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The Removal of Methyl Red from Aqueous Solutions Using Modified Banana Trunk Fibers

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ABSTRACT

Banana trunk fibers (BTF) are abundantly available and are usually discarded as an agricultural waste. However, in recent times, it has used an efficient sorbent for methyl red (MR). Here, we describe the use of modified BTF as an efficient sorbent for MR. The effect of pH, amount of adsorbent and concentrations of adsorbate were studied using modified BTF. The sulphuric acid treated BTF showed the highest adsorption capacity (K_f of 8.74 mg/g) in Freundlich isotherm model.

Keywords: Sorption, Methyl red, Biotransformation, Chemical Modification, Banana trunk fibers.

INTRODUCTION

The effluents from textile, leather, food processing, dyeing, cosmetics, paper and dye manufacturing industries are important sources of dye pollution [1]. Many dyes and their breakdown products may be toxic for living organisms. Therefore, decolorization of dyes becomes an important process in wastewater treatment. However, it is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems. Several biological, physical and chemical methods have been used for the treatment of industrial textile wastewater including microbial biodegradation, membrane filtration, oxidation and ozonation [2]. However, many of these technologies are cost prohibitive, especially when applied for treating large waste streams. Consequently, adsorption techniques seem to have the most potential for future use in industrial wastewater treatment because of their proven efficiency in the removal of organic and mineral pollutants and for economic considerations [3-4]. Activated carbon has been widely used as an adsorbent in wastewater treatment to remove organic and inorganic pollutants due to its high specific surface area, high removal efficiency of most dissolved molecules, good capacity [5]. Nevertheless, the high cost of activated carbon contributes its disadvantages as an absorbent. Therefore, many researchers have been search and study a series of materials in hope to search low cost adsorbent to replace the activated carbon. Therefore, it is important to develop cost efficient adsorbents using agricultural waste. In this paper, banana trunk fibers (BTF) were subjected to modification by means of various known methods (mercerization, acetylation, peroxide treatment, stearic acid treatment and sulphuric acid treatment). The adsorption capacity of the modified fibers for a reactive textile dye: methyl red (MR) were compared with that of the untreated BTF as reported previously by Mas Haris & Kathiresan [6].

MATERIALS AND METHODS

Sorbent

Banana trunks from the family of *Musa acuminate x balbisiana Colla (ABB Group) cv 'Pisang Awak'* were obtained locally. The trunks were chopped into cubes of average size of 2 cm x 2 cm. The cubes were boiled in distilled water for 1 hour and then dried in an oven at 70 °C until a constant weight. The resulting material was grounded using a Waring Commercials high speed blender and sieved to obtain banana trunk fibers of the size 212 -350 microns.

BTF Modification

The BTF were modified according to the methods reported in literature: (i) mercerization (BTF-1), the fibers were immersed in 5% NaOH solution for 48 hr at 25 °C [7], (ii) acetylation (BTF-2), the mercerized fibers were soaked in glacial acetic acid for 1 hr, separated by decantation and then soaked in acetic anhydride containing 2 drops of concentrated H_2S0_4 for 2 min [8], (iii) peroxide treatment (BTF-3) , the mercerized fibers (30 g) were immersed in 1 L of a 6% solution of benzoyl peroxide in acetone for 30 min [8], (iv) stearic acid treatment (BTF-4), a mixture containing 1.0 g of the fibers, 0.2 g of stearic acid, 2 drops of concentrated H_2SO_4 in 100 mL of n-hexane was refluxed in a Dean–Stark apparatus at 65 °C for 6 hr [9], and (v) sulphuric acid treatment (BTF-5), 1 : 1 weight ratio of the fibers : concentrated H_2SO_4 was heated in a muffle furnace for 24 h at 150 °C [10]. All resulting fibers were washed ample amount of water till a pH close to neutral was obtained.

