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RESEARCH ARTICLE

STUDIES ON THE REMOVAL OF METHYL ORANGE FROM AQUEOUS SOLUTION USING MODIFIED BANANA TRUNK FIBRE

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Abstract

Banana trunk fibers are abundantly available and are usually discarded as an agricultural waste. However, in recent times it has used an efficient sorbent for methyl orange. Here, we describe the use of modified BTF as an efficient sorbent for methyl orange. The effect of pH, amount of adsorbent and concentrations of adsorbate were studied using modified Banana trunk fiber. All the experiments were carried out at normal temperature (25-28⁰C) and neutral pH. A set of reading taken by varying pH shows that adsorption capacity also influenced by pH of the two kind of adsorbent prepared, adsorbent prepare by oven drying is found to be more effective than adsorbent by natural drying. A kinetic model applied to the adsorption by banana trunk fiber was evaluated and it was found that the equilibrium data where well described by Type I adsorption model.

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INTRODUCTION

The effluents from textile, leather, food processing, dyeing, cosmetics, paper and dye manufacturing industries are important sources of dye pollution. Many dyes and their breakdown products may be toxic for living organisms. Therefore, decolonization of dyes becomes an important process in wastewater treatment (1-5). 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 (6-12). 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. 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. Nevertheless, the high cost of activated carbon contributes its disadvantages as an adsorbent. 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 (13-20). 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 orange (MO) were compared with that of the untreated BTF.

Reactive dye - methyl orange

Chemical name

: Acid Orange 52; Sodium, Dimethyl amino benzene sulfonate;
4- [Dimethyl amino] phenyl azo benzene sulfonic Acid, sodium salt; Orange III;
Tropaeolin D

Trade name	: Methyl Orange
Molecular formula	: $C_{14}H_{14}N_3NaO_3S$
Molecular weight	: 327.34 g/mole

MATERIALS AND METHODS

Preparation of adsorbent

Banana trunks from the family of *Musa acuminata* 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 70⁰ until a constant weight. The resulting material was grounded using a Waring commercial 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. Mercerization (BTF-1), the fibers were immersed in 5% NaOH solution for 48 hr at 25⁰, acetylating (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 H₂SO₄ for 2 min, 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.

Adsorbate

The molecular structure of MO is depicted in 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 (0.20g) into 2.50 mL Erlenmeyer flasks containing 50 mL of different initial concentrations (100-500 mg/L) of dye solution of pH 5. The flasks were agitated in an isothermal water-bath shaker at 150 rpm and 25⁰ for 2 hours 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 single beam UV/Vis spectrophotometer at 525 nm. The amount of equilibrium adsorption, q_e (mg/g), was calculated by:

$$q_e = (C_0 - C_e) \frac{V}{W}$$

Where, C_0 and C_e (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)

Calculations

A. Initial concentration sample is calculated as follows

$$q_e = (C_0 - C_e) \frac{V}{W}$$

Where,

- q_e = The amount of equilibrium adsorption, (mg/g).
- C_0 = The liquid-phase concentration of dye at initial concentration, (mg/lit).
- C_e = The liquid-phase concentration of dye at equilibrium, (mg/lit).
- V = The volume of solution, (ml).
- W = The mass of dry sorbent, (g).

B. Percentage of colour removal

$$\frac{C_0 - C_e}{C_0} \times 100$$

% of colour removal =

Where,

- C_0 = The liquid-phase concentration of dye at initial concentration, (mg/lit).
- C_e = The liquid-phase concentration of dye at equilibrium, (mg/lit).

RESULTS & DISCUSSION

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 MO on the sulphuric acid treated BTF at different initial dye concentrations. It was observed that increasing initial dye concentration significantly increased the uptake of MO on the adsorbent. These results were also in agreement with previous studies. It was observed that a large amount of MO 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. 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. The removal of higher dye concentrations needed longer contact time than those of lower dye. We observed that a large amount of MO was removed at 300 mg/L of initial concentration for 0.2 g/L of adsorbent dose, pH of 3.

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. 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. 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 °) for 2 h equilibrium time. It was observed that the uptakes were much higher in acidic solutions than those in natural conditions.

