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Evaluation of Utilizing Sulfonated Barely Straw and Coconut Shell Bio-Adsorbents in Removal of Methylene Blue Dye from Aqueous Solutions

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ABSTRACT

In this study, bio-adsorbent from barley straw and coconut shell were used as bio-adsorbent to remove methylene blue (MB) from wastewater, which were prepared by refluxing barely straw (BS) and coconut shell (CS) in concentrated sulfuric acid, and have a specific surface area 1.165 and 11.759 m^2/g for BS-SO_3H and CS-SO_3H respectively. Several parameters are studied such as pH and initial concentration of dye in wastewater, and it is found that the adsorption capacity is improved in the basic medium; also, it is directly proportional to the initial concentration. The results from the adsorption process were found to be more fitted with Langmuir isotherm than the Freundlich isotherm for both adsorbents, so it confirmed that the adsorption process is monolayer. The maximum adsorption capacity was found to be 256.4, and 344.8 mg/g for barley straw and coconut shell respectively, and the design parameters of packed bed column were calculated for batch adsorption process.
Keywords: Adsorption, Bio-adsorbent, Wastewater treatment, Agricultural wastes

1. INTRODUCTION

Water crisis and the high solid waste generation rate are the most important issue nowadays. Water polluted with dyes are generated with high rates as a result from textile industries, so the elimination of dyes using bio-adsorbents is a win – win situation in which water treatment is performed using different treated solid agricultures wastes. Wastewater treatment is the way to restore the desirable quality of water used by people. Treatment includes biological, chemical, or physical processes. Water possibly treated to the desired quality degree; although, the cost of achieving that purity increases as its purity increases [1]. Dyes are essentially organic compounds, often referred to as coloring agents, attachment to the textile surface to impart color. Dyes are widely used in many industries including paper, printing, textiles, foodstuffs, cosmetics, etc. [2]. Adsorption technique is the most popular practice in color removal. This technique was found to be the easiest and most economical one to achieve dyes removal from textile effluents. There have been many researches for the get rid of dyes using numerous low-price materials, including agricultural wastes, and industrial wastes [2].

In adsorption process a higher concentration of materials is found on the interface of two phases. The interface can be liquid-liquid, solid-liquid, liquid-gas or gaseous-solid. Adsorption process has several techniques such as batch fixed bed, continuous fixed bed, continuous moving bed, and continuous fluidized bed [3].

Bio-adsorbent material is mainly composed of carbon atomic and its structure is characterized by complexity and high porosity. It is produced from coconut shell, peat, soft and hard wood and olive pits, and other agricultural wastes [4].

Many studies produced activated carbon from different sources. Bagasse, coconut shells and husks were treated by using nitrogen in a fixed bed reactor. After carbonization, the product was dried, ground and screened [5].

The bio-adsorbents used in the present study were previously prepared by refluxing barley straw and coconut shell with sulfuric acid, where barley straw and coconut shell were treated with reflux by immersing in 94%, 98% sulfuric acid with 10, 4 L/S ratio for 2, 2.5 h respectively, and also, characterized and it was found to be highly efficient bio-adsorbent environmentally friendly, low-cost and sustainable material to be used in wastewater treatment [6].

The objective of this paper is to use the previously acid treated with reflux barely straw and coconut shell as adsorbents to eliminate methylene blue (MB) from wastewater. Several parameters that effect on adsorption capacity are studied such as pH and initial concentration of MB. In this study Langmuir and Freundlich isotherm models are used to analyze the experimental data. Whereas, pseudo-first order and pseudo-second order kinetic models are used to analysis the results of time dependent adsorption.

2. MATERIAL AND METHOD

2.1. Materials

Sulfonated barley straw and sulfonated coconut shell prepared by sulfuric acid reflux, Hydrochloric acid AR and Methylene blue (MB) dye were purchased from Alpha chemika Pharmaceuticals and Chemicals Company, Sodium hydroxide was purchased from El Nasr Pharmaceuticals and Chemicals Company, Cairo, Egypt.

