

Low Cost Adsorbent for Rhodamine B Dyeremoval from Aqueous Solution Using *MESC*

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ABSTRACT: The research of this work was to investigate the removal of Rhodamine B dye from aqueous solution by using *Mimuscopselengi* Stem (*MESC*). Generally, dyes are organic compounds used as colouring products in chemical, textile, paper, printing, leather, plastics and various food industries. The need for the treatment of dye contaminated waste water passed out from the dye industries. *Mimuscopselengi* Stem was studied for its potential use as an adsorbent for removal of a cationic dye Rhodamine B (Rh-B). The various factors affecting adsorption, such as initial dye concentration, contact time, adsorbent dose and effect of temperature were evaluated. The experimental data were fitted into the pseudo-second order kinetic model. The equilibrium of adsorption was modelled by using the Langmuir and Freundlich isotherm models. The objective of the present work suggests the *MESC* may be utilized as a low cost adsorbent for Rhodamine B dye removal from aqueous solution.

KEYWORDS: *Mimuscopselengi* Stem(*MESC*), Rhodamine B(Rh-B),Equilibrium models and Kinetics isotherm.

I. INTRODUCTION

In generally Dyes are used in the textiles, plastics, paper, leather, food industry to color products. In this process of washing and finishing coloured products, waste water contaminated with dyes is generated. The contaminated waste waters are hazardous, which is a great threat to environment [1-3]. Dye contamination in wastewater causes problems in various ways the presence of dyes in water, even in very low quantities, is highly visible and undesirable color interferes with penetration of sunlight into waters retards photosynthesis, inhibits the growth of aquatic biota and interferes with gas solubility in water bodies. These materials are the complicated organic compounds and they resist against light, washing and microbial invasions [4-7]. The need for the treatment of dye contaminated waste water arose from the environmental impact [8]. Activated minerals are one of the most popular adsorbents used for the removal of toxic substances from waste water. This could be related to their extended surface area [9]. The major use of *Mimuscopselengi* Stem is in solution purification and for the removal of colour, odors and other unpleasant impurities from liquids, water supplies and vegetable and animal oils. In recent years it has been increasingly used for the prevention of environmental pollution and antipollution laws have increased the sales of low-cost activated minerals for control of the air and water pollution. Various techniques like precipitation, ion exchange, chemical oxidation and adsorption have been used for the removal of toxic pollutant from, wastewater. Rhodamine B (Rh-B) is selected as a model compound for evaluating the potential of *MESC* to remove dye from aqueous solution.

II. MATERIALS AND METHODS

Adsorption studies

Rhodamine B (Rh-B) was employed for the adsorbate in the adsorption experiments. An aqueous solution with a concentration of 25-125 mg/L was prepared by mixing an appropriate amount of Rh-B with distilled water adsorption experiments were conducted by placing 0.025 g of the *MESC* samples and 50 ml of the aqueous solution in a 250 ml of glass-stoppered flask. The flask was then put in a constant-temperature shaker bath with a shaker speed of 150 rpm. The isothermal adsorption experiments were performed at $30 \pm 2^\circ\text{C}$.

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***Mimuscopselengi* Stem**

The *Mimuscopselengi* Stem collected from agricultural area nearby Thanjavur district was Carbonized with concentrated Sulphuric Acid and washed with water and activated around 700°C in a muffle furnace for 6hrs the it was taken out, ground well to fine powder and stored in a vacuum desiccators.

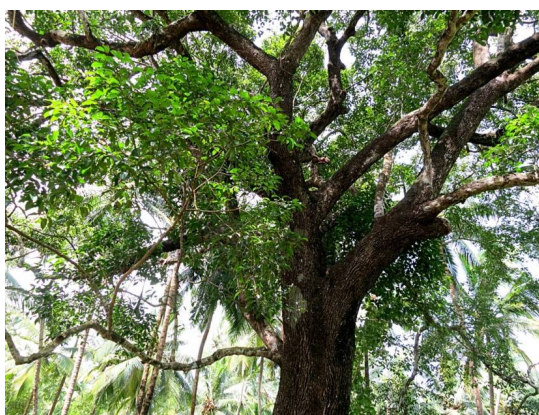


Fig.1 *Mimuscopselengi*

Preparation of adsorbate

Rhodamine B was chosen in the present work because of its strong adsorption onto solids. It recognized usefulness in characterizing adsorptive material ^[10 and 11] Rhodamine B is employed to evaluate the adsorption characteristics of carbon. A known weight of 1000 mg of Rh-B was dissolved in about one litre of distilled water to get the stock solution.