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. A similar observation was also seen for the adsorption of acid red 183 and acid green 25 onto shells of bittim and removal of acid blue 62 (AB62) on aqueous solution using calculated colemanite ore waste.

Effect of sorbent dose

The effects of sorbent dose on the removal of MO are shown. As the sorbent dose was increased from 0.4 to 1.2 g/1, percentages of MO sorbed on the modified banana trunk fibers increased. Increase in the sorption percentage of MO 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. The linear form of Langmuir isotherm equation is given in equation.

$$\frac{c_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e$$

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_0 and b are 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 $1/Q_0$ was obtained. The value of Q_0 was determined from the Langmuir plot at the concentration range 100 to 500 mg/L and then the b value was calculated and tabulated in Table 1/ Q_0 . 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.

$$R_L = \frac{1}{1 + b C_0}$$

The values of R_L were found to be 0.389, 0.268, and 0.370, for BTF-1, BTF-2, and BTF-3, respectively suggesting the isotherm to be favorable at the concentrations studied. The Freundlich isotherm model considers a heterogeneous adsorption surface that has unequal available sites with different energies of adsorption and can be represented by equation.

$$\log q_e = \log K_f + n(\log C_e)$$

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 $\log C_e$ and are presented in. 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. In this work, it is found that K_f , increased in the order of BTF-3 (22.787 mg/g) < BTF-1 (22.38 mg/g) < BTF-2 (46.45 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 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.

EFFECT OF INITIAL CONCENTRATION

Mass of adsorbent	: 0.2 mg / lit
Dye concentration	: 100~500 mg / lit
Constant	: Time, Pressure
Time	: 2 hours

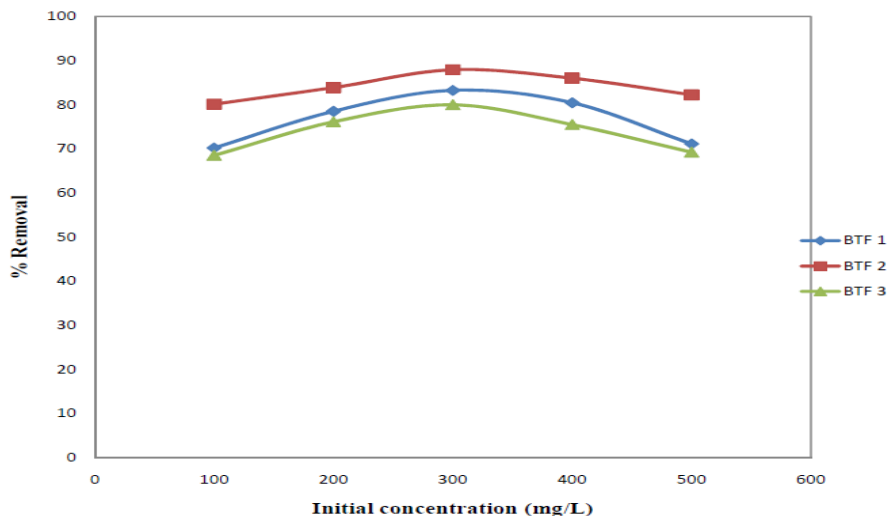


Figure 1: Effect of MO concentration on the adsorption of MO on acetylation treated banana trunk fibres (weight fibres=0.20 g, temp=25-27 °, stirring rate 150 rpm and pH 3)

EFFECT OF pH

Dye concentration	: 500 mg / lit
pH Concentration	: Variable
Constant	: Concentration, Time
Time	: 2 Hours