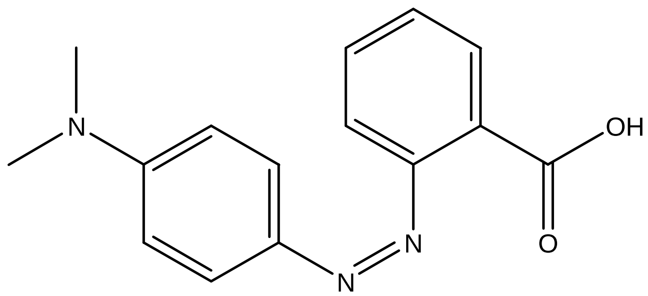

Figure 1: Molecular Structure of Methyl Red (MR)

Adsorbate

The molecular structure of MR is depicted in Figure 1. A stock solution of 500 mg/L 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.

Equilibrium studies

Batch equilibrium studies were carried out by adding a fixed amount of sorbent (0.20 g) into 250 mL Erlenmeyer flasks containing 50 mL of different initial concentrations (100–500 mg/L) of dye solution at pH 5. The flasks were agitated in an isothermal water-bath shaker at 150 rpm and 25 °C for 2 h until equilibrium was reached. Aqueous samples were taken from the solutions and the concentrations were analyzed. At time t = 0 and at equilibrium, the dye concentrations were measured by a by a single beam UV/vis spectrophotometer (Genesys 20 Thermo Spectronic, Krackeler Scientific, USA) at 525 nm. The amount of equilibrium adsorption, qe (mg/g), was calculated by:

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

where Co and Ce (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V is the volume of the solution (L) and W is the mass of dry sorbent used (g).

RESULTS AND DISCUSSION

Effect of pH on Dye Adsorption

The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption capacity [11]. The effects of pH on acid dye sorption have been studied extensively and the results indicated that pH of a solution plays a significant role to influence biosorption process [12-13]. The effect of pH on acid dye sorption using BTF were studied with 500 mg/L initial dye concentration with 4 g/L adsorbent mass at ambient temperature (25 - 27 ºC) for 2 h equilibrium time (Figure 2). It was observed that the uptakes were much higher in acidic solutions than those in neutral conditions.

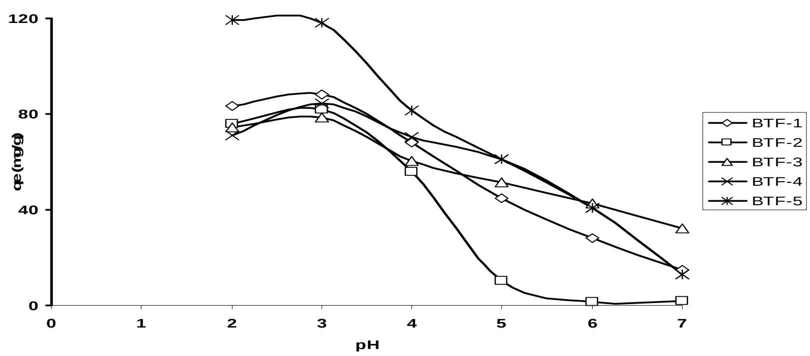

Figure 2: Effect of pH on the adsorption of MR on the modified banana trunk fibers (C_0 = 500 mg/L, temp. = 25 - 27 ºC, stirring rate 150 rpm, contact time 120 min and weight of fibers = 0.20)

As the pH of the system decreased, the number of negatively charged surface sites decreased and the number of positively charged surface sites increased and this favors the adsorption of dye anions due to electrostatic attraction [14]. A similar observation was also seen for the adsorption of acid red 183 and acid green 25 onto shells of bittim [15] and removal of acid blue 62 (AB62) on aqueous solution using calcinated colemanite ore waste [16].