Adsorption dynamic experiments

The adsorption experiments were carried out in a batch process at 30, 40, 50 and 60° C. A known weight of *MESC* was added to 50 ml of the dye solutions with an initial concentration of 25 mg/L to 125 mg/L, which is prepared from 1000 mg/L of Rhodamine B stock solution. The contents were shaken thoroughly using a mechanical shaker with a speed of 150 rpm. The solution was then filtered at present time intervals and the residual dye concentration was measured.

III. RESULTS AND DISCUSSION

Characteristics of the adsorbent

Mimuscops elengi Stem is an effective adsorbent for the abatement of many pollutant compounds (organic, inorganic, and biological) of concern in water and wastewater treatment. Most of the solid adsorbents possess micro porous fine structure, high adsorption capacity, high surface area and high degree of surface, which consists of pores of different sizes and shapes ^[12]. The chemical nature and pore structure usually determines the sorption activity. The physico-chemical properties of the chosen adsorbent are listed in Table-1. The wide usefulness of *MESC* is a result of their specific surface area, high chemical and mechanical stability.

Effect of solution pH

The adsorption capacity can be attributed to the chemical form of dye in the solution at specific pH. In addition due to different functional groups on the adsorbent surface, which become active sites for the dye binding at a specific pH the effect of adsorption can vary substantially. Therefore, an increase in pH may cause an increase or decrease in the adsorption, resulting different optimum pH values dependent on the type of adsorbent. To examine the effect of pH on the % removal of Rh-B dye, the solution pH were varied from 2.0 to 10.0 by adding acid and base to the stock solution This increases may be due to the presence of negative charge on the surface of the adsorbent *MESC* that may be responds for the dye binding. However, as the pH is lowered, the hydrogen ions compete with dye for the adsorption

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sites in the adsorbent *MESC*, the overall surface charge on the particles become positive and hinders the binding of positively charged dye. The decrease in the adsorption under $\text{pH} > 6.3$ may be due to occupation of the adsorption sites by OH^- ions which retard the approach of such dye further toward the adsorbent *MESC* surface. From the experimental results, the optimum pH range for the adsorption of the Rh-B dye is 2.0 to 6.5 shown in Fig.1.

Adsorption isotherms

Langmuir isotherm

The theoretical Langmuir isotherm is used for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Therefore, the Langmuir isotherm model was chosen for estimation of the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. The Langmuir non-linear equation is commonly expressed as

$$C_{eq}/Q_{eq} = 1/Q_m b + C_{eq}/Q_m \dots\dots\dots (1)$$

Where C_{eq} is the equilibrium concentration of adsorbate in the solution (mg/L), Q_{eq} is the amount adsorbed at equilibrium (mg/g), Q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption, respectively. The linear plots of C_{eq}/Q_{eq} vs. C_{eq} suggest the applicability of the Langmuir isotherms (Fig.3). The values of Q_m and b were calculated from slope and intercepts of the plots are given in Table-3. From the results, it is obvious that the value of adsorption efficiency Q_m and adsorption energy b of the *MESC* increases on increasing the temperature. The values can conclude that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with endothermic nature of adsorption^[17]. To confirm the favorability of the adsorption process, the separation factor (RL) was determined and given in Table-4.