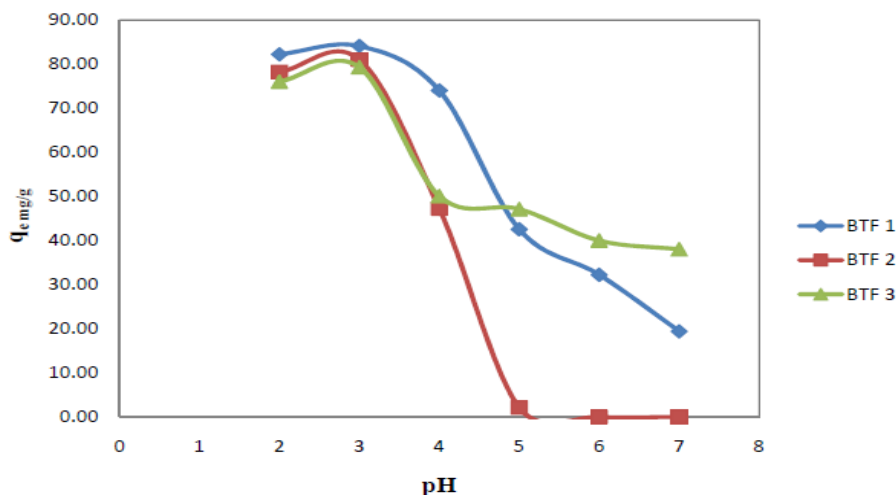


Figure 2: Effect of pH concentration on the adsorption of MO on treated banana trunk fibre (Initial concentration=500 mg/L, weight fibres=0.20 g, temp=25-27 °C, stirring rate 150 rpm and time 120 min)

ADSORPTION ISOTHERMS

Langmuir Isotherm Model

Dye concentration	: 100-500 mg / lit
Dose concentration	: 0.2g
Temperature	: 25-27 ⁰ C

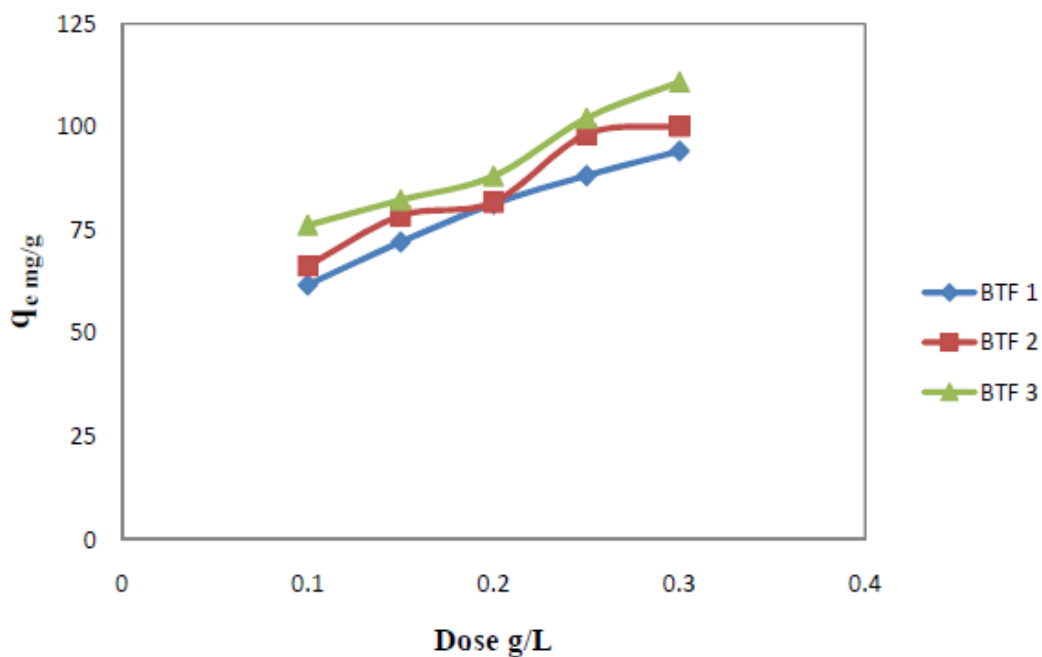


Figure 3: Effect of adsorbent dose on the adsorption of MO on treated banana trunk fibres (Initial concentration=500 mg/L, temp=25-27 °, stirring rate 150 rpm and pH 3)