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2.2. Batch adsorption experiments

The effect of the pH on the adsorption of MB is examined by putting 40 ml of 600 ppm MB solution in a range of pH (3.5-13.5) with 40 mg of BS-SO_3H or CS-SO_3H for 24 h. Sodium hydroxide and hydrochloric acid 1 M are used for pH adjustment. pH is measured by using pH meter.

The effect of initial concentration of methylene blue is examined by putting 40 ml of MB in a range of concentration (100-500 ppm, pH=11.5) with 40 mg of BS-SO_3H or CS-SO_3H for 24 h.

The optical density of MB dye was measured at 630 nm to calculate dye concentration using Ultraviolet – visible spectrophotometer (model SPECTRO DR 2800) in National Research Centre NRC**.**

Langmuir and Freundlich isotherm models are used to analyze the experimental data. Whereas, pseudo-first and second order kinetic models are used to analyze the results of time dependent adsorption. Langmuir isotherm is preferred to use in case of adsorption in monolayer the adsorbent. The isotherm models were expressed by the following equations:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{K_L Q_m} \qquad (1)$$

$$lnQ_e = \frac{1}{n} \ln C_e + \ln K_f \qquad (2)$$

C_e: the equilibrium concentrations (mg /L), Q_e and Q_m: the equilibrium and maximum adsorption capacities (mg/g), K_L (L/mg): the Langmuir constant, K_F and n: Freundlich constants.

The kinetic models were expressed by the following equations:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_2 Q_e 2} \qquad (3)$$

$$loq\ (Q_e - Q_t) = loq\ Q_e - \frac{K_1 t}{2.303} \qquad (4)$$

Q_t: the adsorption capacity (mg /g) at time t (min), K_1: the pseudo-first order (min^{-1}), and K_2: the pseudo-second-order rate constants (g/ mg. min)

The equilibrium adsorption capacity was studied by the following equation:

$$Q_e = \frac{C_0 - C_e}{m} * V \qquad (5)$$

C_0: the concentrations of the dyes (mg/L) at the beginning, C_t: the concentrations of the dyes (mg/L) at time t, m: the mass of the adsorbent (g), V: the volume of dye solution (L) [7].

3. RESULTS AND DISCUSSION

3.1. Effect of pH

The equilibrium adsorption capacity of MB is performed experimentally in pH range from 3.5 to 13.5. It was noticed that the adsorption capacity increased from 220 mg/g to 560 mg/g with increasing pH up to 11.5 as displayed in Figures (1), (2). There is no significant change in the adsorption capacity at higher pH. Methylene blue is a cationic dye which is attracted to the negative charge on the bio-adsorbents.