The Freundlich isotherm

The Freundlich isotherm model is the earliest known equation describing the adsorption process. It is an empirical equation and can be used for non-ideal sorption that involves heterogeneous adsorption. The Freundlich equation was employed for the adsorption of Rhodamine B dye on the adsorbent. The Freundlich isotherm was represented by the following equation.

$$\log Q_e = \log K_f + 1/n \log C_e \dots\dots\dots (2)$$

Where Q_e is the amount of Rhodamine B dye adsorbed (mg/g), C_e is the equilibrium concentration of dye in solution (mg/L), and K_f and n are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption respectively. Linear plots of $\log Q_e$ versus $\log C_e$ shows that the adsorption of Rhodamine B obeys the linear plots of $\log Q_e$ versus $\log C_e$ shows that the adsorption of Rhodamine B dye obeys the Freundlich adsorption isotherm. The values of K_f and n are given in Table-4 shows that the increase of negative charges on the adsorbent surface makes electrostatic force like van der Waal's between the *MESC* surface and dye ion. The molecular weight and size either limit or increase the possibility of the adsorption of the dye onto adsorbent. However, the values clearly show the dominance in adsorption capacity. The intensity of adsorption is an indication of the bond energies between dye and adsorbent, and the possibility of slight chemisorptions rather than physisorption^[17]. The effect of temperature on the adsorption of dye adsorption by *MESC*, the experiments was performed at temperatures of 30, 40, 50, 60°C. As it was observed that, the equilibrium adsorption capacity of Rh-B onto *MESC* was found to increase with increasing temperature, especially in higher equilibrium concentration, or lower adsorbent dose because of high driving force of adsorption. This fact indicates that the mobility of dye molecules increased with the temperature. The adsorbent shows the endothermic nature of adsorption. The adsorption capacity of the *MECS* increased with increase of the temperature in the system from 30° to 60°C. Thermodynamic parameters such as change in free energy (G°) (kJ/mol), enthalpy (H°) (kJ/mol) and entropy (S°) (J/K/mol) were determined using the following equations.

$$K^0 = C_{solid}/C_{liquid} \dots\dots\dots (3)$$

$$G^\circ = -RT \ln K^0 \dots\dots\dots (4)$$

$$\log K^0 = S^\circ / (2.303R) - H^\circ / (2.303RT) \dots\dots\dots (5)$$

Where K^0 is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin, and R is the gas constant. The H° and

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S° values obtained from the slope and intercept of Van't Hoff plots are given in Table 5. The values of H° is the range of 9 to 17 kJ/mol, indicate the physisorption. The results show that physisorption is much feasible for the adsorption of Rhodamine B (Rh-B). The positive values of H° show the endothermic nature of adsorption which governs the possibility of physical adsorption. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of dye adsorption increases, there is no possibility of chemisorption. The negative values of G° (Table -5) show that the adsorption is highly favourable and spontaneous. The positive values of S° (Table-5) show the increased disorder and randomness at the solid solution interface of Rhodamine B with *MESC* adsorbent. The enhancement of adsorption capacity of the *MESC* at higher temperatures was described to the enlargement of pore size and activation of the adsorbent surface^[19].

Adsorption kinetics

The study of adsorption dynamics describes the solute up take rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Rh-B dye adsorption on the *MESC* were analyzed using pseudo second-order^[20]Elovich^[21] and intra-particle diffusion kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation co- efficient ($\square\square$) and the values are close or equal to 1. A relatively high correlation coefficient (\square) value indicates that the pseudo second-order model successfully describes the kinetics of Rh-B dye adsorption.

The pseudo second- order equation

The pseudo second-order adsorption kinetic rate equation is expressed as

$$dq/dt = k_2(q_e - qt)^2 \dots\dots\dots(6)$$

Where k_2 is the rate constant of pseudo second- order adsorption (g mg/min). For the boundary conditions $t = 0$ to $t = t$ and $qt = 0$ to $qt = qt$ the integrated form of Eq. (6) becomes:

$$1/(q_e - qt) = 1/q_e + K_2t \dots\dots\dots (7)$$

This is the integrated rate law for a pseudo second-order reaction. Equation (7) can be rearranged to obtain Eq.(8), which has a linear form:

$$t/qt = (1/k_2q_e^2) + ((1/q_e)t \dots\dots\dots(8)$$

If the initial adsorption rate (h)(mg g-1min-1) is :

$$h = k_2q_e^2 \dots\dots\dots (9)$$

Equation (8) and (9) becomes,

$$t / qt = 1 / h + 1 / q_e t \dots\dots\dots \dots(10)$$

The plot of (t/qt) and t of Eq. (10) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively. The pseudo-second order rate constants K_2 , the calculated h values, and the correlation coefficients (\square) are summarized in Table-(5). At all studied initial Rh-B dye concentrations, the straight lines with extremely high correlation co-efficient (>0.99) were obtained. From table 5, the values of the rate constant k decrease with in increasing initial Rh-B dye concentration for *MESC* powder. This is shows that the sorption of Rh-B dye on *MESC* follows pseudo second order kinetic model^[20].

