

Removal of Methyl Orange from Solutions using Yam Leaf Fibers

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Abstract: This work aims to investigate the removal of methyl orange, a mutagenic azodye from various aqueous solutions using ground yam leaf fibers of the size 212-350 microns. The parameters studied were the effect of pH, amount of adsorbent, contact time and concentration of adsorbate. Equilibrium data were fitted to the Langmuir, Freundlich and Temkin - Pyzhev isotherm models. The data were best represented by the Freundlich model with an adsorption capacity and adsorption intensity of 2.40 and 1.14, respectively.

Keywords: Sorption; Methyl red; Biotransformation; Monoazo; Yam Leaf Fibers.

Introduction

Progress in industrialization in particular textile industries have 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 [1]. A majority of the used dyes are azo reactive dyes which are bright in color due to the presence of one or several azo ($-N=N-$) groups associated with substituted aromatic structures [2]. These dyes or their breakdown products are toxic to living organisms [3]. 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 [4]. 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 [5-7]. This has prompted enormous research interest in the

use of agricultural waste as starting materials because of their low-cost and widespread availability.

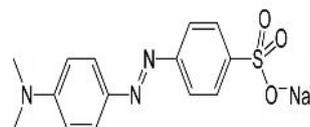


Figure 1. Molecular structure of Methyl Orange

Methyl orange (MO) is a commonly used monoazo dye in laboratory assays, textiles and other commercial products and has to be removed from water due to its toxicity [8-9].

Yam Leaf is of the genus *Colocasia* and is considered toxic due to presence of oxalate and as such, the leaf is often considered a waste. In the present work, application of ground yam leaf fibers of the size 212 - 350 micron for the removal of MO from various aqueous solutions has been studied.

Materials and Methods

Sorbent

Leaf of Yam plant from the family *Colocasia* were obtained locally and were boiled in distilled water for 1 hour and then dried in an oven at 70 °C until a constant weight was obtained. The resulting material was ground using a Waring Commercial high speed blender and sieved to isolate fibers of the size 212 - 350 micron.

Adsorbate

Methyl Orange, 4-dimethylaminoazobenzene-4'-sulfonic acid (MO), a bright orange crystalline powder with a molecular weight of 327.34 and melting point around 300 °C, was purchased from LABCHEM and used without further purification. The molecular structure of MO a water soluble dye is shown in Figure 1. MO is dark red in aqueous solution below pH 3 and the color brightens to orange as pH increases. A stock solution of MO (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

Adsorption experiments were carried out by adding 0.2 g of sorbent into 250-mL Erlenmeyer flasks containing 50 mL solutions of different concentrations (1, 10 and 100 mg/L) of MO. The temperature was controlled at 25 °C. Agitation speed was kept constant at 150 rpm for 180 min, which was sufficient to reach equilibrium. Since MO 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 500nm. The pH was adjusted by adding appropriate amount of

Results and Discussion

Effect of pH on biosorption

The efficiency of sorption is dependent on the pH of the solution [10] because variation in pH leads to the variation in the surface properties of the sorbent and the degree of ionization [11]. Thus, comparative experiments were performed over a pH range 2.0 – 8.0 to obtain the optimum pH for dye adsorption. The result depicted in Figure 2 shows that the sorption of MO increased from the initial pH 2 up to pH 3.0 and then decreased over the pH range of 4 – 8. This is attributed to the protonation of the fibers at low pH [12-13]. H⁺ ions provide a significantly strong electrostatic attraction between the fibers surface and the dye molecules leading to maximum adsorption.

either 0.1 M NaOH or 0.1 M HCl solution before each experiment. When the equilibrium was established, the supernatant was carefully filtered through Whatman filter paper (No. 1) which was pre-saturated with distilled water. It was then computed to dye concentration using standard calibration curve. The adsorption at equilibrium, q_e (mg/g), was calculated using equation (1).

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

where C_o and C_e (mg/L) are the liquid-phase concentrations of metals at initial and equilibrium, respectively. V is the volume (L) of the solution and W is the weight (g) of dry sorbent. For the determination of rate of sorption and the sorption equilibrium time, the residual metal in the supernatant was determined by allowing MO- fibers contact for different periods between 5 and 120 min. The MO-fibers sorption suspension was equilibrated at different pH values of 2 –8. For the adsorption isotherms studies, MO concentrations used for sorption ranged between 50 and 500 mg/L. The quantity of biomass was varied between 0.1 and 0.3 g to determine the BTF required for optimum level of sorption.