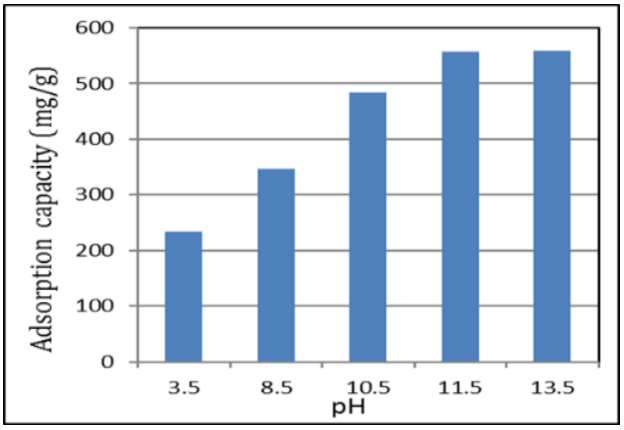

Figure 1: Effect of pH on the adsorption capacity of BS-SO_3H towards MB

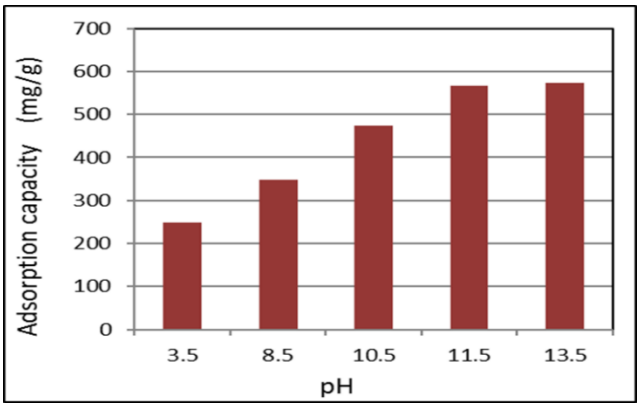

Figure 2: Effect of pH on the adsorption capacity of CS-SO_3H towards MB

3.2. Effect of initial concentration on the adsorption of MB

The effect of initial concentration on equilibrium adsorption capacity was studied at pH 11.5, it was observed that the adsorption capacity of BS-SO_3H gradually increase from 66 to 277 mg/g with increasing initial concentration of MB dye from 100 to 500 ppm ,while the adsorption capacity of CS-SO_3H increase from 73 to 289 mg/g with increasing initial concentration of MB dye from 100 to 500 ppm as shown in Figures (3),(4).The increase in adsorption capacity is due to the greater concentration driving forces [8].

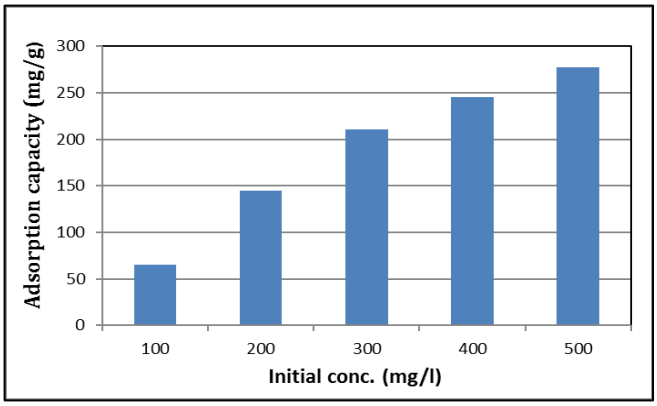

Figure 3: Effect of initial concentration on the adsorption capacity of BS-SO_3H towards MB

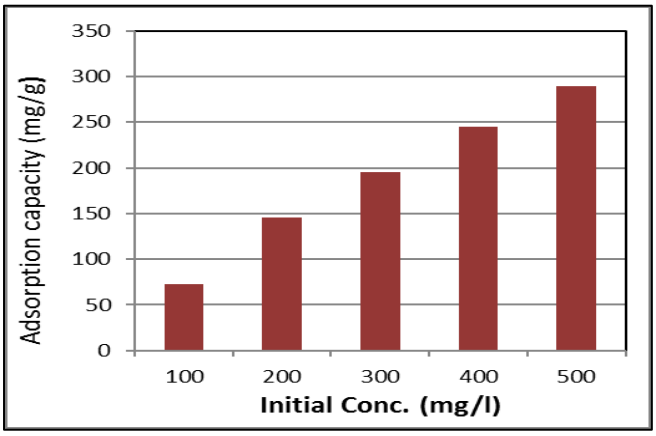

Figure 4: Effect of initial concentration on the adsorption capacity of CS-SO_3H towards MB

3.3. Adsorption isotherms

The adsorption isotherm of MB dye was studied using Langmuir and Freundlich models, it was observed that the Langmuir model isotherm for adsorption of MB by BS-SO_3H is more fitted (R^2=0.986) than Freundlich model isotherm (R^2=0.68) as shown in Figures (5), (6).It indicated that the adsorption of MB is characterized by monolayer adsorption. The maximum adsorption capacity (Q_{max}) was calculated to be 256.4 mg/g for MB at pH 11.5.