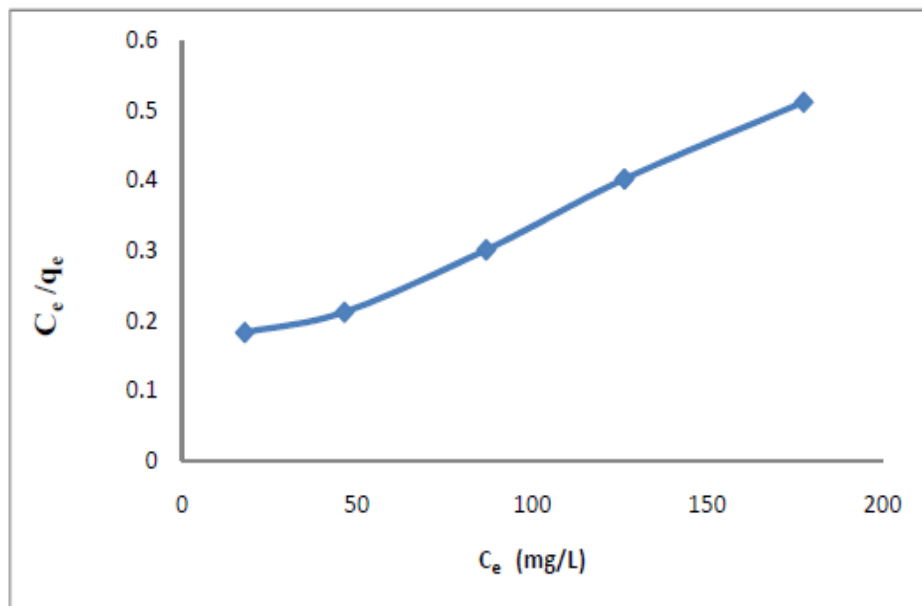


Figure 4: Langmuir isotherm for MO sorption unto the modified banana trunk fibers at ambient temperature (25-27⁰ C) for BTF 1

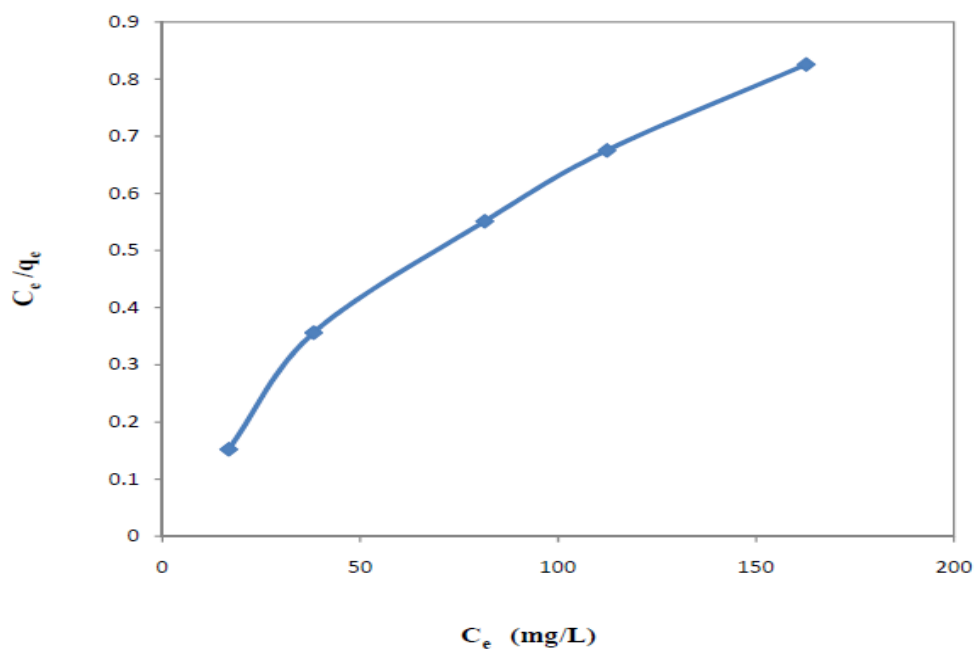


Figure 5: Langmuir isotherm for MO sorption unto the modified banana trunk fibers at ambient temperature (25-27⁰ C) for BTF 2

ADSORPTION ISOTHERMS
Freundlich Isotherm Model

Dye concentration	: 100-500 mg / lit
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Dose concentration	: 0.2g
Temperature	: 25-27⁰ C