Spectroscopic study.

Fourier Transform Infrared (FTIR) spectrophotometer was used in this study to identify the characteristic functional groups in the yam leaf fibers. 5 mg of the fibers sample was mixed with dry potassium bromide (KBr). The mixture was thoroughly mixed and pressed at pressure of 4500 psi to form a KBr thin disc. Then the disc was measured to check the IR spectrum by 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

However, at pH above 3 the degree of protonation of the surface of the fibers will be less which results in the decrease in diffusion and adsorption thereby due to electrostatic repulsion [14-15]. The lower adsorption of the direct dyes in alkaline medium can also be attributed to the competition from hydroxide ions (OH⁻) with the anionic dye molecules for the adsorption sites. In this work, we also 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 2002 [16]. Therefore, all subsequent studies were carried out at pH 3 as the optimum pH.

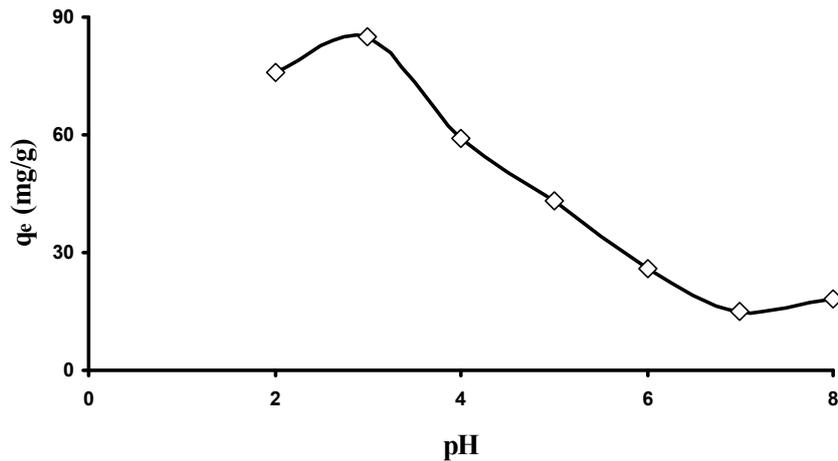


Figure 2. Effect of pH on the adsorption of MO on Yam Leaf fibers ($C_0 = 500 \text{ mg L}^{-1}$, Temp. =25-27°C, stirring rate 150 rpm, contact time 120 mins and weight of fibers = 0.20 g)

Effect of contact time and adsorbent dose on biosorption

The effect of contact time on the amount of MO adsorbed on the fibers was investigated at initial concentration of 500 mg/L. The system was subjected to an agitation speed of 150 rpm for 120 min. Figure 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 MO molecules via chemisorption [17]. Results shown in Figure 3 show that as the dosage of

adsorbent increases the adsorption increases proportionately. The increase of dosage increases adsorbent sites thus surface area of contact with the dyes increases. Therefore the amount of dye uptakes increases and consequently leads to a better adsorption [18]. This observed trend is mainly due to the increase in sorptive surface area and availability of more adsorption site [19].