Effect of initial dye concentration

Initial dye concentrations provide an important driving force to overcome all mass transfer resistance of dye between the aqueous and solid phases. The adsorption of MR on the sulphuric acid treated BTF at different initial dye concentrations is shown in Figure 3. It was observed that increasing initial dye concentration significantly increased the uptake of MR on the adsorbent. These results were also in agreement with previous studies [17-18]. It was observed that a large amount of MR was rapidly removed by modified BTF during the first 45 min. Subsequently, the rate of removal of dyes slowed down gradually until the equilibrium state. The two-stage sorption, the first stage which is quantitatively predominant and the second slower stage which is quantitatively insignificant, has been extensively reported in literature [19]. The rapid stage is attributed to the abundant availability of active sites on the biomass and with the gradual occupancy of these sites; the sorption becomes less efficient in the slower stage [20]. The removal of higher dye concentrations needed longer contact time than those of lower dye.

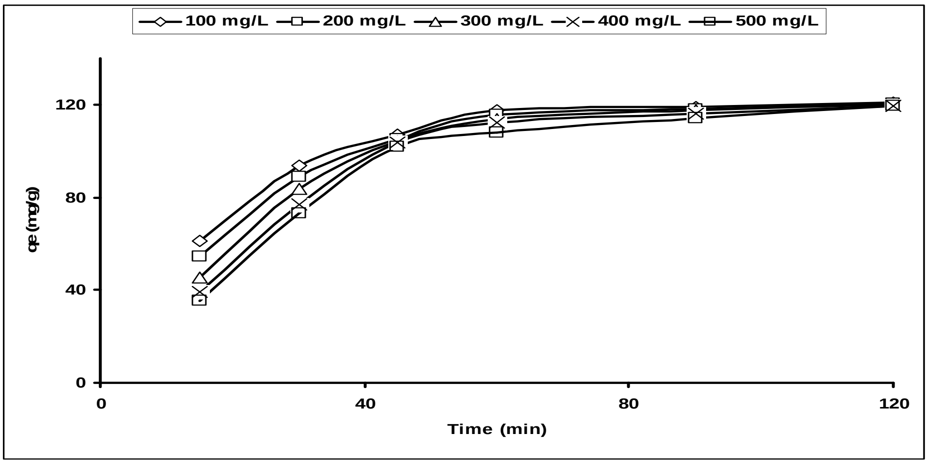

Figure 3: Effect of MR concentration on the adsorption of MR on sulphuric acid treated banana trunk fibers (weight of fibers = 0.20 g, temp. = 25 - 27 ºC, stirring rate 150 rpm and pH 3)

Effect of sorbent dose

The effects of sorbent dose on the removal of MR are shown Figure 4. As the sorbent dose was increased from 0.4 to 1.2 g/l, the percentages of MR sorbed on the modified banana trunk fibers increased. Increase in the sorption percentage of MR with sorbent dose could be attributed to increased sorbent surface area and availability of more sorption sites.

Adsorption Isotherms

Langmuir isotherm model assumes the uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [21].The linear form of Langmuir isotherm equation is given in equation (2).