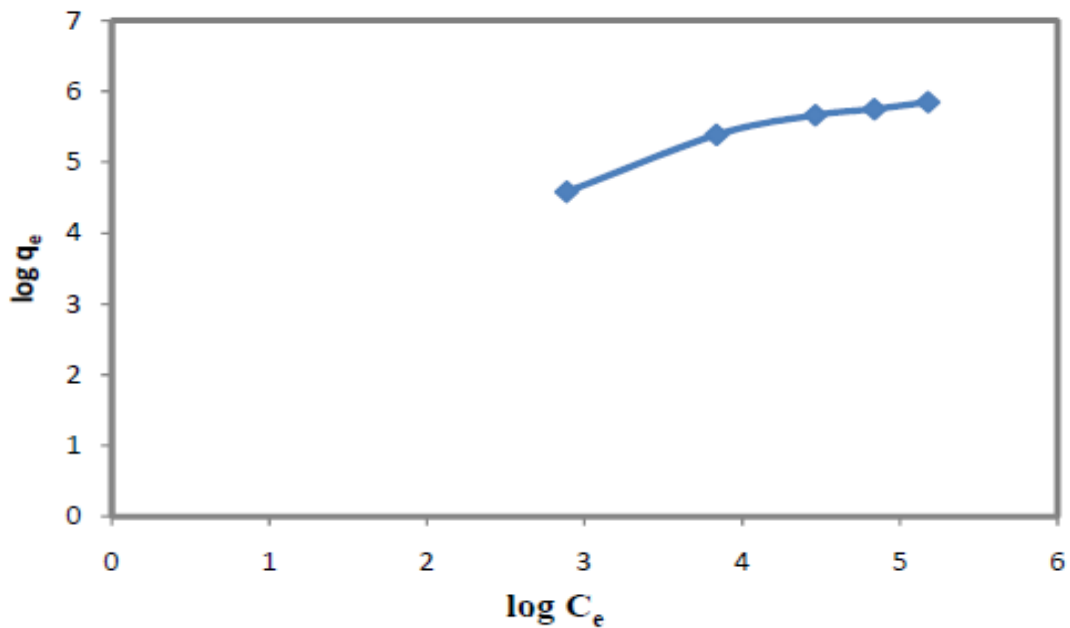


Figure 7: Freundlich isotherm for MO sorption unto the modified banana trunk fibers at ambient temperature (25-27⁰ C) for BTF 2

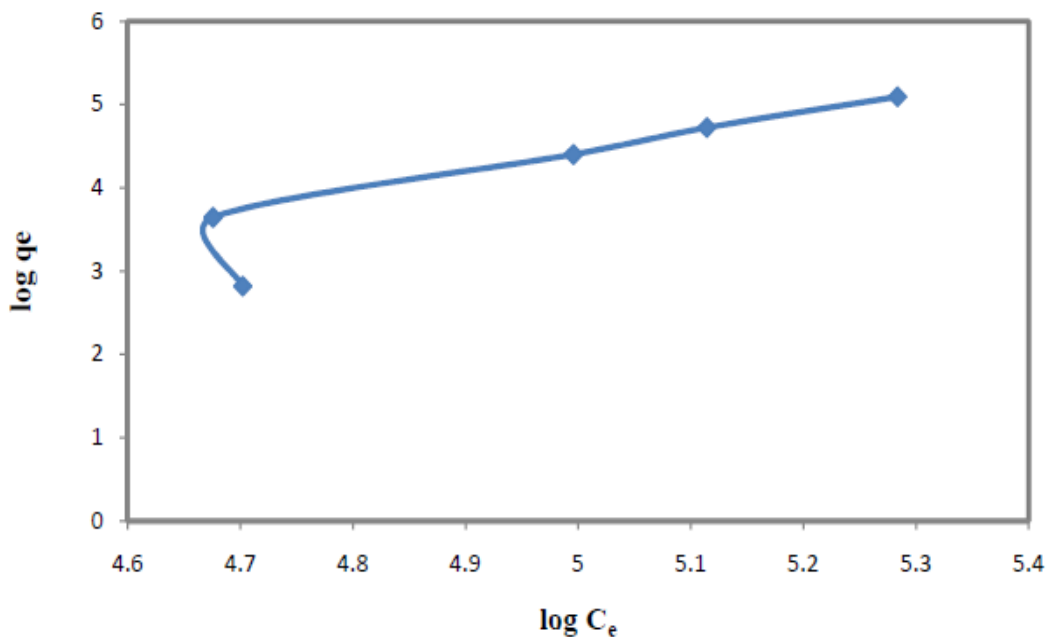


Figure 8: Freundlich isotherm for MO sorption unto the modified banana trunk fibers at ambient temperature (25-27⁰ C) for BTF 2

