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Enhancement removal of methylene blue from water by using modified beetroot fibers-SDS (Sodium dodecyl sulfonates)

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ABSTRACT

Beetroot was used to clean water contaminated by methylene Blue (MB). Parameters such as particle size of fibers, initial concentrations, pH of the solutions and rates of effluent were studied to optimize the conditions of removal dyes from industrial wastewater. It has been observed that the efficiency of dyes removal increases when fiber's size decreases (from 100 to 50 microns). The pH value to remove maximum of methylene blue is 6.5. Adsorption parameters were determined using both Langmuir and Freundlich isotherms. The chemical modification of fibers by an anionic surfactant such as sodium dodecyl sulfate (SDS) increases the efficiency of the dye's elimination two times.

KEYWORDS

Adsorption;
Beetroot fibers;
Methylene blue (MB);
Industrial colored water;
Sodium dodecyl sulfonate (SDS).

INTRODUCTION

Dyes have long been used in dyeing paper and pulp, textiles, plastics, leather, cosmetics and food industries[1]. Color stuff discharged from these industries poses certain hazards and environmental problems. Colored compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem[2]. These dyes such as methylene blue (MB) are also harmful to aquatic life. MB dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion, and painful[3,4].

Removing color from wastewater can be done via several methods namely chemical, biological and physical[5-9].

Chemical methods use coagulation or flocculation[10] combined with flotation and filtration, precipitation-flocculation, electro flotation, electro kinetic coagulation and ozonation[11] to remove color.

Biological color treatment utilizes fungi, bacteria or other biomass (either dead or alive) and is widely accepted due to its economical advantage. Recently, work has been carried out over different biological alternatives for the adsorption of various dyes. For example Sargassum muticum algae[12], marine green alga *Ulva lactuca*[13], and *Chara aspera* algae[14], have been tested for removal of methylene blue.

Physical methods often applied are either using membrane filtration or adsorption techniques. Various treatment systems have been developed using activated carbon as the sorbent[15]. Researchers have studied the production of activated carbon from palm-tree cobs[4], plum kernels[16], cassava peel[17], bagasse[18], jute fiber[19], rice husks[20], olive stones[21], date pits[22], fruit stones and nutshells[23] and bamboo activated with potassium hydroxide (KOH) and carbon dioxide (CO_2)[24]. The advantage of using agricultural by-products as raw materials for manufacturing activated carbon is that these raw materials are renewable and potentially less expensive to manufacture.

While carbon has been used successfully to remove dyes from solution, it is, however, expensive. Alternative, cheaper sorbent materials such as bark[25], rice husk[26], coal, bentonite clay, cotton waste[27,28], biogas slurry waste[29] moss[30], banana pith[31] and coconut husks[32] have been used with varying degrees of success.

The present work deals with the adsorption of MB by beetroot fibers. Modified beetroot fiber was by SDS was used to increase the hydrophobic characteristics in order to increase the efficiency of MB removal from contaminated water.

MATERIALS AND METHODS

Chemicals and reagents

Methylene blue (MB) supplied by Sigma–Aldrich (M) Sdn Bhd. Beetroot fibers were collected from Bekaa (Lebanon), was used as an adsorbate after purification by ionized water. The fibers were cut into small pieces, air-dried and powdered in a grinder. The samples obtained were first sieved through a 100 μm sieve and then through a 50 μm sieve Sodium Dodecyl Sulfonate SDS was supplied from Fischer Scientific Co.

The fiber powder was soaked in distilled water for 24 hrs at room temperature, and air-dried then stored for use. Double distilled water was employed for preparing all the solutions and reagents. All reagents used for the preparation of solutions were of analytical grade.

Instruments

The UV absorption measurements were performed on a Shimadzu UV- 1650 PC. With 10 mm quartz cells were used for spectrophotometric measurements. The concentration of methylene blue solution, after and before adsorption was determined using a double beam UV spectrophotometer (Shimadzu, Japan) at 664 nm. It was found that the blank (water filtered through the beetroot fibers did not exhibit any absorbance at this wavelength and also that the calibration curve was very reproducible and linear over the concentration range used in this work. The IR spectrum was recorded on a FTIR spectrometer (UNICAM).