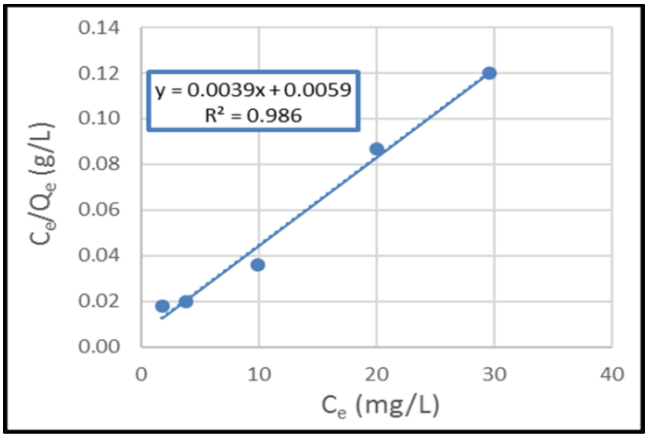

Figure 5: Langmuir isotherms for the adsorption of MB onto BS-SO_3H

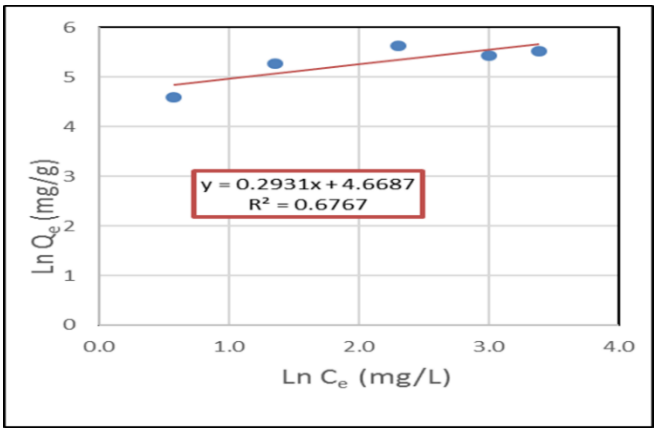

Figure 6: Freundlich isotherms for the adsorption of MB onto BS-SO_3H

The adsorption isotherm of MB dye was investigated using Langmuir and Freundlich models, It was noticed that the Langmuir model isotherm for the adsorption of MB by CS-SO_3H is more fitted (R^2=0.94) than Freundlich model isotherm (R^2=0.8) as displayed in Figures (7), (8).Which indicated that the adsorption of MB is characterized by monolayer adsorption. The maximum adsorption capacity (Q_{max}) was calculated to be 344.8 mg/g for MB at pH 11.5.