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

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

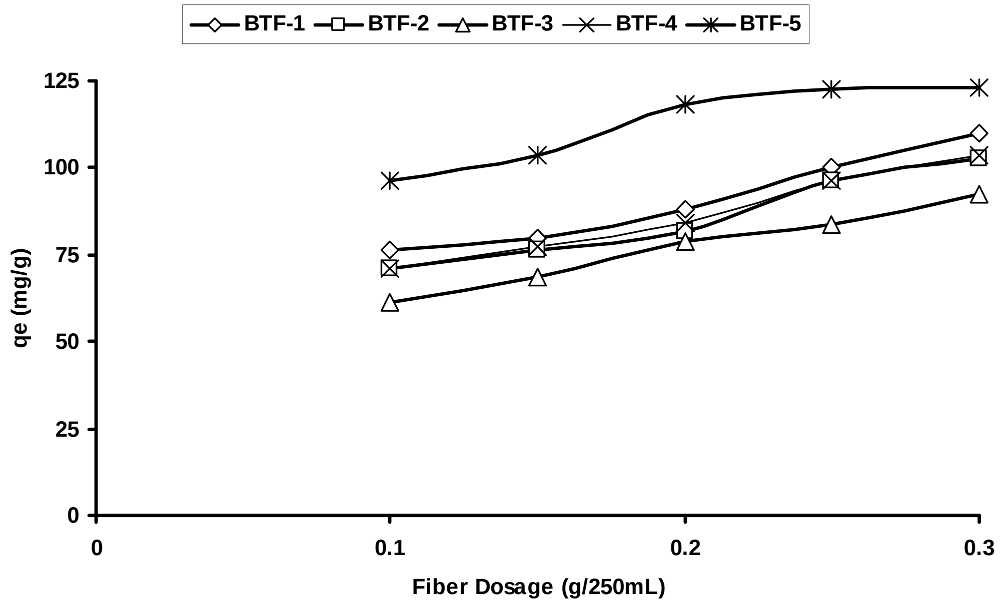

Figure 4: Effect of adsorbent dose on the adsorption of MR on the modified banana trunk fibers (C_0 = 500 mg/L, temp. = 25 - 27 ºC, stirring rate 150 rpm and pH 3)

When C_e/q_e was plotted against C_e, a straight line with slope of $1/Q_o$ was obtained. The value of Q_o was determined from the Langmuir plot at the concentration range 100 to 500 mg/L (Figure 5a) and then the b value was calculated and tabulated in Table 1. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given in equation (3).

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

The values of R_L were found to be 0.598, 0.415, 0.566, 0.511and 0.0950 for BTF-1, BTF-2, BTF-3, BTF-4 and BTF-5, respectively suggesting the isotherm to be favorable at the concentrations studied. The Freundlich isotherm model [22] considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption and can be represented by equation (4).

