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Adsorption study of methylene blue dye on basil seeds in aqueous solutions

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Abstract : Environmental pollution as a result of the dye presence led to serious health problems. In this study, the adsorption by basil seeds was investigated. The adsorption behavior of basil seeds with Methylene Blue dye has been studies by batch method to consider its application in this field The effects of various experimental parameters like contact time, dosage of weld seeds, initial concentration of the Methylene Blue, pH and temperature have been investigated. The removal percentage is a pH dependent and decrease with increase in temperature, the best removal was at 293K. The adsorption kinetic data are best described by pseudo- second-order kinetic model with good correlation coefficient. The experimental results indicate that freundlich isotherm describes the biosorption of methylene blue onto the basil seeds better than others at all the temperature studied. The calculated thermodynamic parameters (ΔG°, ΔH° and ΔS°) show that its adsorption is spontaneous and exothermic in nature.
Keyword : methylene blue, basil seeds, adsorption, isotherm, kinetic.

Introduction

Water pollution has become a global concern due to the disposal of toxic contaminants/dyes in water and the fast growth of industries. The presence of toxic substance in water affects symbiotic methods by reducing the photosynthetic action. Therefore it is imperious to treat the polluted water, through ecofriendly, and techno economically feasible processes. Many physic-chemical techniques have already been built up for separation of toxic substance from aqueous environment [1, 2].

Dyes are basically natural or synthetic chemical compounds have complex aromatic molecular structure and are generally resistant to light, temperature and oxidizers [3]. Dyes are also widely used in many industries such as rubber, paper, plastic, cosmetic etc. There are more than 10,000 commercially [4]. Methylene blue (MB) is a Cationic toxic dye mainly used for dyeing cotton, leather, wool, silk, paper, plastics, as well as for the production of ink, copying paper [5]. MB can cause eye burns, and if swallowed, it causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea, profuse sweating, mental confusion. It can give rise to short periods of rapid or difficult breathing. Acute exposure to methylene blue may increase heart and methemoglobinemia, Heinz body formation, cyanosis, jaundice quadriplegia, and tissue necrosis in humans [6, 7]. Various physical and chemical treatment methods have been used for the removal of dyes [8]. photo/ferrioxalate system , photo catalytic and electrochemical combined treatments, photo-catalytic degradation using UV/TiO_2,sono chemical degradation, Fenton biological treatment, biodegradation, activated carbon, photo Fenton processes, integrated chemical biological degradation, electrochemical degradation, chemical oxidation adsorption process, coagulation/flocculation, ozonation, cloud point extraction, nano filtration, chemical precipitation, and ion exchange [9].

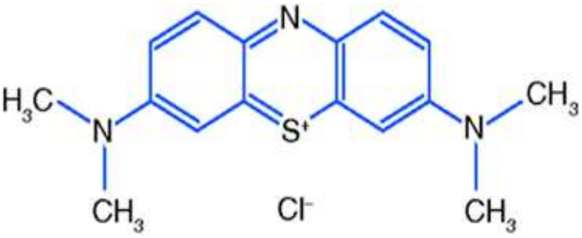

Figure-1: The molecular structure of methylene blue.

The main aim of this research work is to develop a cost effective and environmentally friendly basil seeds based adsorbent and its applications in the removal of toxic methylene blue from its aqueous solution by adsorption. The effectiveness of these biomass adsorbents has been justified by kinetics and isotherm mechanism, study under different physico-chemical conditions and calculate the thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) for the practical ofbasil seeds.

2: Experimental

2.1: Materials

Basil seeds were purchased from the local market, the plants producing these seeds grown extensively in Iran. methylene blue (MB)[3,7 bis(Dimethylamino)-phenazathionium chloride tetra methylthionine chloride; chemical formula =$(C_{16}H_{18}N_3S)^+CI^-$ molecular weight = 319.85 g mol-1; nature = basic blue] A stock solution of 100 ppm was prepared by dissolving 0.0250g in 250 ml volumetric flask using distilled water as a solvent Other concentration needed were prepared by dilution of stock solution.

A series of solutions were prepared by fresh diluting of the stock solution. The required quantity of seeds were washed with distilled water then allowed for 10 min and directly used as adsorbent Figure (2):

Figure 2: Basil plants and seeds.