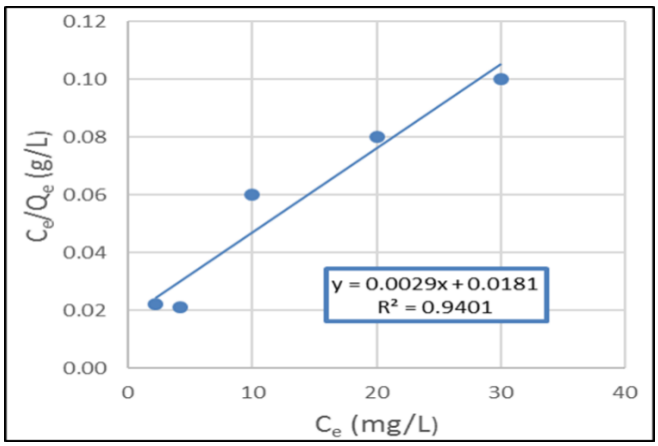

Figure 7: Langmuir isotherms for the adsorption of MB onto CS-SO_3H

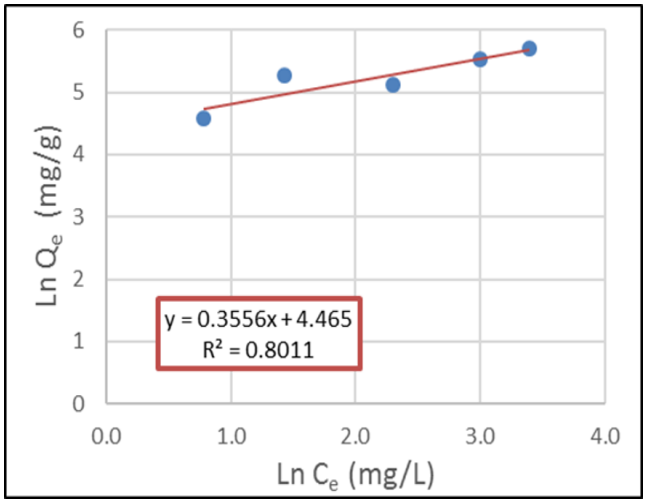

Figure 8: Freundlich isotherms for the adsorption of MB onto CS-SO_3H

3.4. Adsorption kinetics

The adsorption kinetics of MB on BS-SO_3H and CS-SO_3H were investigated by pseudo-first order and pseudo- second-order models. Figures (9),(10) shows the linear form of the pseudo-second-order kinetic model for BS-SO_3H and CS-SO_3H. The correlation coefficients R^2=1 for both BS-SO_3H and CS-SO_3H.This suggested that the adsorption followed the pseudo-second-order kinetic model. The values of pseudo-second-order rate constants of MB adsorption were calculated to be 0.2 and 0.26 [g/mg.min] for BS-SO_3H and CS-SO_3H respectively, the equilibrium adsorption capacities (Q_e) were calculated to be 100,74.6 mg/g for BS-SO_3H and CS-SO_3H respectively which is almost the same value obtained from experimental work. The linear form of the pseudo-first order kinetic model, applied on the experimental data gave a bad R^2 for BS-SO_3H and CS-SO_3H as shown in Figures (11),(12)**.** The constants of the adsorption isotherms and kinetics are presented in table (1)