Preparation of the modified fibers

20g of fibers were transferred into a Beaker 500 ml containing 100 ml of aqueous SDS salt solution with 2.9g.L^{-1}. The mixture was then heated at 50°C and stirred for 4 hours. After filtration the fibers were washed by distilled water several times then dried at100°C for 24 hours.

Column procedures to remove TDS and heavy metals

The column consisted of a Plexiglas tubing (30 cm height, φ 4.0 cm) perforated at the bottom and connected to a pumping system. In order to assure homogeneity and reproducibility of the results, the column was filled by 30 g of fibers. The material was compressed inside the column to reach a density of o.4 g/ cubic centimeter. The flow rate of liquid was 4GPM (gallons per minute) at a pressure of 15 PSI. Also, we proceeded with the passage of 50 mL of solution, through the biomass filter and we have made about 10 passages from the same initial solution to study the saturation of fibers by metal cations.

Methylene blue solutions of different concentrations (1000 ppm, 300ppm, 200 ppm 100 ppm and 50 ppm) were prepared. The pH values were adjusted by the addition of aqueous HCl.

RESULTS AND DISCUSSION

FTIR for beetroot and SDS-beetroot

The natural fibers contain several chemical functions like hydroxyl, carboxylic, aldehyde, ketone and C=N as shown in the FTIR of the fibers in figure 1. These chemical functions will play an important role in the grafting of SDS molecules and the subsequent complexation of MB dye on the surface of fibers.

The fibers modified by sodium dodecyl sulfonate show shift of some lines and apparition of mew lines as shown in figures 2 and figure 3 Beetroot-SDS with peaks.

Effect of pH on the retention efficiency

To study the influence of pH on retention of beetroot fibers efficiency, we filtered a solution of BM (100ppm) through the filter at different pH starting from 1.5 to 7.

The solutions were filtered through the biofilters under the same conditions of mass filter and the volume of the MB solutions.

The optimal pH for the maximum of removal was at pH = 6.5.

Evolution of the UV-visible absorption spectra of methylene blue solution (100 ppm), filtered by unmodified beetroot fiber

Treatment of water polluted by MB using beetroot fibers has been tested by monitoring the evolution of MB before and after filtering the solutions by the fibers. The initial concentration of the MB was 100 ppm.

Spectrum shows a maximum absorption has λ_{max} = 664nm with an A = 1, 11 absorbance. 50 ml of BM was filtered through 20 g of beetroot unmodified fibers. Recovery after filtering solution has been tested by spectrophotometry.

Figure 4 represents the evolution of the MB spectra based on the number of passages from 1 until 5 (MB zero is the spectrum of the initial solution).

As shown in this spectrum, more than 98% of the MB was eliminated after the first filtration.

Percentage of retention of BM 100ppm by beet fibers non-modified according to the number of passages

The MB amount retained by the bio filter has been determined in a quantitative way by measuring after each passage the absorbance of the filtrate at 664 nm. The results are present in figure 5.

This figure shows that the first pass elimination was 99.6% while at the 5th passage the bio filter is still efficient and decreased slightly to 95% as elimination rates.

According to the results observed above the bio filter has yet important MB elimination efficiency and its saturation is still very far. This led us to work at higher concentration of MB.

Retention efficiency of MB 1000 ppm by beetroot fibers in function of the number of passages

To study the saturation of the beetroot fibers, solutions of MB (1000 ppm) were filtered through the beetroot fibers. Figure 6 shows changes of the percentage of retention of MB 1000ppm filtered through the fibers according to the number of passages of BM.

We note that after 6 passages, the effectiveness of the retention of the bio filter decreases 97% to 72%.