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

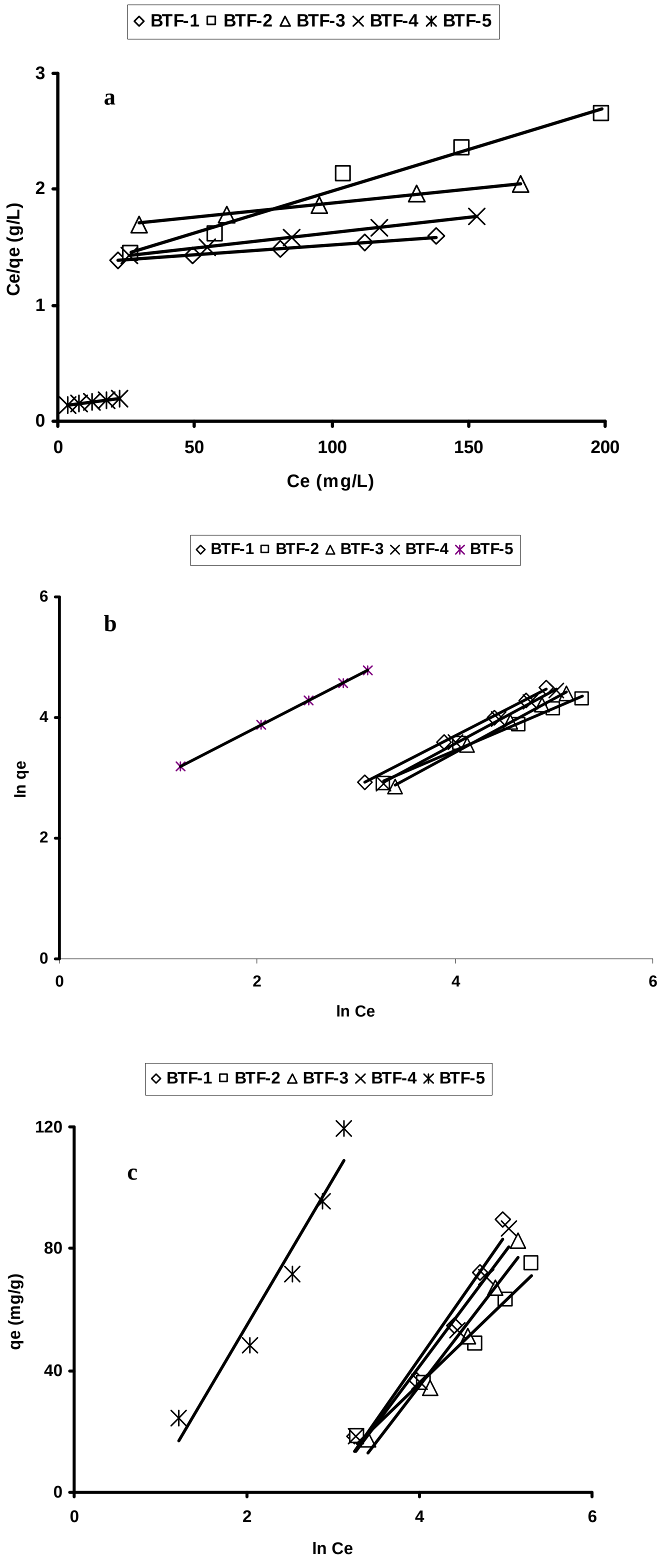

Figure 5: Langmuir (a),Freundlich (b) and Tempkin-Pyzhev isotherm for methyl red sorption unto the modified banana trunk fibers at ambient temperature (25 - 27 ºC)

Table 1: Langmuir, Freundlich and Temkin-Pyzhev isotherm constants and correlation coefficients for sorption of methyl red

Isotherms	Modified Banana Trunk Fibers					
Langmuir		BTF-1	BTF-2	BTF-3	BTF-4	BTF-5
Q_0 (mg/g)		555.56	322.6	400.0	384.6	384.5
b (mg/L)		0.0013	0.0028	0.0015	0.0019	0.0019
R^2		0.989	0.976	0.996	0.995	0.944
Freundlich						
K_f (mg/g)		0.94	2.00	0.85	1.04	8.74
n		1.33	1.45	1.12	1.13	1.20
R^2		0.999	0.992	0.999	0.999	0.999
Temkin-Pyzhev						
A		0.05	0.06	0.05	0.05	0.42
B		40.65	27.57	36.88	38.12	48.54
R^2		0.958	0.978	0.961	0.962	0.948

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), K_f and n are Freundlich constants. The Freundlich constants were derived from the slopes and intercepts of log q_e versus log C_e (Figure 5b) and are presented in Table 1. K_f can be defined as the adsorption capacity that represents the quantity of anionic dye ions adsorbed onto the fibers for a unit equilibrium concentration and value of $n > 1$ giving an indication of favorability of the adsorption process [28]. In this work, it is found that K_f, increased in the order of BTF-3(0.85 mg/g) < BTF-1 (0.94 mg/g) < BTF-4 (1.04 mg/g) < BTF-2 (2.00 mg/g) < BTF-5 (8.74 mg/g). Theoretically, adsorbent has finite number of sites and once all these sites are occupied by adsorbed molecules further adsorption cannot take place. Temkin-Pyzhev [23] considered the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. Temkin isotherm is expressed as equation (5).

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

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

A representative plot of qe versus ln Ce (Figure 5c) enables the determination of the constants A and B. The constant B is related to the heat of adsorption. The constant A and B together with the R^2 values for the MR study are shown in Table 1. As seen from the Table 1, a high regression correlation coefficient, R^2, was shown by the Freundlich model. This indicates that the Freundlich model is very suitable for describing the sorption equilibrium of the dye by modified

BTF. When the linearity of the plots of the Langmuir, Freundlich and Temkin-Pyzhev T models was compared, it is found that the Freundlich model has a better fit. Thus it is reasonable to conclude that the adsorption of the colored substance on the fibers that consist of heterogeneous adsorption sites that are very similar to each other in respect of adsorption phenomenon.

CONCLUSION

The present work establishes that modified banana trunk fibers, in particular sulphuric acid treated is an efficient biosorbent in the removal of methyl red from aqueous solutions at pH 3. The amount of MR sorbed was above 96% over a range from 100 to 5000 mg/l of dye concentration when 1.2 g/l of sorbent was used. Banana trunk fibers are very cheap, easily available and renewable. This study revealed that this biosorbent could be used as a tool for the development of low-cost biomaterial-for the treatment of coloured dye.

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