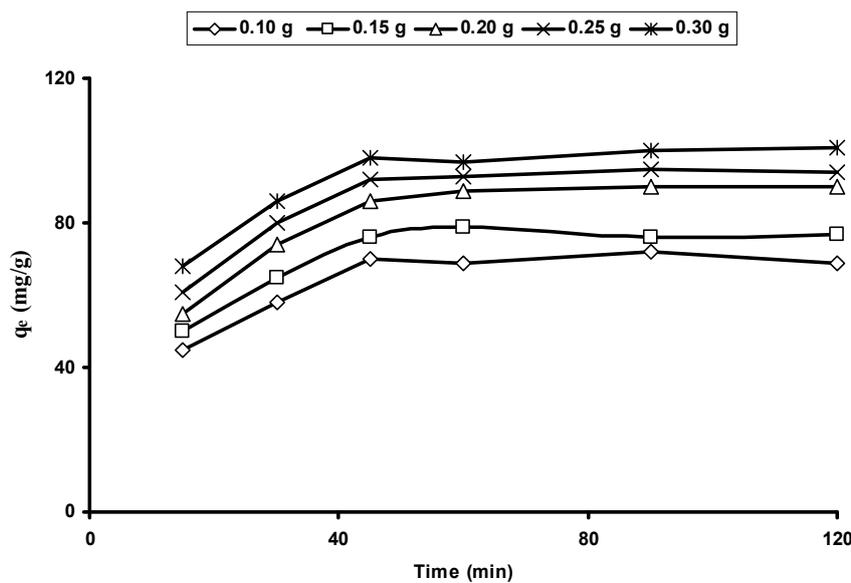


Figure 3. Effect of adsorbent dose on the adsorption of MO on Yam Leaf fibers ($C_0 = 500 \text{ mg L}^{-1}$, Temp. = 25-27°C, stirring rate 150 rpm and pH 3)

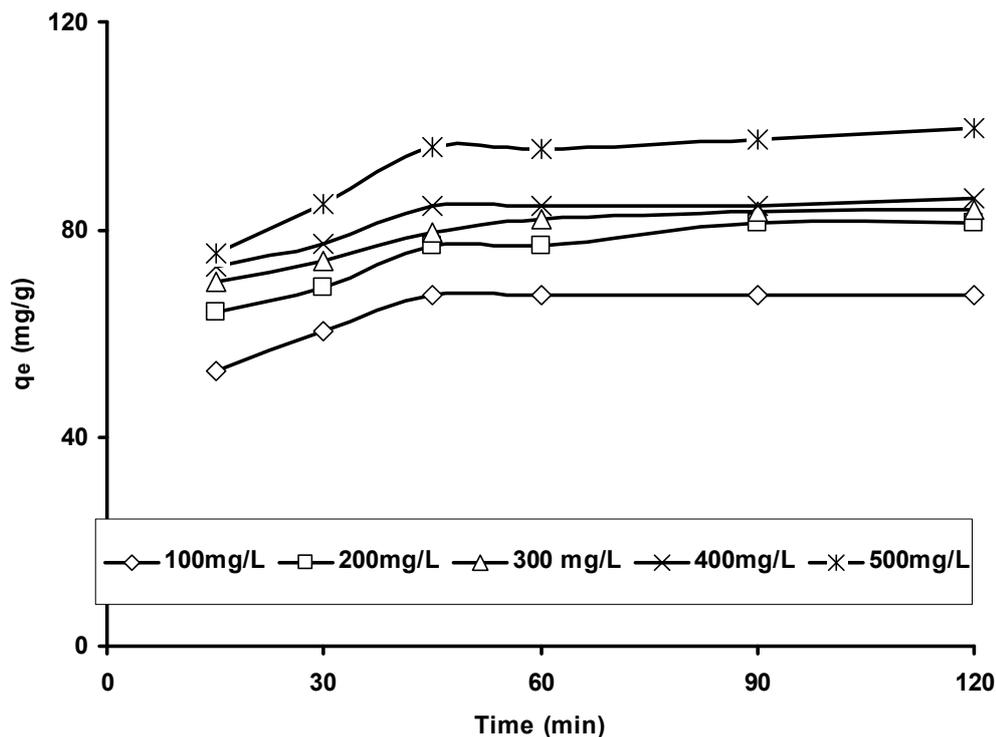


Figure 4. Effect of MO concentration on the adsorption of MO on Yam Leaf fibers (weight of fibers = 0.2g, Temp. = 25-27°C, agitation rate 150 rpm and pH 3)

Effect of initial MO concentration.

The results displayed in Figure 4 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 [14]. In addition, increasing the initial dye concentration increases the number of collisions between dye molecules and the adsorbent, which enhances the adsorption process.

Adsorption Isotherm studies.

Adsorption isotherm describes how solutes interact with adsorbents. Three isotherm models, Langmuir, Freundlich and Temkin-Pyzhev models were chosen to fit the equilibrium data. The applicability of the isotherm models to the adsorption study done was compared by judging the correlation coefficients, R^2 values. This will show 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 model that can be used for design purposes [20].