Size effect of the beetroot fibers on the retention efficiency of MB (1000 ppm) in function of the number of passages

This section deals with the size effect of the fibers on the retention efficiency of the MB. MB solutions (1000ppm) were filtered through the beetroot fibers under the same conditions as section 4-3 except varying the size of fibers using 100 and 50 micron.

TABLE 2 summarizes the retention efficiency of MB (1000 ppm) by the fibers in function of the sizes and the number of passages.

According to the figure 7, we observe that 50 micron-sized fibers have a greater retention efficiency than those 100 micron fibers and than normal size fibers labeled XL. Effective retention fibers 50 micron after 6 passages is 87 %, which of 100 micron fiber is 80 % while one XL fiber decreases up to 72%. Therefore, the particle size of fibers is an important factor influencing on the retention of the BM.

Retention of MB 1000 ppm by beetroot XL, 100 and 50 micron using modified fibers by SDS (Sodium dodecyl sulfonate),in function of the number of passages

The fibers XL, 100 and 50 micron are modified according to the method mentioned in the section 2-3. Then, MB 1000ppm solution was filtered through these

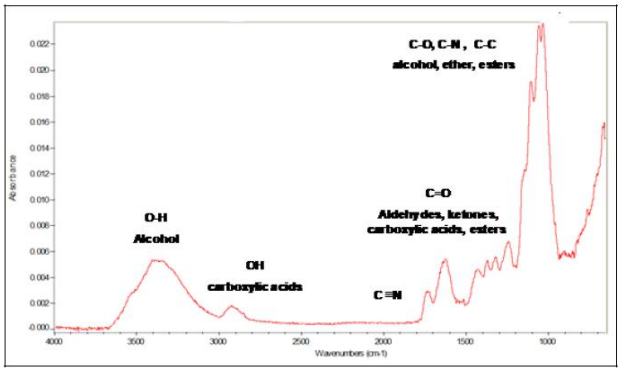

Figure 1 : FTIR Spectrum of Beetroot fiber showing different chemical functions

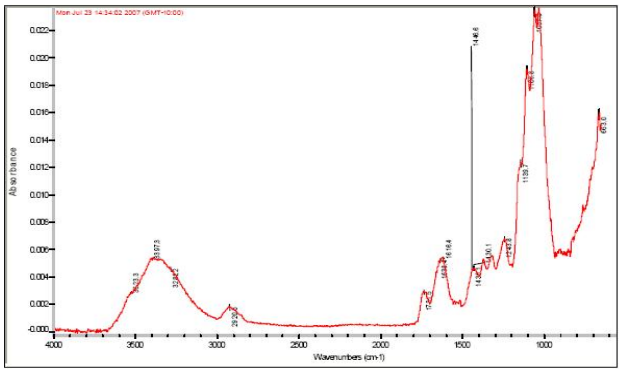

Figure 2 : FTIR Spectrum of Beetroot fiber showing different chemical functions with peacks

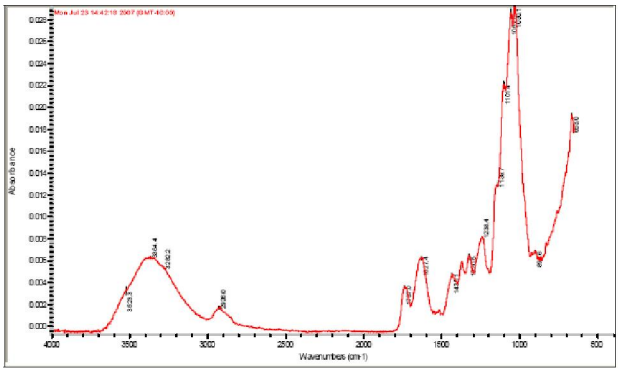

Figure 3 : FTIR Spectrum of Beetroot fiber modified by SDS showing different chemical functions with peacks shift lines and new lines attributed to the attachments of SDS chains