2.2: Methods

The adsorption experiments were carried out by batch equilibrium method. Drenched seeds were taken in 250 ml round bottom flask containing 200ml of methylene blue solution. The flasks were placed on a rotary shaker (BS-11; Korea)and shaken at 150 rpm at 293K. At the end of predetermined time intervals, the supernatant were measured by UV-Vis spectrophotometer (Shimadzu UV-1800) Germany to determine the final concentration of (MB). The adsorbent at equilibrium (q_e) was calculated using the following equation (1):

$$q_e = \frac{(Co - C_e)V}{m} \qquad (1)$$

Where: q_e is the amount of (MB) adsorbed in mg/g, C_o is the initial (MB) concentration in mg/g , C_e is the concentration at equilibrium in mg/L and V is the total volume of solution in Liter and W is the mass of the adsorbent (basil seeds) used in gram.

Removal percentage or adsorption percentage was calculated using equation (2):

$$\%R = \frac{(Co - C_e)}{Co} \times 100 \qquad (2)$$

3.Results and Discussions

3.1: Effect of various parameters on Adsorption

3.1.1: Effect of contact time:

The mixture of weld seeds (1g) and MB dyes solution (5mg/L) were agitated 293Kfor different time (5, 10, 15, 20, 25, 30, 40, 50, 60, 75, 90, 105, and 120) minutes. MB concentrations were determined at each time. The effect of the contact time on the adsorption of (MB) is shown in figure -3. The equilibrium was attained after shaking for 25 min therefor 25 min was accepted as optimal time for adsorption of MB on basil seeds. Further increase in contact time did not show any increase in adsorption due to saturation in a surface sites [10].

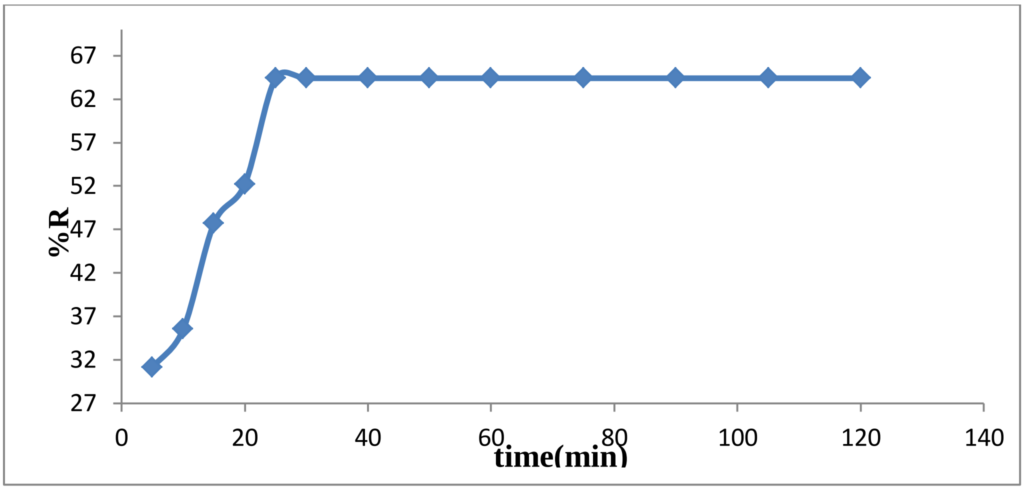

Figure-3: Effect of contact time on adsorption of MB dye onto basil seeds.

3.1.2: Effect of adsorbent dose

Initial MB concentration of(5mg/L) were used in conjunction with different amount of weld seeds of (0.1, 0.3, 0.5, 0.7, 1, and 1.3gm), the other parameters were kept constant; contact time 25 min ,agitation speed 150 rpm; temperature 293K, and pH=6.92. MB uptake was found to increase with increase in B.S dosage up to 1 gm. are show in figure-4. The optimum absorbent dose was chosen as 1 gram for the subsequent experiment, this is due to the increase in availability of surface active sites resulting from the increased dose [11].

