Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 13 (3) 237-252: Fall 2016
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

Adsorption of Malachite Green Dye from Aqueous Solutions Using Roots of Azolla Filiculoides

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Received October 2016; Accepted December 2016

ABSTRACT

Pollution of water resources by various pollutants is nowadays a global environmental issue. Among the different type of water pollutants, dye represents a major polluting group. In this study, *Azolla filiculides* roots have been used for adsorption of Malachite Green (MG), a cationic dyed from aqueous solution. In this study, effects of operating parameters such as initial concentration of dye (5-30 mg/L), contact time (5-120 min), adsorbent dosage (0.05- 0.5) and pH (6-11) in the batch system investigated. The adsorption process data successfully were described by Langmuir, Freundlich, Temkin and BET isotherms. The kinetics of the adsorption data were analyzed using 3 kinetic models such as pseudo second- order, Intra-particle diffusion and Elovich to understand the adsorption behavior of Malachite Green onto *Azolla filiculoides* roots. The result showed the removal of MG was increased by increasing contact time and adsorbent dose, and pH. According to the analysis of the different kinetic models for adsorption of MG on *Azolla filiculoides* roots follows of Pseudo second – order kinetic. The Temkin model described the adsorption result very well. This study indicated can be used as an effective and inexpensive adsorbent to removal of Malachite Green from aqueous solution. The positive value of change in enthalpy shows that the adsorption MG dye onto *Azolla filiculoides* roots is endothermic. Furthermore, the negative value of indicated that the adsorption MG dye was thermodynamically spontaneous.

Keywords: Azolla filiculoides; Cationic Dye; Adsorption Kinetics; BET Thermodynamic

1. INTRODUCTION

Dye is widely used in industries such as textiles, rubber, plastics, printing, leather, cosmetics, etc., to color their products. As a result, they generate a considerable amount of colored wastewater. There are more than 10.000 commercially available dyes with over tone of dye stuff produced annually. It is estimated that 2% of dyes produced annually is discharged in effluents from associated industries [1]. Some of the dyes present in wastewater even decompose into carcinogenic aromatic amines under anaerobic conditions and cause serious health problems to human beings as well as other animals. Many died and there by- products break down into products, which are toxic for living organisms [2].Malachite green is environmentally persistent and acutely toxic to a wide range of aquatic and

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terrestrial animals. Several studies have shown MG to be highly lethal to fresh water fish, in both acute and chronic exposures. It causes serious public health hazards and also poses potential environmental problems. Both clinical and experimental observations reported to so far reveal that, MG is a multi-organ toxin. It decreases food intake, growth and fertility rates; cause damage to liver, spleen, kidney and heart; It inflicts lesions on skin, eyes, lungs and bones and produces teratogenic effects. Malachite green is highly cytotoxic to mammalian cells. Incidences of tumor in lungs, breast and ovary have been also reported from rats exposed to MG. It also acts as a respiratory enzyme poison decrease in RBC count (dyscrasia), H_b (anemia) and HTC (%); increases in WBC count (leucocytosis) and delay in blood coagulation were observed after exposure [3-4-5].

Among the advanced wastewater treatment methods used for dye removal (advanced oxidation, membrane separation, adsorption, bio sorption, photocatalysis, ion exchange and others), adsorption is one of the most effective, due to its low cost, low energy requirements and simple operation [6]. Adsorption by the adsorbent material cost as an effective and economical process for the removal of dyes known [7-8].

The adsorption processes are more efficient methods for removing pollutants from wastewater. It also provides an alternative treatment method, especially if the adsorbent is inexpensive and readily available [9]. The most perfect adsorbent used for color removal is an activated carbon, but it is expensive and its regeneration is time consuming additionally powdered activated carbon requires filtration and centrifugation for its separation after use [10]. In this regard agriculture waste material like: Coffee beans [11] Lemon's peel [12] Almond shell [13] Mango bean [14] Rice husk [15] Sawdust [16] Peanut husk [17] was tried successfully. Azolla filiculoides is a floating aquatic fern which is growing rapidly in stagnant wetlands and cover the surface of water. Therefore, it is a risk for aquatic life, especially in ANZALI wetlands in north of Iran [18] The cell wall of plant biomass has proteins, lipids, carbohydrate polymers (cellulose, x y lane, mannan, etc.) and inorganic ions of Ca^{2+}, Mg^{2+}, etc. The carboxylic and phosphate groups in the cell wall are acidic functional groups of biomass and this functional groups direct affect the adsorption capacity of the biomass [19]

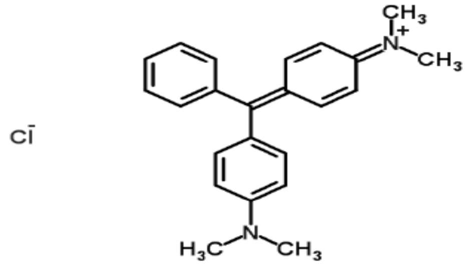
Therefore, the main aim of this work has focused their attentions to find out low-cost adsorbent for the removal malachite green dye from aqueous solution. The Azolla filiculoides roots as inexpensive adsorbent for removal MG dyed is used. Because previous studies on the removal MG dye by Azolla filiculoides roots, no research has been done, so the aim of this study was to evaluate the removal of MG by fern Azolla filiculoides roots in aqueous solution. The effective parameters on the batch technique such as initial pH, contact time, dosage, and initial concentration have been investigated. The adsorption isotherm and kinetic are investigated to study the removal capacity of MG dye by adsorbent.