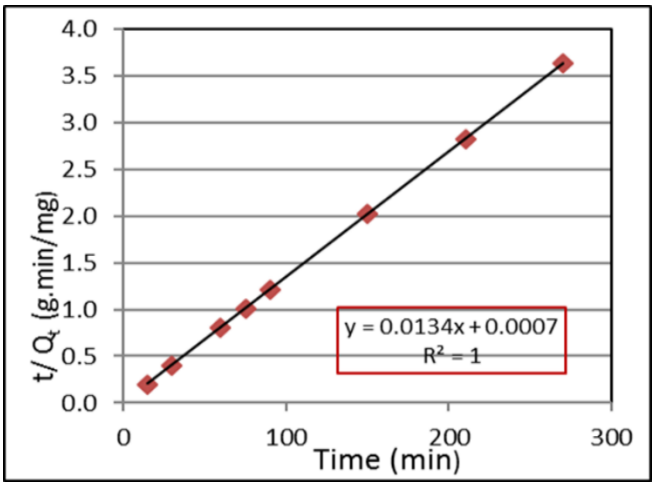

Figure 9: Pseudo-second-order kinetics for the adsorption of MB onto BS-SO_3H

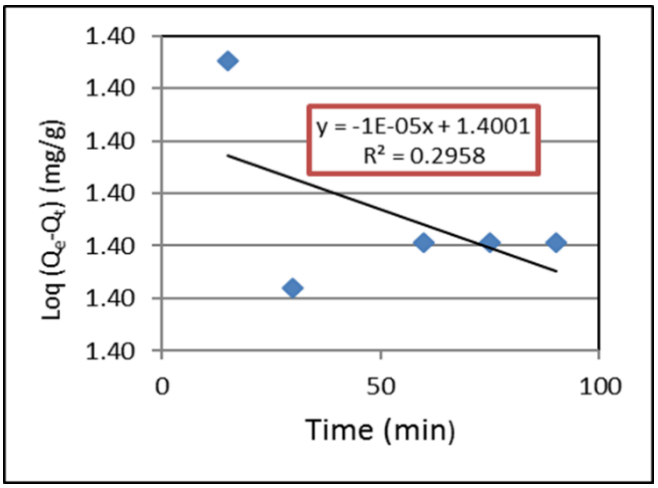

Figure 12: pseudo-first-order kinetics for the adsorption of MB onto CS-SO_3

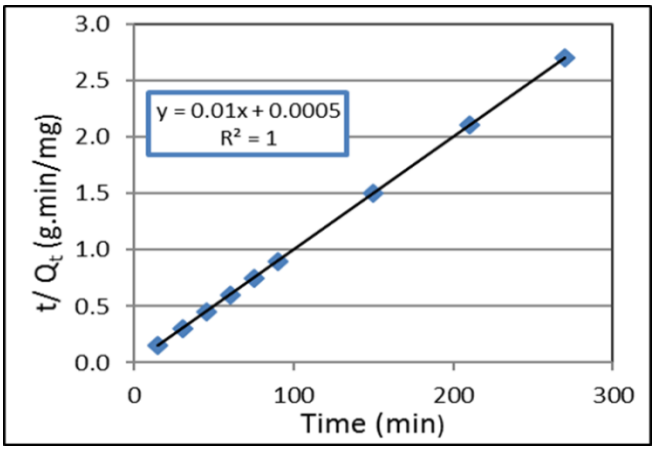

Figure 10: Pseudo-second-order kinetics for the adsorption of MB onto CS-SO_3H

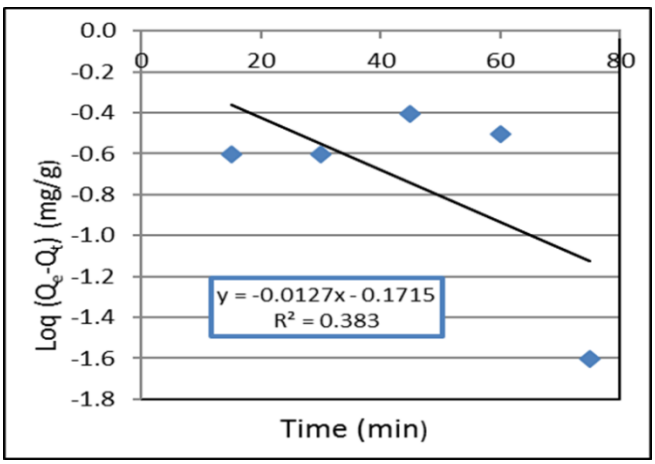

Figure 11: Pseudo-first-order kinetics for the adsorption of MB onto BS-SO_3H

Table 1: The constants of adsorption isotherms and kinetics

Adsorption isotherms						
	Langmuir model			Freundlich model		
Adsorbent	Q_{max} (mg/g)	K_L	R^2	n	K_f	R^2
BS-SO_3H	256.4	0.66	0.98	3.4	106.6	0.68
CS-SO_3H	344.8	0.16	0.94	2.8	86.92	0.8
Adsorption kinetics						
	Pseudo-first-order model			Pseudo-second-order model		
Adsorbent	Q_e (mg/g)	K_1	R^2	Q_e (mg/g)	K_2	R^2
BS-SO_3H	0.674	0.0292	0.38	100	0.2	1
CS-SO_3H	0.99	-3.22	0.29	74.6	0.257	1

3.5. The difference between the adsorption capacities and other adsorbents

Studies that were done before for the adsorptive removal of MB from aqueous solution using low-cost based materials were illustrated in Table (**2**). The BS-SO_3H and CS-SO_3H have better adsorption capacities than barely straw, coconut shell, coconut shell loaded by silver nanoparticles and chemically modified barley straw. Therefore, the utilization of BS-SO_3H and CS-SO_3H as bio-adsorbent is more profitable.