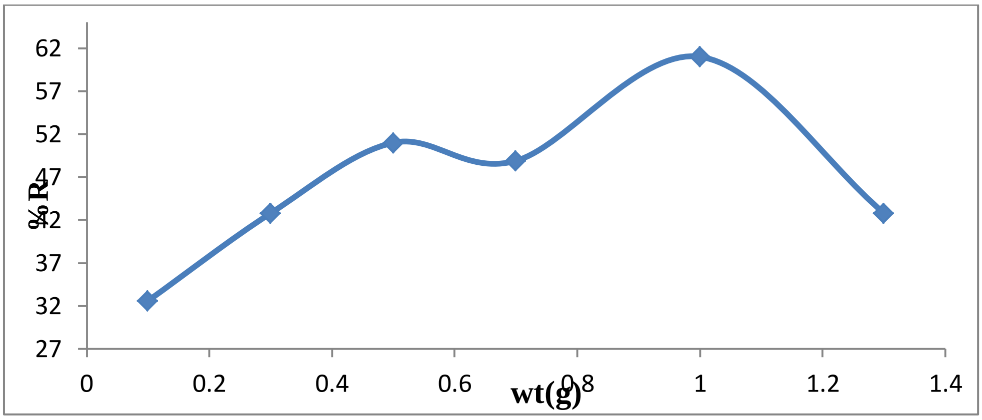

Figure-4: Effect of adsorbent dose on adsorption of MB onto basil seeds at 25 min.

3.1.3: Effect of initial MB dye concentration

The experimental values for adsorption of different concentration of MB dye (1, 2, 3, 4, 5, 6, 7, 8, 9, and 10) mg/L are shown in figure-5. As the concentration of MB dye increase, more and more surface sites are covered and hence at higher concentration, the capacity of the adsorbent get exhausted due to non-availability of the surface sites**.** The initial concentration of adsorbate in solution provides an important driving force in overcoming mass transfer resistance between the aqueous and the solid phases. Equilibrium adsorption studies have been performed to determine the capacity of the adsorbent, and the equilibrium is established when the concentration of adsorbate in the bulk solution is in dynamic balance with that on the surface [12] best concentration was 4 mg/L.

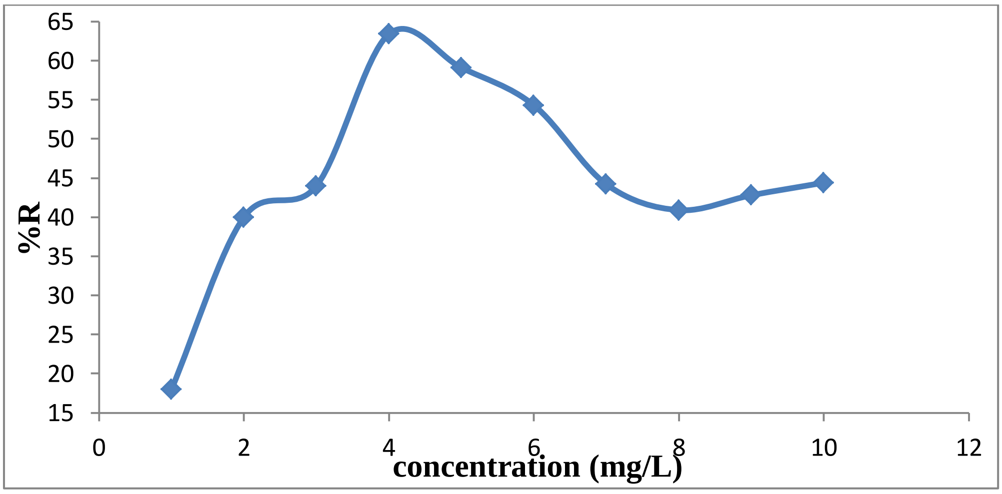

Figure-5: Effect of initial concentration of MB adsorption onto basil seeds.

3.1.4: Effect of pH

MB dye uptake was found to be pH dependent in its aqueous solution. Solutions were pH adjusted at (1, 3.5, 6.92, 11 and 13). MB uptake was found to be maximum at pH=6.92 Lower adsorption of methylene blue at low pH is probably due to the presence of excess pH ions competing with cation groups on the dye for the adsorption sites. The percentage removal of the hydrolyzed reactive dyes decreased with further increase in pH (above PH=9), and the maximum removal rate was achieved under acidic conditions (pH=3) [7].