The Elovich equation

The Elovich model equation is generally expressed as

$$dq / dt = \alpha \exp (-\beta qt) \dots\dots\dots(11)$$

Where α is the initial adsorption rate (mg g-1 min-1) and β is the desorption constant (g/mg) during any one experiment. To simplify the Elovichequation [26]. assumed $\square\square t \gg t$ and by applying boundary conditions $qt = 0$ at $t = 0$ and $qt = qt$ at $t = t$ Eq.(11) becomes:

$$qt = 1/\square \ln (\square\square) + 1/\square \ln t \dots\dots\dots (12)$$

If Rh-B dye adsorption fits with the Elovichmodel, a plot of qt vs. $\ln(t)$ should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)\ln (\alpha\beta)$. The Elovich model parameters α , β , and correlation coefficient (\square) are summarized in Table-5. The experimental data such as the initial adsorption rate (\square) adsorption constant (β) and the correlation co-efficient (γ) calculated from this model indicates that the initial adsorption (α) increases with temperature

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similar to that of initial adsorption rate (h) in pseudo-second-order kinetics models. This may be due to increase the pore or active site on the *MESC* adsorbent.

The intra particle diffusion model

The intra-particle diffusion model used here refers to the theory proposed by Weber and Morris [27] based on the following equation for the rate constant:

$$qt = k_{id} t^{1/2} + C \dots \dots \dots (13)$$

Where k_{id} is the intra-particle diffusion rate constant (mg/g/min) and C is the constant. If the rate limiting step is intra-particle diffusion, then the graph drawn between (qt) (mg/g) versus square root of the contact time $(t^{1/2})$ should yield a straight line passing through the origin [22]. The slope of the will give the value of the intra-particle diffusion coefficient (k_{id}) and correlation coefficient (\square) indicate the fitness of this model. The value of C gives an idea about the thickness of the boundary layer. From these data the intercept value indicate that the line were not passing through origin, there are some other process affect the adsorption. But the correlation coefficient (γ) value is very high, so that the intra-particle diffusion takes place along with other process that may affect the adsorption. The values are given in Table-5.

TABLES AND GRAPH

**Table: 1. EQUILIBRIUM PARAMETERS FOR THE ADSORPTION OF Rh-B
Dye ONTO *MESC***

M_0	Ce (mg / L)				Qe (mg / L)				Removal %			
	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C	30°C	40°C	50°C	60°C
25	3.64	3.03	2.54	2.73	92.70	93.92	94.90	94.52	92.72	93.92	94.90	94.52
50	11.43	10.46	8.47	7.56	177.1	179.0	183.0	184.8	88.56	89.53	91.52	92.43
75	25.74	22.36	19.64	17.36	248.5	255.2	260.7	265.2	82.83	85.08	86.90	88.42
100	47.84	43.64	19.64	36.67	304.3	312.7	360.7	326.6	76.07	78.17	90.17	81.66
125	73.88	69.93	40.64	60.90	352.2	360.1	418.7	378.19	70.44	72.02	83.74	75.63

Table: 2. Langmuir and Freundlich isotherm parameters for the adsorption of RhB onto *MESC*

Temp. (°C)	Langmuir parameter		Freundlich parameter	
	Q_m	b	K_f	n
30	353.78	0.0850	67.551	2.8060
40	364.51	0.0943	71.896	2.8079
50	497.46	0.0733	66.291	2.1230
60	384.05	0.1224	81.635	2.7997

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Table: 3. Dimensionless separation factor (R_L) for the adsorption of RhB dye onto MESC