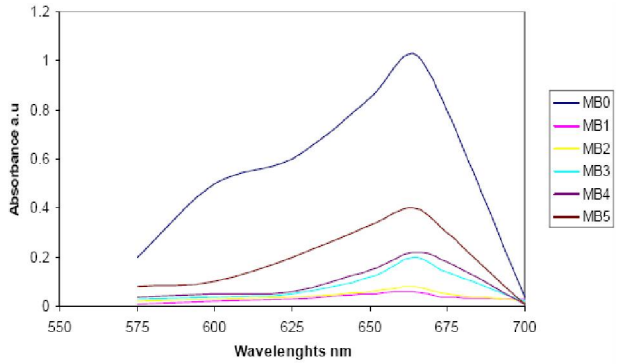

Figure 4 : UV-visible Spectra of MB before and after filtration by unmodified beetroot fibers

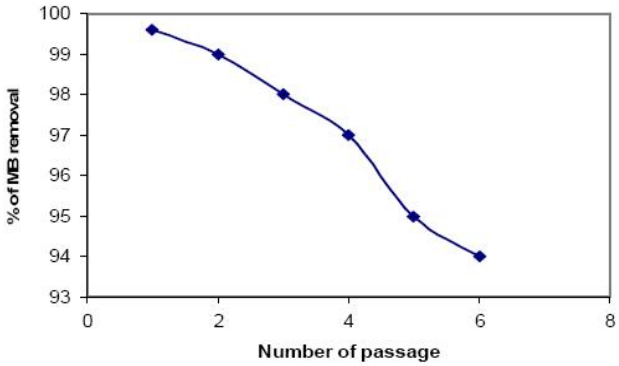

Figure 5 : Percentage of retention of MB at 100 pm by non modified beetroot in function of passage numbers

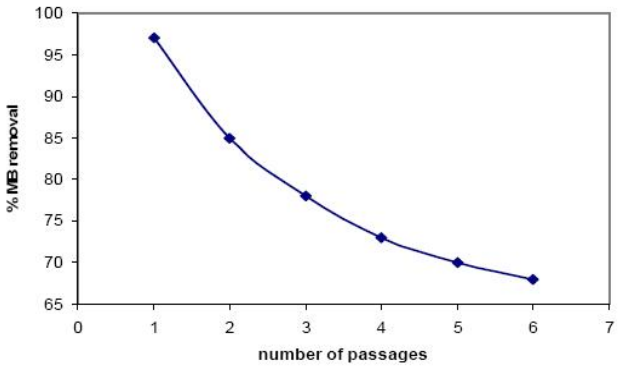

Figure 6 : Retention efficiency of MB 1000ppm filtered through the beetroot fibers according to the number of passages retention percentage

modified fibers.

TABLE 3 illustrates the retention efficiency of the fibers modified according to the number of passages and the sizes if the fibers.

The results of retention efficiency of fibers modified by SDS are shown in figure 8, After 6 passages; the elimination of MB 1000ppm was remarkable capacity ranging from 100% and 99% with the 50 microns. With the fibers 100 microns the capacity of elimination was ranging between 100 % and 95%, for modified XL fibers the efficiency was ranging from 99 to 83%. Therefore, smaller modified fibers have better retention of MB (1000ppm).

Effect of the modification of the by SDS on the retention efficiency of MB 1000ppm

The comparison between the retention efficiencies

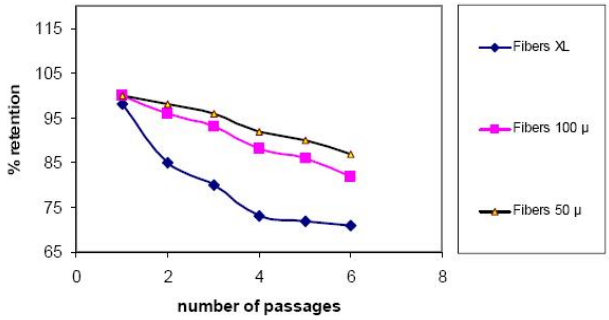

Figure 7 : Retention efficiency of MB by different sizes of fibers in function of number of passages (XL, 100 microns , 50 microns)