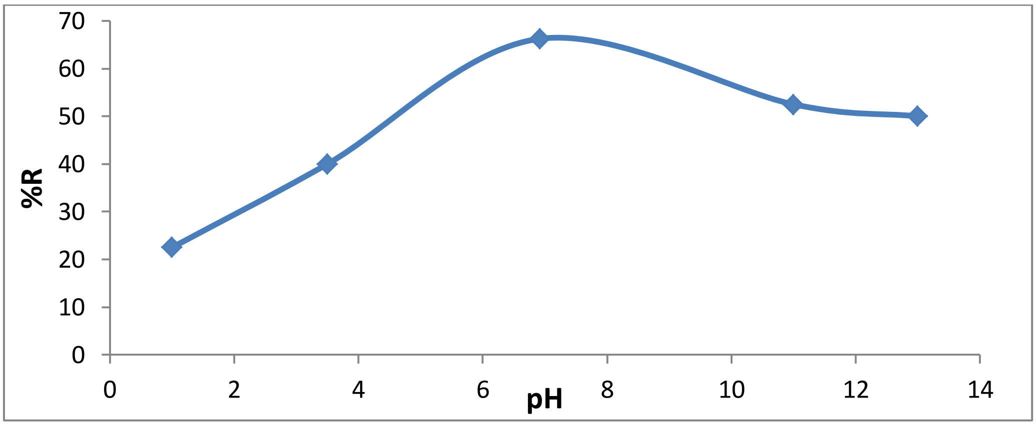

Figure-6: Effect of pH on adsorption of MB onto basil seeds.

3.1.5: Effect of temperature

Experiments were carried out at different temperature 293, 298, 303, 308 and 313K in conjunction with the optimum other parameters, contact time 25 min, adsorbent dose 1 gm , agitation speed 150rpm, and pH=6.92.293K was the best temperature..

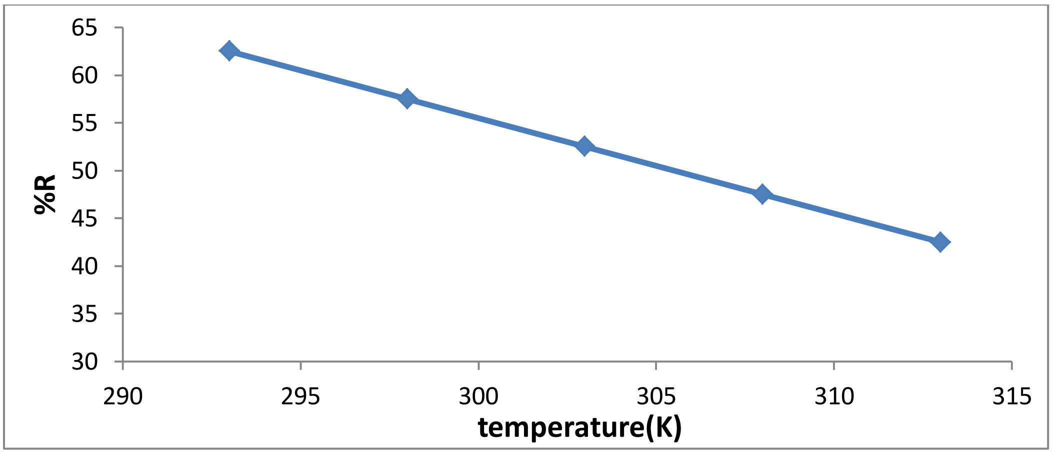

Figure-7: Effect of temperature in MB onto basil seeds.

3.2: Adsorption isotherms

To determine the adsorption capacity and potential for selecting the adsorbent for the removal of MB dye, the study of adsorption isotherm is essential in selecting the adsorbent. From all the batch experiment carried out, the optimum parameters selected were; pH 6.92, basil seeds dose 1gm, contact time 25 min, and agitation speed 150rpm**.** Adsorption isotherm study was carried out at five different temperature which were (293, 298,303,308 and 313) K.Two most common isotherm models were employed for describing the adsorption data, which were Langmuir and freundlich isotherm. The equilibrium values obtained are depicted in table -1.

Table -1: Equilibrium parameters for the adsorption of MB dye onto basil seeds.

MB C_O mg/L	Temperature (K)									
	293		298		303		308		313	
	C_e mg/L	Q_e mg/g	C_e mg/L	Q_e mg/g	C_e mg/L	Q_e mg/L	C_e mg/L	Q_e mg/L	C_e mg/L	Q_e mg/g
3	0.95	0.41	1.00	0.40	1.30	0.34	1.50	0.30	1.60	0.28
4	1.20	0.56	1.23	0.55	1.41	0.51	1.53	0.49	1.62	0.47
5	1.65	0.67	1.83	0.63	2.10	0.58	2.40	0.52	2.60	0.48
6	2.25	0.75	2.30	0.74	2.90	0.62	3.15	0.57	3.30	0.54
7	2.70	0.86	2.85	0.83	3.40	0.72	3.77	0.64	3.90	0.62
8	3.40	0.92	3.50	0.90	4.00	0.80	4.40	0.72	4.50	0.70
9	3.60	1.08	3.85	1.03	4.60	0.88	4.90	0.82	5.20	0.76
10	4.20	1.16	4.30	1.14	5.20	0.96	5.60	0.88	5.80	0.84