C_0	Temperature °C			
	30°C	40°C	50°C	60°C
50	0.1904	0.1750	0.2144	0.1405
100	0.1052	0.0959	0.1200	0.0756
150	0.0727	0.0660	0.0834	0.0517
200	0.0555	0.0504	0.0639	0.0393
250	0.0449	0.0407	0.0517	0.0317

Table:4. Thermodynamic parameters for the adsorption RhB onto MESC

C_0	ΔG^0				ΔH^0	ΔS^0
	30°C	40°C	50°C	60°C		
50	-7118.4	-7739.2	-8374.6	-8911.5	11.123	60.248
100	-4735.0	-5262.0	-6022.4	-6724.6	15.641	67.066
150	-3531.3	-4044.7	-4609.7	-5196.2	13.305	55.505
200	-2277.7	-2637.8	-5500.2	-3498.5	18.173	68.090
250	-1451.9	-1754.4	-3814.8	-2412.2	14.008	51.466

C_0 -Initial concentration of RhB dye

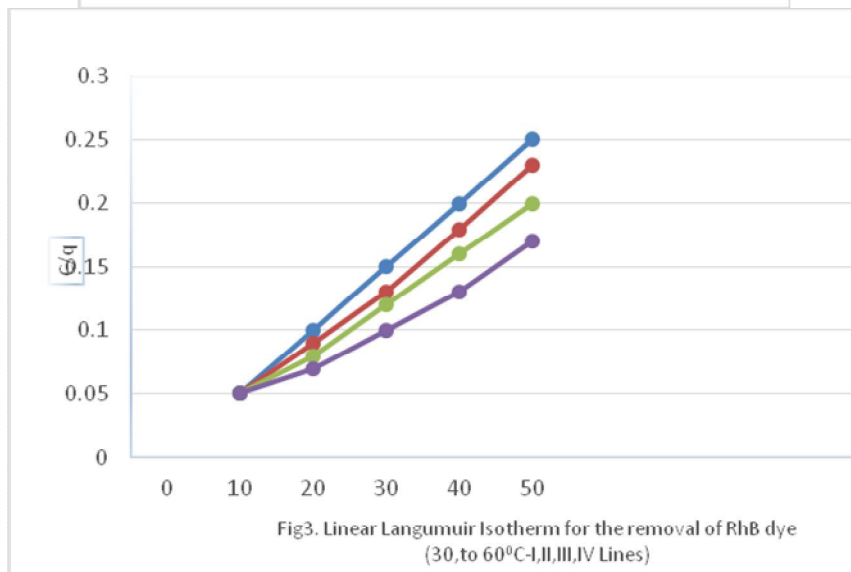
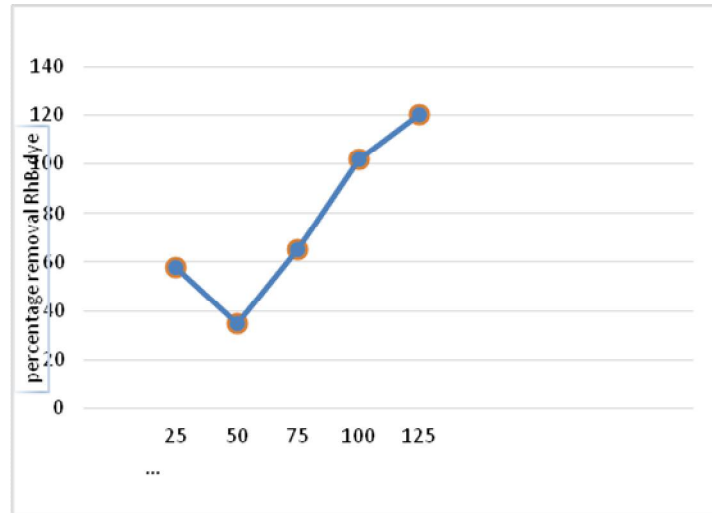
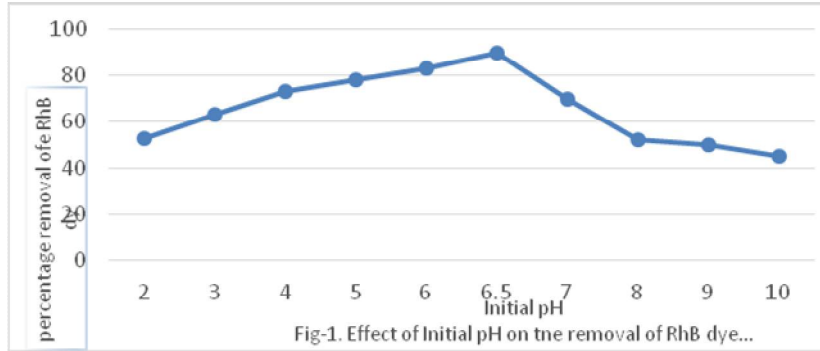
Table: 5. The kinetic parameters for the adsorption of RhB dye onto MESC