Table 2: The difference between the adsorption capacities and other adsorbents

Adsorbent	Q_{max} (mg/g)	References
Barely straw	27.72	[9]
Coconut shell	4.159	[10]
Coconut Shell Loaded by Silver Nanoparticles	71.29	[11]
Chemically modified barely straw	51.91	[12]
BS-SO_3H	256.4	Present work
CS-SO_3H	344.8	Present work

3.6. Design of Batch Adsorber

The following section includes the design outline of the batch adsorber. At first, mass balance of adsorbate in the fluid flowing as shown in Figure (13) is performed to get equation (6)

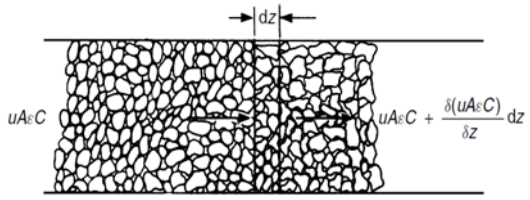

Figure 13: Flowing the adsorbate through the packed bed

Input – output = accumulation + loss by adsorption (6)

$$uA\varepsilon C - [uA\varepsilon C + \frac{\partial(uA\varepsilon C)}{\partial z}dz] = \frac{\partial(\varepsilon ACdz)}{\partial t} + Loss \quad (7)\ [13]$$

By knowing that the rate of loss by adsorption from the fluid phase equals the rate of gain in the adsorbed phase and equals to:

$$Rate\ of\ adsorption\ = \frac{\partial[(1-\varepsilon)AC_s dz]}{\partial t} \quad (8)$$

Equation (7) becomes:

$$-\frac{\partial(uC)}{\partial z}dz = \frac{\partial C}{\partial t}dz + \frac{\frac{1}{\varepsilon}\partial C_s dz - \partial C_s dz}{\partial t} \quad (9)$$

The equations may be rearranged to give:

$$(\frac{\partial(uc)}{\partial z})_t + (\frac{\partial C}{\partial t})_z = -\frac{1}{m}\left(\frac{\partial C_s}{\partial t}\right)_z \quad (10)$$

Where: $m = \frac{\varepsilon}{1-\varepsilon}$ (11)

$$and\ \ \rho_B = (1-\varepsilon)\rho_p \quad (12)$$

When the adsorbate content of the inlet stream is small, the fluid velocity is virtually constant along the bed.

$$u(\frac{\partial c}{\partial z})_t + (\frac{\partial C}{\partial t})_z = -\frac{1}{m}\left(\frac{\partial C_s}{\partial t}\right)_z \quad (13)$$

At all positions in the bed, concentrations in the fluid and adsorbed phases are related to the adsorption isotherm. This implies that there is no resistance to the transfer of molecules of adsorbate from bulk fluid to adsorption site.

If the adsorption isotherm is written as Cs = f'(C), equation (13) may be rewritten as:

$$u\frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} = -\frac{1}{m}\frac{\partial C_s}{\partial C}\frac{\partial C}{\partial t} = -\frac{1}{m}f'(C)\frac{\partial C}{\partial t} \quad (14)$$

after integration at constant C:

$$\frac{ut}{1+\frac{1}{m}f'(C)} = z - z_0 \quad (15)$$

Where: f′(C) = Slope of an adsorption isotherm.
ε: Intrapellet void fraction
m: Intrapellet void ratio and it is equals to ε/ (1 − ε).
t: Time (minute).
u: Intrapellet velocity of the fluid (m/min).
Z: Distance along the bed (m).
Z_0: Initial position of the adsorption (m).
ρ_B: Bulk density of an adsorbent pellet (g/cm^3).
ρ_p: Particle density of an adsorbent pellet (g/cm^3).

a) The design of the batch adsorber for the bio-adsorbent produced from barely straw