3.2.1:Langmuir isotherm

The Langmuir isotherm is valid for monolayer adsorption on to a surface with a finite number of identical sites. It is based on assumption of adsorption homogeneity, such as equally available adsorption sites, monolayer surface coverage and no interaction between adsorbed species [13].According to the Langmuir adsorption isotherm, the adsorption process can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{q_m k_l} + \left(\frac{1}{q_m}\right).C_e \qquad (3)$$

Where c_e (mg/L) is the equilibrium concentration of MB dye in solution, q_e (mg/g) is the amount adsorbed per unit weight at equilibrium, q_m (mg/g) the maximum adsorption capacity and K_L express the affinity between the adsorbent and adsorbate. The linear plots of C_e/q_e VS C_e suggest the applicability of the Langmuir isotherm; (figure -8). The values of q_m and K_L were calculated from the slope and intercept of the plot are listed in Table-2. Langmuir constants relates to the adsorption capacity and rate of adsorption, respectively.

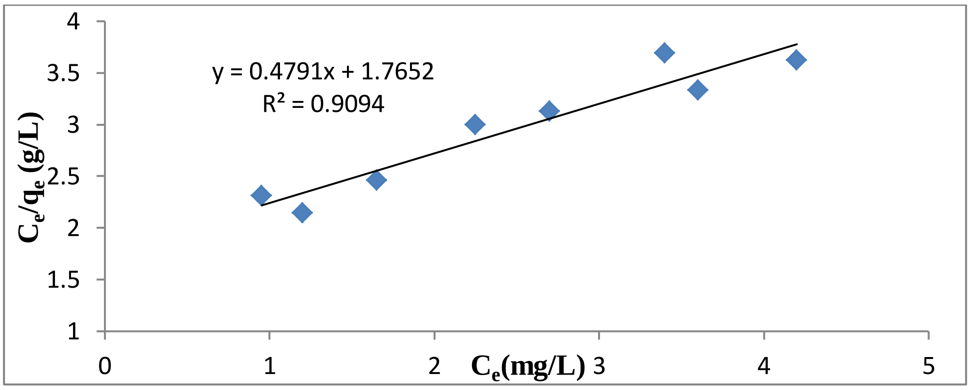

Figure-8: Langmuir plot of C_e/q_e versus C_e for MB onto basil seeds at 293K.

The essential characteristic of the Langmuir isotherm can be expressed by a dimensionless separation factor (R_L), and were determined by the following equation.

$$R_L = 1/1+K_LC_O \qquad (4)$$

Where: K_L is the Langmuir constant (L/mg). C_0 is the initial concentration (mg/L) .The value of R_L indicates the shape of the isotherm to be either unfavorable (R_L> 1), linear (R_L=1), favorable (0<R_L< 1) or irreversible (R_L= 0). Since RL values lies between 0 and 1 for all the five temperature studied, it indicates that the adsorption is favorable, favorable sticking of adsorbate to adsorbent-physisorption mechanism predominant [14].

3.2.2:Freundlich isotherm

Batch isotherm data fitted to the linear form of the freundlich isotherm which is commonly expressed by the following equation.

$$\text{Log } Q_e = \log K_f + 1/n \log C_e \qquad (5)$$

The values of k_F and n were calculated from figure-9 and the data are provided in Table -2. These are the indicators of the adsorption capacity and adsorption intensity, respectively. This supports the applicability of freundlich adsorption isotherm indicating that the adsorption by weld seeds may be governed by physisorption. From the values of the regression coefficient R^2 listed in Table-2, Freundlich isotherm gave good and better fit to the experimental data than Langmuir.