C_0	Temp °C	Pseudo- second- order				Elovich model			Intra-particle diffusion		
		q_e	k_2	γ	h	α	β	γ	K_{id}	γ	C
50	30	101.50	0.0012	0.992	13.363	123.46	0.0691	0.992	1.6367	0.990	0.1795
	40	101.63	0.0013	0.991	14.131	164.84	0.0724	0.992	1.6581	0.992	0.1690
	50	101.79	0.0014	0.993	15.076	224.65	0.0758	0.996	1.6783	0.994	0.1593
	60	102.38	0.0014	0.996	15.035	211.21	0.0745	0.999	1.6768	0.995	0.1614
100	30	187.25	0.0006	0.997	23.807	199.77	0.0367	0.992	1.5906	0.996	0.1846
	40	190.35	0.0006	0.998	24.732	236.35	0.0371	0.993	1.6095	0.997	0.1782
	50	193.98	0.0007	0.995	27.251	317.20	0.0379	0.991	1.6283	0.998	0.1689
	60	197.73	0.0007	0.993	27.984	314.89	0.0370	0.990	1.6451	0.999	0.1702
150	30	260.80	0.0004	0.992	29.127	182.07	0.0246	0.993	1.5189	0.995	0.2027
	40	266.70	0.0004	0.992	32.170	236.58	0.0250	0.996	1.5520	0.994	0.1921
	50	273.83	0.0004	0.990	35.152	293.17	0.0251	0.997	1.5802	0.995	0.1846
	60	278.33	0.0003	0.9921	29.891	365.61	0.0268	0.991	1.5962	0.991	0.1699
200	30	309.27	0.0002	0.9931	27.522	108.42	0.0183	0.993	1.3822	0.995	0.2433
	40	316.91	0.0002	0.9919	30.043	134.50	0.0186	0.994	1.4200	0.994	0.2301
	50	325.77	0.0003	0.9910	32.706	162.28	0.0186	0.993	1.4527	0.996	0.2201
	60	333.49	0.0003	0.9920	37.295	218.69	0.0190	0.994	1.4947	0.997	0.2066
250	30	343.43	0.0002	0.993	24.626	73.030	0.0150	0.995	1.2410	0.998	0.2848
	40	354.92	0.0002	0.994	26.334	81.643	0.0148	0.991	1.2715	0.992	0.2761
	50	367.86	0.0001	0.995	26.914	83.024	0.0141	0.992	1.2847	0.993	0.2786
	60	375.68	0.0002	0.996	30.856	106.62	0.0145	0.997	1.3353	0.992	0.2580

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IV. CONCLUSION

In this work shown the effectiveness of using *MESC* in the removal of Rhodamine B of the aqueous solution *Mimuscops elengi* Stem in different forms has a great role in modern life to systematical surroundings. *Mimuscops elengi* Stem can be good precursors for producing highly porous *Mimuscops elengi* Stem by simple preparative methods. An adsorption test has been carried out for industrial pollutants (Rhodamine B (Rh-B) under different experimental conditions. The adsorption of Rhodamine B was dependent on adsorbent surface characteristics, adsorbent dose, Rh B concentration, contact time and temperature. A study of the kinetic models on sorption showed that sorption fitted the pseudo second-order kinetics model. The G, H, and S reveal the favorability of adsorption. The thermodynamic parameters suggested that the adsorption on *MESC* was a spontaneous and endothermic process

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