To apply the previous equations on the bio-adsorbent produced from barely straw, the slope of the suitable isotherm should be obtained. Thus, the linear form of the Langmuir adsorption isotherm model is determined and from which the first derivative (f'(c)) is obtained as shown in equations (16) and (17) respectively.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m}C_e + \frac{1}{K\,Q_m} \quad (16)$$

$$f'(c) = \frac{dQ_e}{dC_e} = \frac{K\,Q_m}{(KC_e+1)^2} \quad (17)$$

By substituting the values of Q_m, K, and the optimum C_e with 256.4, 0.66, and 9.52 ppm respectively in equation (17), it is found that f'(c) equals 3.19. Also, by determine the bulk and particle density of the bio-adsorbent produced from barely straw experimentally, which are 0.352 and 0.713 g/cm^3 respectively, and by compensation in equation (11), (12) , it is found that $\varepsilon\ and\ m\ equal$ 0.506 ,1.024 respectively.

Taking into consideration the assumption that the height of the packed material is 0.5 m and the ratio of height to diameter is 3:1, therefore of diameter of the packed bed column is equal 0.17 m. Also, the length of the packed bed column will be 0.7 m as we will leave 0.1 m from top and bottom to fix the packed material and for the links to the entrance and exit of the column.

The value of U will be obtained as 0.0206 m/min by substituting in equation (15) with the optimum time from the kinetics study 100 min.

Also, the flow rate of the treated water could be obtained by knowing that the diameter of adsorber is 0.17 m from the following equations:

$$A=\pi r^2 = 0.0227\ m^2 \quad (18)$$

$$Q = UA\varepsilon = 2.364*10^{-4}\frac{m^3}{min} = 14.18\ \frac{L}{h} \quad (19)$$

b) The design of the batch adsorber for the bio-adsorbent produced from coconut shell

The same procedure followed in the previous section is repeated using another bio-adsorbent material, by substituting the values of Q_m, K, and the optimum C_e with 344.83,0.16, and

11.52 ppm respectively in equation (17), it is found that f'(c) equals 6.83. Also, by determine the bulk and particle density of the bio-adsorbent produced from coconut shell experimentally which are 0.675 and 1.2 g/cm^3 respectively, by compensation in equation (11),(12) , it is found that $\varepsilon \; and \; m \; equal$ 0.438 ,0.779 respectively.

The value of U will be obtained as 0.0814 m/min by substituting in equation (15) with the optimum time from the kinetics study 60 min. Also, the flowrate of the treated water could be obtained by knowing that the diameter of adsorber is 0.17 m from the following equations:

$$Q = UA\varepsilon = 8.093*10^{-4}\frac{m^3}{min} = 48.6\ \frac{L}{h} \quad (20)$$

4. CONCLUSION

The utilization of previously prepared and characterized bio-adsorbent from barely straw and coconut shell using concentrated sulfuric acid with reflux is one of the most effective method in removal of methylene blue dye from wastewater. The maximum adsorption of MB by BS-SO_3H and CS-SO_3H were found at pH 11.5 at equilibrium and increased by increasing initial dye concentration up to 500 ppm. The maximum adsorption capacities were found to be 256.4 mg/g, and 344.8 mg/g for BS-SO_3H and CS-SO_3H respectively. The adsorption of MB by BS-SO_3H and CS-SO_3H followed the Langmuir isotherm model which is more fitted than the Freundlich model. The pseudo-second-order kinetic model was in best fit with the experimental results. The equilibrium adsorption capacities (Q_e) obtained from kinetics were calculated to be 100, and 74.6 mg/g for BS-SO_3H and CS-SO_3H respectively which is almost the same value obtained from experimental work. The flow rate of the treated water obtained by knowing that the diameter of adsorber is 0.17 m could be $14.18, and\ 48.6\ L/h$ for BS-SO_3H and CS-SO_3H respectively.

Credit Authorship Contribution Statement

Sabah Mohamed Farouk: Methodology, literature review, results analysis *N.A. Mostafa:* Supervision, writing review*; S.M.S. Abdelhamid:* Supervision, writing review, resources; *Aliaa Monazie:* Supervision, validation, formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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