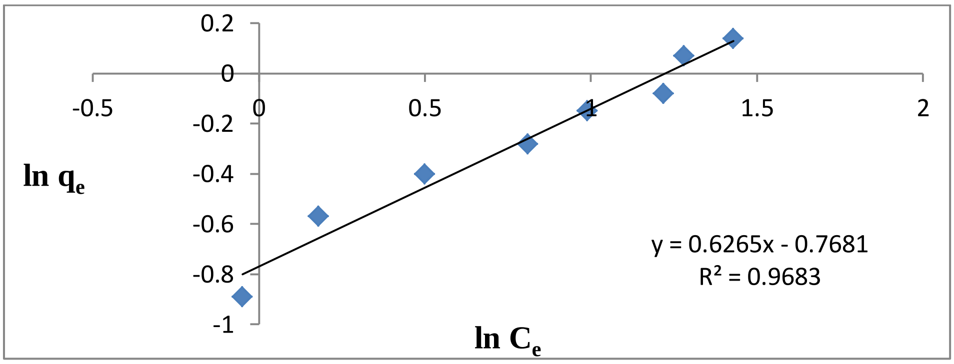

Figure-9: Freundlich plot of $\ln q_e$ versus $\ln C_e$ for MB onto basil seeds at 293K.

Table -2: Langmuir and, freundlich isotherm model parameters and their correlation coefficient of the adsorption of MB dye onto basil seeds.

Temperature (K)	Langmuir Results			Freundlich Results			Dimension less Separation Factor R_L MB C_o (4mg/L)
	q_m mg/g^{-1}	K_L L.mg	R^2	K_f	n	R^2	
293	2.087	0.271	0.9094	0.4638	1.5961	0.9683	0.4794
298	2.084	0.247	0.9068	0.4367	1.5837	0.9697	0.5028
303	1.722	0.223	0.8843	0.3488	1.6398	0.911	0.5278
308	1.703	0.177	0.7174	0.2945	1.5982	0.8526	0.5854
313	1.573	0.178	0.7687	0.2633	1.5427	0.8413	0.5831

3.3: Adsorption thermodynamic

Thermodynamic parameters, change in Gibbs free energy ΔG^0, enthalpy change ΔH^0, and entropy change ΔS^0 were calculated according to following equation.

$$\Delta G^o = -RT\ln K_{eq} \qquad (6)$$

$$\text{Ln } k_{eq} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (7)$$

Where:K_{eq} is the equilibrium constant, q_e is the solid phase concentration at equilibrium (mg/g), C_e is the liquid phase concentration at equilibrium (mg/L) and T is an absolute temperature, and R is the gas constant [15]. ΔH^0 and ΔS^0 values were obtained from the slope and intercept of vant Hoff plots Figure-11, and are given in table- 3.

Table- 3: thermodynamic parameters of MB dye sorption onto basil seeds.

Temperature (K)	K_{eq}	lnK_{eq}	ΔG^0 ($J.mol^{-1}$)	ΔH^0 ($J.mol^{-1}$)	ΔS^0 ($J. mol^{-1}.K^{-1}$)
293	2.33	0.845	-2058.42	-19115.5	-58.215
298	2.23	0.802	-1987.01		
303	1.80	0.587	-1478.73		
308	1.60	0.470	-1203.53		
313	1.46	0.378	-983.66		

When the temperature of the system increase, the extent of adsorption decrease, this become obvious from the values of K_{eq} which decrease with increase in temperature that means the process is exothermic, this is confirmed by the negative values of ΔH°. The negative value of entropy change ΔS° suggests a high degree of the order at the solid-solution interface during the adsorption process. The negative value of ΔG° indicates that the adsorption is spontaneous and became more spontaneous at low temperature.

3.4: Adsorption kinetics

In order to investigate the adsorption kinetics of MB dye onto basil seeds, the pseudo–first order equation of lagergreen equation and, pseudo second order equation [15]**.** Were applied to the experimental data:

$$\ln(qe - qt) = \ln qe - k_1 t \quad (8)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q} + \left[\frac{1}{q_e}\right] t \quad (9)$$

Where q_e and q_t is the amount Adsorbed at equilibrium and at time t respectively.k_1 is the first – order rate constant (min^{-1}). K_2 is the second –order rate constant (g/mg. min) and t is the time in min. The parameters obtained by the application of the two kinetic models were reported in Table-4.

Table-4: parameters of kinetic models for adsorption of MB dye onto basil seeds at 293K.