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).

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

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_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. 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).

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

The values of R_L were found to be 0.476 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).

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

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 Table 1. K_f can be defined as the adsorption capacity that represents the quantity of metal 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 and n values

were 2.40 and 1.14, respectively. Temkin-Pyzhev model [23] considers 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)

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

$$\text{where } B = \frac{RT}{b}$$

A plot of q_e versus $\ln C_e$ 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 MO are shown in Table 1. As seen from Table 1; very high regression correlation coefficient was shown by the Freundlich model compare to the other isotherm models. This indicates that the adsorption data of MO onto fiber at all ratios studied were best fitted to the Freundlich isotherm model. The applicability of Freundlich sorption model is also evident for non uniform surface of the fibers.

Table 1: Langmuir, Freundlich and Temkin-Pyzhev isotherm constants and correlation coefficients for the adsorption of MO on Yam Leaf Fibers

Isotherms	Parameters
Langmuir:	
Q_0 (mg g ⁻¹)	357.14
b (mg L ⁻¹)	0.002
R^2	0.979
Freundlich:	
K_f (mg g ⁻¹)	2.40
n	1.14
R^2	0.999
Temkin- Pyzhev	
A	0.05
B	37.65
R^2	0.967

Kinetics studies.

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 [24] as depicted in equation (6).

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

where q_e and q_t are the amounts of MO adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the rate constant. Values of k_1 at ambient temperature were calculated from the plots of $\log(q_e - q_t)$ versus t for different initial concentrations of MO. 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 2). On the other hand, the pseudo-second-order equation based on equilibrium adsorption [25] is expressed as equation (7):

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

where k_2 (g/mg min) is the rate constant of second-order adsorption. The linear plot of t/q_t versus t at ambient temperature, yielded set of R^2 values that are greater than 0.984 for all MO concentrations as shown

in Table 2. It also showed a good agreement between the experimental and the calculated q_e values (Table 2), indicating the applicability of this model to describe the adsorption process of MO onto the fibers.

Spectroscopic studies.

Fourier transform spectroscopy (FTIR) is done at the end of the study to determine the functional groups that exists on the fibers. The IR spectrum of Yam Leaf fibers in the form of KBr pallet is shown in Figure 5. Identification of the characteristic peaks is based on previous studies of banana stem fibers [26]. The typical functional groups and their corresponding IR signals are listed in Table 3. The band at 3290 cm^{-1} is due to the stretching of hydroxyl groups that are present in the yam leaf fibers. The bands at 2850 and 2918 cm^{-1} is due to the C-H symmetrical and asymmetrical stretching of saturated (sp^3) carbon, respectively. The band at 1644 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 [27-28]. The band at 1615 cm^{-1} is due to C=C stretching associated with the aromatic skeletal mode of fibers containing lignin [29]. The weak bands at 1373 and 1250 cm^{-1} are assigned to C-O stretching and O-H bending, respectively. The bands at 1072 and 782 cm^{-1} are assigned to C-OH bending and CH_2 rocking, respectively.