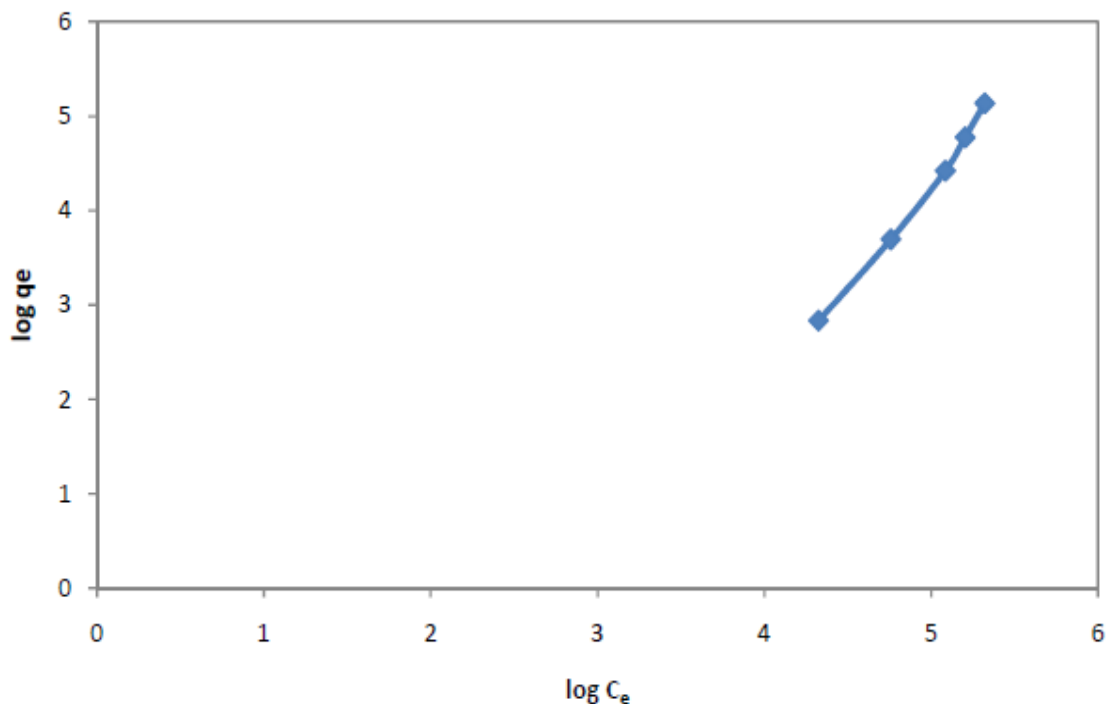


Figure 9: Freundlich isotherm for MO sorption unto the modified banana trunk fibers at ambient temperature (25-27^o C) for BTF 3

Isotherms	Modified banana trunk fibers		
	BTF 1	BTF 2	BTF 3
Langmuir			
Q ₀ (mg/g)	500	250	333.33
B (mg/L)	0.0157	0.0273	0.0170
R ²	0.996	0.960	0.996
Freundlich			
K _f (mg/g)	22.38	46.45	22.387
N	0.436	0.269	0.436
R ²	0.993	0.862	0.993

Table 1: Langmuir and Freundlich isotherm constants and correlation coefficients for sorption of methyl orange

CONCLUSION

This work was concluded with that modified BTF can be used as efficient sorbent for MO and the results will be helpful in studies of industrial effluents comprising MO. Nowadays dye based industries are polluting the water bodies. Here presently there are many methods for sorbing heavy metals and toxic compounds from the industrial effluents but need for efficient method paved way for utilizing agricultural wastes as sorbents. K.S. Lee et al worked with banana pith to sorb electroplating waste and synthetic solutions while here in this work it has been shown how modified banana trunk fibers acts as adsorbent at different pH and dose.

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