MB dye C_0 mg/L	Pseudo first order		Pseudo second-order	
	K_1	R^2	K_2	R^2
3	0.2036	0.9183	0.3047	0.9694
4	0.1684	0.8997	0.2980	0.9801
5	0.137	0.9714	0.3475	0.9969
6	0.106	0.9422	0.2880	0.9886
7	0.0794	0.9005	0.2619	0.9831
8	0.0632	0.8585	0.2256	0.9695
9	0.034	0.9698	0.2475	0.9593
10	0.049	0.9932	0.1471	0.9685

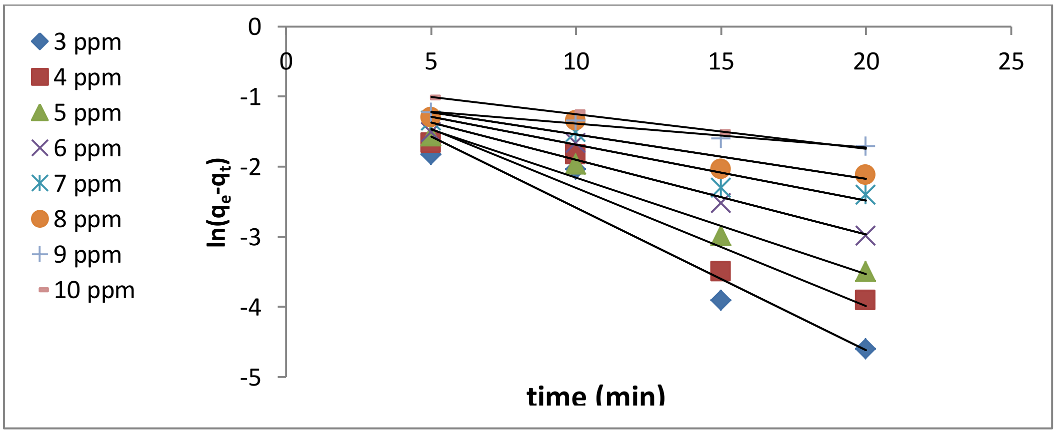

Figure-11: first-order kinetic equation model for adsorption of MB dye onto basil seeds at 293K.

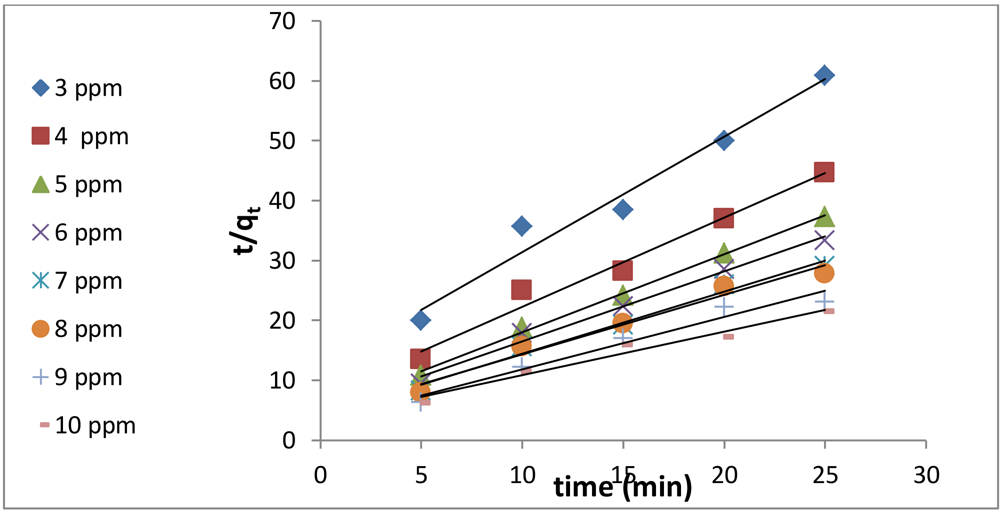

Figure-12: second-order kinetic equation model for adsorption of MB dye onto basil seeds at 293K.

The value of the rate constant calculated from the first-order and second order kinetic equation are found to be greater for the second order, therefore the second kinetic equation can be employed to calculate the rate constant for the adsorption process of MB onto weld seeds, and Linear plots were obtained with high correlation coefficient (R^2), suggesting that the interaction between the adsorbent and the MB follow the pseudo-second order mechanism.

Conclusion:

This study confirmed that basil seeds can be used effectively for the removal of MB dye from aqueous solution. The removal efficiency reaches %63 in some instances. The adsorption process based on solution pH and effect of temperature.

The process of adsorption was best fitted by Freundlich model, and second order model fitted the kinetics. According to the results, basil seeds are recommended as an available and safe biosorbent to the removal of toxic dyes.

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