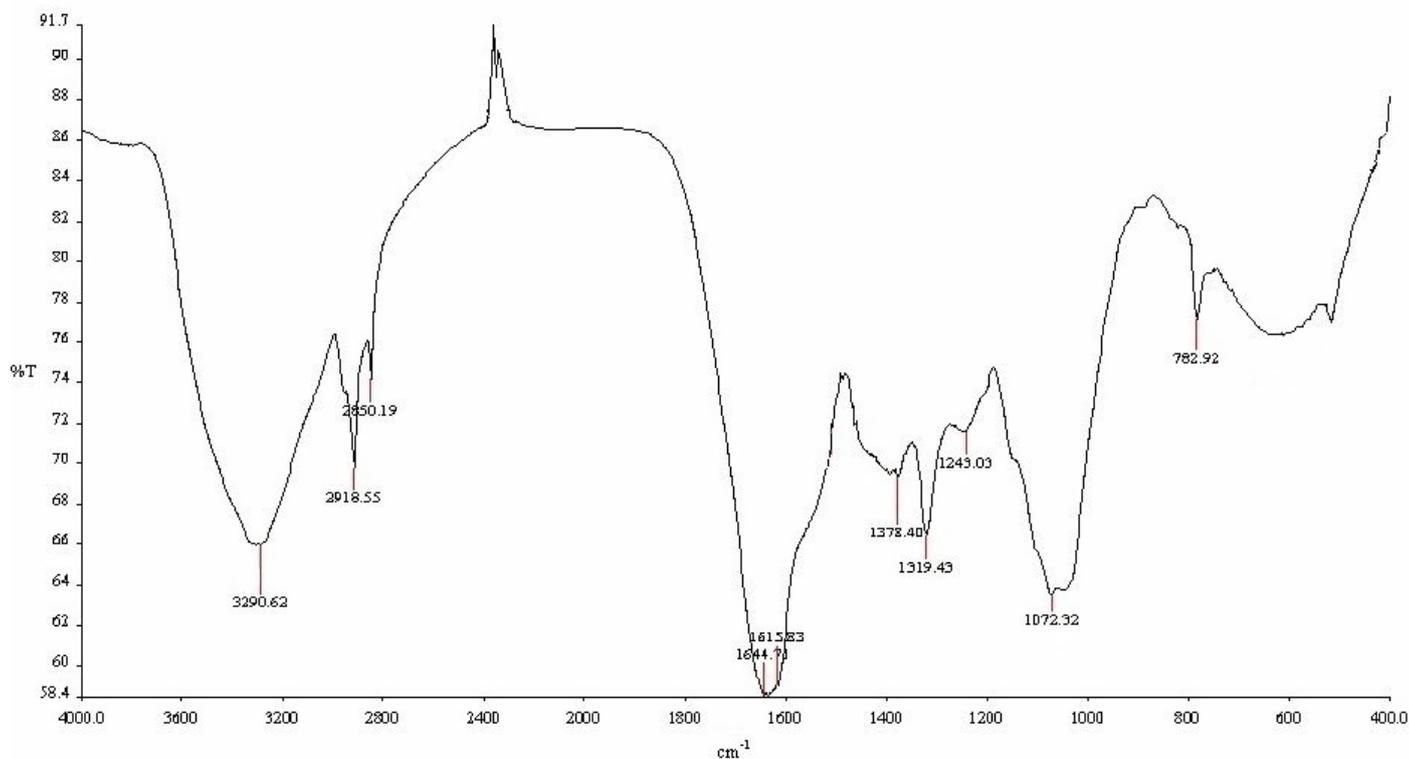
Table 2: Comparison of the pseudo first-order, pseudo second order adsorption rate constants and calculated and experimental q_e values obtained at different initial MO concentrations

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	24.265	1.3817	0.000	0.7497	4.6621	26.132	0.9992
200	43.795	1.9792	0.034	0.642	0.0196	46.795	0.9897
300	60.026	1.4793	0.035	0.9059	0.0122	64.026	0.9892
400	72.180	1.8145	0.001	0.8486	0.0326	71.150	0.9841
500	82.413	1.4575	0.004	0.9989	0.1164	82.193	0.9931

Table 3: Infrared spectrum data of yam leaf fibers

Frequency, cm-1	Assignment
3290.62	OH stretching
2850 ms	C-H stretching
1644.70, 1615.83 w	C = O stretching
1636 ms	O-H bending (of H ₂ O)
1618 s	C = C stretching
782.93 w	CH ₂ bending
1373 w	O-H bending
1318 m	C-C and C-O stretching
1249 w	C-O 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

**Figure 5. Infrared spectra of Yam Leaf fibers**

Conclusion

The use of yam leaf fibers of the size 212 - 350 micron for the removal of MO from aqueous solutions was investigated. The effect of various parameters such as pH, sorbent dose, contact time and dye concentration was studied. The kinetics of direct dye adsorption of MO on the banana pseudostem fibers follows the pseudo-second-order model. The equilibrium data fit well in the Freundlich model of adsorption, which clearly suggests a heterogeneous coverage of the dye molecules at the outer surface of the fibers. The

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present work demonstrates that Yam Leafs, which are abundantly available but generally considered as agricultural waste, can be utilized as efficient sorbents for the removal of MO from aqueous solutions.

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