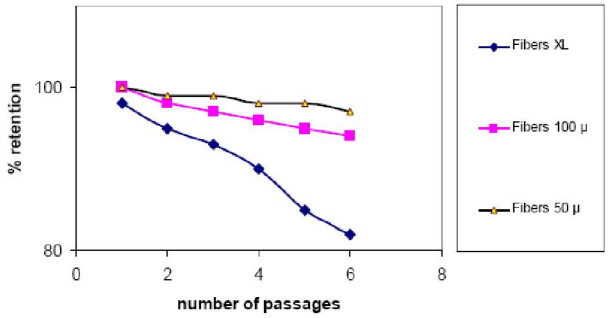

Figure 8 : Evolution of retention of MB by modified fibers at different sizes (XL, 100µm, and 50µm) in function of number of passages

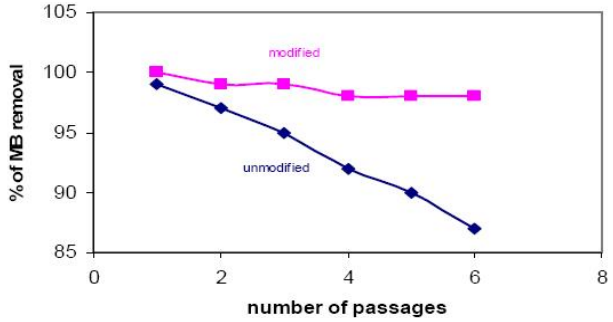

Figure 9 : Evolution of the retention capacities of modified and unmodified fibers (50 microns) of MB (1000ppm) in function of number of passages

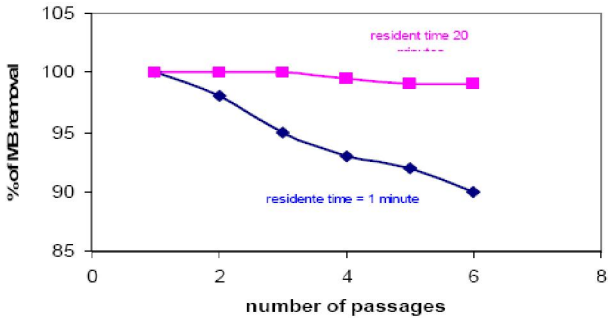

Figure 10 : Percentage of retention of MB 1000ppm by beetroot fibers in function of resident time (20 minutes Free filtration ; 1 minute forced filtration by special pump)

of the same size of fibers (50 µm) but different types. The first type was modified by SDS and the second type was unmodified

After 6 passages of MB (1000 ppm) through 20g of fibers 50 µm, the capacity of elimination was 87%, while the capacity of the modified fibers by SDS reaches the 90% after the 6th passage.

Effect of residence time on the effectiveness of the retention

The same process was applied during all our experiences. A volume of 50 ml of BM is filtered through a mass 20 g of fibers. Filtration is done either by free filtration $t_{\text{free time}}$ = 20 min or by forced filtration using a special pump $t_{\text{forced filtration,}}$ = 1 minute. Figure 10 shows that if the efficiency of retention is much better if the resident time increases.

Adsorption isotherms

Two important physiochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibrium of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent. The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. There are two types of adsorption isotherms: Langmuir adsorption isotherms and Freundlich adsorption isotherms.

(a) Langmuir isotherm

The Langmuir adsorption isotherm is often used for adsorption of a solute from a liquid solution. The Langmuir adsorption isotherm is often expressed as:

$$\mathbf{Q_e = X_m KC_e/(1+KC_e)}$$

where, Q_e is the adsorption density at the equilibrium solute concentration C_e (mg of adsorbate per g of adsorbent). C_e is the concentration of adsorbate in solution (mg/L). X_m is the maximum adsorption capacity corresponding to complete monolayer coverage (mg of solute adsorbed per g of adsorbent). K is the Langmuir constant related to energy of adsorption (L of adsorbent per mg of adsorbate). The above equation can be rearranged to the following linear form:

TABLE 1 : Summarizes the wavelenghts in both spectra of modified and non-modified beetroot fibers

No Lines	Beetroot wavelenghts cm^{-1}	Beetroot modified fibers wavelenghts cm^{-1}
1	3523	3523
2	3397	3364
3	3282	3282
4	2920	2926
5	1701	1731
6	1638	1627
7	1616	-
8	1430	1430
9	1243	1320
10	1239	1239
11	1106	1139
12	-	1101
13	1057	1046

TABLE 2 : Retention efficiency of MB by beetroot fibers: normal fibers (XL), 100 µm; 50 µm

Number of passages	% of retention of MB by the beetroot fibers	% of retention of MB by the beetroot fibers 100 µm	% of retention of MB by the beetroot fibers 50 µm
1	97	98	99
2	86	94	96
3	80	92	95
4	73	88	90
5	72	85	89
6	72	80	87

TABLE 3 : Retention efficiency of modified fibers at different sizes (XL, 100 µm, and 50 µm)

Number of passages	% of MB retention using modified XL fibers by SDS	% of MB retention using modified fibers by SDS (100 microns)	% of MB retention using modified fibers by SDS (50 microns)
1	99	100	100
2	95	98	99.5
3	92	97	99.3
4	90	97	99.2
5	85	96	99
6	83	95	99

$$C_e/Q_e = 1/X_mK + C_e/X_m$$

The linear form can be used for linearization of experimental data by plotting C_e/Q_e against C_e. The Langmuir constants X_m and K can be evaluated from the slope and intercept of linear equation.

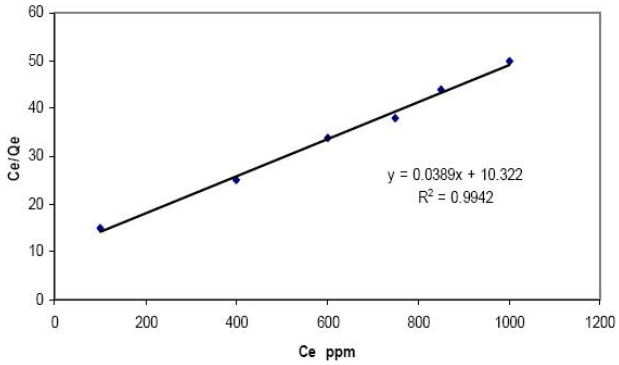

Figure 11a : Adsorption Langmuir isotherm of modified fibers 50 µm

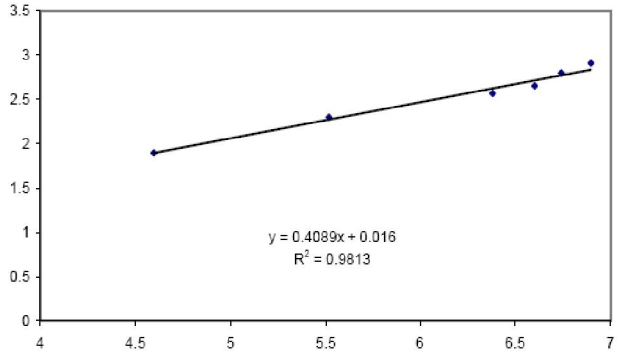

Figure 11b : Adsorption Freundlich isotherm modified fibers 50 µm

(b) Freundlich isotherm

The Freundlich isotherm is the relationship describing the adsorption equation and is often expressed as:

$$Q_e = K_f C_e^{1/n}$$

where, Q_e is the adsorption density (mg of adsorbate per g of adsorbent). C_e is the concentration of adsorbate in solution (mg/L). K_f and n are the empirical constants dependent on several environmental factors and n is greater than one.

This equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\ln Q_e = \ln Kf + 1/n \ln C_e$$

A plot of $\ln C_e$ against $\ln Q_e$ yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constants can be determined from the slope and the intercept.

