar to each other in respect of adsorption phenomenon.

Adsorption kinetics: Two simplified kinetic models were adopted to examine the mechanism of the adsorption process. First, the kinetics of adsorption was analyzed by the Lagergren pseudo-first-order equation[53] as depicted in Eq. 5:

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1 t}{2.303} \qquad (5)$$

Where:

q_e and q_t = The amounts of MR adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively
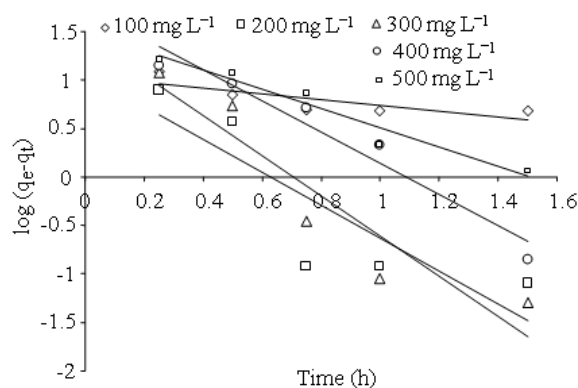
k_1 (min^{-1}) = The rate constant

Fig. 8: Pseudo first order for MR sorption onto banana pseudostem fibers at ambient temperature (25-27°C)
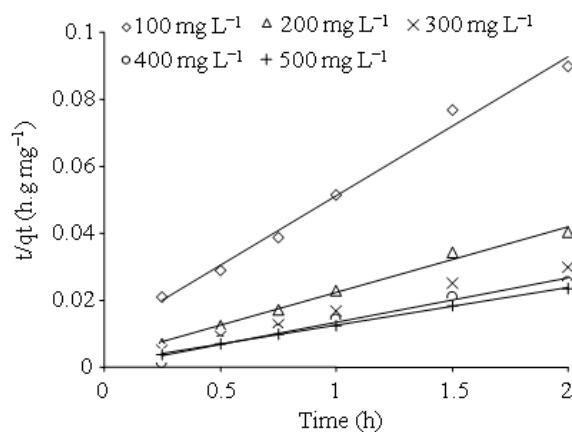

Fig. 9: Pseudo second order for MR sorption onto banana pseudostem fibers at ambient temperature (25-27°C)

Values of k_1 at ambient temperature were calculated from the plots of log (q_e-q_t) versus t (Fig. 8) for different initial concentrations of MR. The set of R^2 values obtained were poor and the experimental q_e values did not agree with the calculated values obtained from the linear plots (Table 4). On the other hand, the pseudo-second-order equation based on equilibrium adsorption[54] is expressed as Eq. 6:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (6)$$

where, k_2 (g mg^{-1} min) is the rate constant of second-order adsorption. The linear plot of t/q_t versus t at ambient temperature, as shown in Fig. 9, yielded set of

Table 4: Comparison of the pseudo-first-order, pseudo-second-order adsorption rate constants and calculated and experimental q_e values obtained at different initial MR concentrations

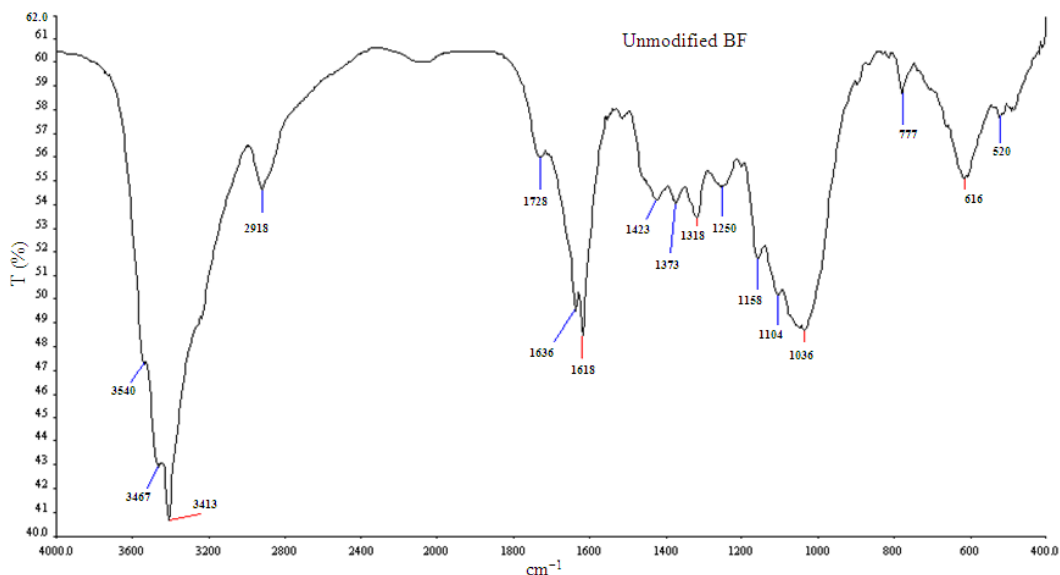| Initial concentrations (mg L^{-1})	$q_{e\,(Exp)}$	Pseudo first order kinetic model			Pseudo second order kinetic model		
		k_1	$q_{e\,(Cal)}$	R^2	k_2	$q_{e\,(Cal)}$	R^2
100	24.27	0.829	11.90	0.849	0.185	23.980	0.990
200	43.80	3.915	11.65	0.741	0.137	51.020	0.990
300	60.03	4.756	28.41	0.876	0.111	68.970	0.993
400	72.18	3.703	55.78	0.830	0.581	75.760	0.971
500	82.41	2.251	29.72	0.977	0.098	88.500	0.999

Fig. 10: Infrared spectra of banana pseudostem fibers

R^2 values that are greater than 0.970 for all MR concentrations. It also showed a good agreement between the experimental and the calculated q_e values (Table 4), indicating the applicability of this model to describe the adsorption process of MR onto the fibers.