(c) Method used for adsorption test

The method used for the adsorption tests for different methylen blue concentrations is as follows:

TABLE 4 : Experimental results of retention capacities obtained for different sizes of fibers modified and unmodified

Passages	MB removed by XL fibers each passage	MB removed by 100 microns fibers each passage	MB removed by 50 microns fibers each passage	MB removed by XL modified fibers each passage	MB removed by 100 micros modified fibers each passage	MB removed by 50 microns fibers each passage
1	48	49	49,5	49,5	50	50
2	43	47	48	47,5	49	49,75
3	35	46	47,5	46	48,5	49,65
4	30	44	45	45	48,5	49,6
5	28	42,5	44,5	35	48	49,5
6	22	40	43,5	30	47	49,5
7	18	28	30	25	30	48
8	15	20	25	15	20	47
9	12	15	22	15	15	37
10	10	15	20	12	15	35
11	10	10	20	10	10	35
Total mass (mg)	271	356,5	395	330	381	500
Total Mass of MB(mg) removed by g of fibers	13.5	17,8	19.75	16.5	19.05	25

(1) 20g of fibers as an adsorbent were transferred into a column and different concentrations of MB were filtered through the column.

(2) For each concentration, the MB was filtered through the modified fiber several times until complete saturation of the filter fiber. The concentrations that has been tested were 1000, 850, 750, 600 and 400 ppm.

(3) Q_e was determined and C_e/Q_e vs C_e and $\ln Q_e$ vs $\ln C_e$ were plotted.

The Langmuir constant X_m (maximum adsorption capacity) and the Freundlich constant K_f were obtained from the linear equations. The values are summarized in TABLE 4. The Langmuir and Freundlich plots are presented in figure 11a and 11b respectively.

For both isotherms model we observed that the estimated adsorbed quantities of the MB are fitted.

We have selected modified fibers (100 microns) to study Langmuir and Freundlich equations where the maxima of retentions and the concentrations at the equilibrium were summarized in TABLE 5.

The Langmuir and Freundlich isotherms are presented in the figure 11a and 11b.

Langmuir constant Xm (Maximum capacity of adsorption) and Freundlich constant Kf were obtained using their linear equations. The results are summarized in the TABLE 6.

In the two models Freundlich and Langmuir, the amount absorbed by fibers provides acceptable linearity which confirms the accuracy of our experimental results.

CONCLUSION

In this study, unmodified and SDS-modified beetroot fibers have been tested for the removal of MB from polluted water. The modification of fibers using SDS has been shown to enhance the removal capacity compared to the unmodified fibers. Removal of MB from polluted water is highly pH dependent and the best results were obtained at pH 6.5. The removal efficiency was found to increase significantly with the decrease of fiber size. The modified beetroot fibers presented a higher efficiency compared to both the unmodified beetroot fibers.

The isotherms of both Freundlich and Langmuir were established and they described the removal process indicating favorable elimination of MB from polluted water.

This removal mechanism involves either complexation by chemical functions of fibers and adsorption by electrostatic Van Der Waals interactions. The presence

TABLE 5 : Maxima of retentions and the concentrations at the equilibrium

Ce ppm	Qe	Ce/Qe	LnQe	Ln Ce
1000	19.05	52.49	2.947	6.9
850	16.5	43	2.8	6.74
750	14.5	39	2.6	6.6
600	11.5	31	2.44	6.38
400	7.6	21	2.028	5.99
100	7.1	14.08	1.96	4.6

TABLE 6 : Constants of Langmuir and Freundlich modified fibers 50 microns

Aqueous solution of MB	Langmuir constants			Freundlich constants		
Parameters	Xm (mg/g)	K (L/mg)	R^2	K_f	1/n	R^2
	24.5	0.0037	0.9942	1.016	0.4089	0.98
Equations	y = 0.0389x + 10.322			y = 0.4089x + 0.016		

of the chain of dodecyl sulfonate increases the hydrophobecic charateritics and then the efficiency of the MB removal.

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