Spectroscopic study: The aim of using FTIR analysis is to determine the existence of functional groups that exists on the fibers. The IR spectrum of banana pseudostem fibers in the form of KBr pallet is shown in Fig. 10. Identification of the characteristic peaks is based on previous studies of banana and coconut fibers[55], sugarcane bagasse cellulose[56], rice straw[57], perennial ryegrass leaves[58] and hemicellulose, cellulose and lignin[59]. The typical functional groups and their corresponding IR signals are listed in Table 5. The absorptions at 3540, 3467, 3413 and 3238 cm^{-1} are due to the stretching of hydroxyl groups of cellulose, hemicellulose and lignin that are present in the banana pseudostem fibers. The medium strong band at 2918 cm^{-1} is due to the C-H stretching of saturated (sp^3) carbon.

Table 5: Infrared spectrum data of banana pseudostem fibers

Frequency, cm^{-1}	Assignment
3540 w, 3467 w, 3413 s, 3238 vw	OH stretching
2918 ms	C-H stretching
1728 w	C = O stretching
1636 ms	O-H bending (of H_2O)
1618 s	C = C stretching
1423 w	CH_2 bending
1373 w	O-H bending
1318 w	C-C and C-O stretching
1250 w	C-O stretching
1158 w	C-O antisymmetric stretching
1104 w	C-O-H (OH association)
1036 w	C-O-C stretching (pyranose ring skeletal)

w: weak; s: strong; vw: very weak; ms: medium strong

The weak band at 1728 cm^{-1} corresponds to the absorption of carbonyl group of carboxylic acids of the hemicellulose which is a minor component of the fibers. The band at 1636 cm^{-1} is assigned to the bending mode of absorbed water since fibers with hemicellulose component are known to have a strong affinity for water[58,60]. The band at 1618 cm^{-1} is due to C = C stretching associated with the aromatic skeletal mode of fibers containing lignin[59]. The weak bands at 1423,
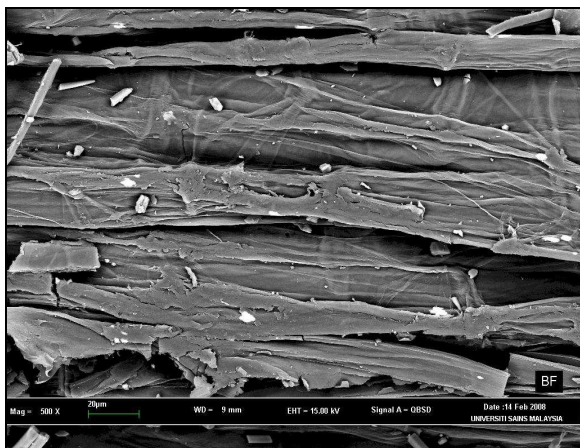
Fig. 11: SEM micrograph of banana pseudostem fibers

1373 and 1250 cm^{-1} are assigned to C-H bending, C-O stretching and O-H bending, respectively[60]. The bands at 1318 and 1158 cm^{-1} are assigned to O-H bending and C-O skeletal vibrations, respectively.

Morphological analysis: Studies of the fibers surface topography could provide vital information on the level of interfacial adhesion that would exist between the fibers and the dye molecules. Figure 11 shows the SEM micrograph of the banana pseudostem fibers. Some minor impurities can be observed as tiny white specks on the surface of the fibers. On the whole, however, the surface of the fibers appears to be clean but with fairly rough texture which is ideal for surface adsorption. Bilba *et al*.[55] reported that the banana pseudostem fibers were made of rough particles. Each particle was formed of hollow not cylindrical fibers whose walls presented hazardous porosities whose size is smaller than 1 µm. The walls which made of fibrils embedded in a homogeneous matrix. The fibrils were probably composed of cellulose that constitutes the skeleton of cellular wall, the homogenous matrix a mixture of various polysaccharide acids, neutral hemicelluloses and lignin.

CONCLUSION

The use of ground banana pseudostems fibers of the size 212-350 micron for the removal of MR from aqueous solutions was investigated. The effect of various parameters such as pH, sorbent dose, contact time, dye concentration and agitation speed was studied. The kinetics of direct dye adsorption of MR on the banana pseudostem fibers follows the pseudo-second-order model. The equilibrium data fit well in the Freundlich model of adsorption, which suggests a heterogeneous coverage of the dye molecules at the outer surface of the fibers. The present research demonstrates that banana pseudostems, which are abundantly available but generally discarded as agricultural waste, can be utilized as efficient sorbents for the removal of MR from aqueous solutions.

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