2. MATERIALS AND METHODS

1.2. Methods

Malachite-Green dye, $NaOH$ and HCl solutions were provided from Merk chemical company. Table1 summarizes the physical- chemical properties of Malachite-Green dye [20].

Table 1. Characteristics of MG dye

C.I. Name	Empirical Formula	Molecular weight	Maximum Adsorption Wavelength	Chemical Structure
Basic Green 4	**$C_{23}H_{25}ClN_2$**	**364.91 g/mol**	**615 nm**	

3.2. Instruments

A UV-Vis spectrophotometer (models: Lamda 25 and WPA) were used in the determination of the MG dye concentrations. A pH meter (model: Metrohm) was employed for pH measurements of the MG dye solutions. Furthermore, a shaker (model: Heidolph 1010) was used for shaking materials. An FTIR (BRUKER) was used for characterization of adsorbent. The BET isotherm was measured by nitrogen adsorption at 77 K (model: Belsorp mini II, BelJapan).

4.2. Methods

Preparation of adsorbent

Azolla filiculoides roots were collected from ANZALI Wetland in north Iran on 14 Apr 2014. The root of this plant was washed with tap water and finally rinsed with distilled water to remove impurities. The adsorbent was dried in the sun for a week. The material was sieved by the mesh size 100.

5.2. Preparation of dye stock solution

The stock solution was prepared by dissolving 0.1g of MG in distilled water at a concentration of 100 mg/L.

6.2. Adsorption process

A mount of 0.1 g Azolla filiculoides roots added to 25 ml 0f MG dyed solutions at of pH= 9 (opt) initial concentration of MG dyed was ranged between (5- 10 – 15- 20-30) mg/L in the investigation of initial concentration. The batch experiments were performed in orbital shaker for 120 min and 5 rpm. The amount of dye adsorbed on Azolla filiculoides roots obtain as follows (2) and the percent of dye removal, the following equation was used (1)

$$\%R = C_0 - C_e / C_e \times 100 \quad (1)$$

$$Q_e = (C_0 - C_e) \times V / W \quad (2)$$

Where is the equilibrium capacity of dye in the adsorbent (mg-1), is the initial concentration of dye solution (mg L−1), C_e is the equilibrium concentration of dye solution (mg L−1), V is the volume of dye solution used (L) and W is the weight of adsorbent (g) used [21].

3. RESULTS AND DISCUSSION

1.3. Characterization of adsorbent

The FTIR spectrum of Azolla filiculoides roots is presented in figure 1. The range of different functional groups can be seen. The broad band at around 3474.56 Cm-1 is typically attributed to hydroxyl groups. The peak values in 1700, 1625.94, 1257.91 and 1063.77 Cm-1 confirm the functional groups such as C=O stretch, C=C, C-C, CH bending respectively. These groups have negative charge. Where can be sites for adsorption of Malachite-Green dye onto Azolla filiculoides roots.

2.3. Effect of pH

One of the most important parameters for adsorption of any adsorbate is pH, which influences the adsorption. Effect of pH on adsorption of Malachite green was investigated at the initial pH ranged between 6 and 11 for initial dye concentration 25 ppm, the agitation speed (5rpm) and contact time (120 min). A sample of 0.1 g of adsorbent was used, and the desired pH value was adjusted using 0.1 N $NaOH$ and HCl solution. Figure 2 shows the effect of pH on removal percentage of MG by Azolla filiculoides roots. According to results illustrated in figure 1, the removal percentage of Malachite green was increasing of solution pH values from 6.0 to 9.0. Hence, optimum pH values were selected to be 9.0 for the adsorption of Malachite green by Azolla filiculoides roots. With increasing pH the number of positively charged sites decreased and the number of negatively charged sites increased. This phenomenon favours the sorption of positively charged to dye due to electrostatic attraction [22].

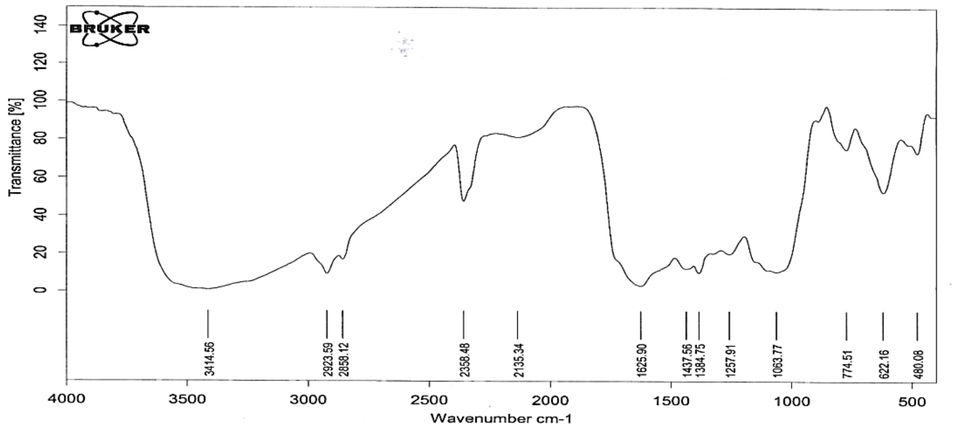


Fig. 1. FT-IR spectrum of Azolla filiculoides roots.

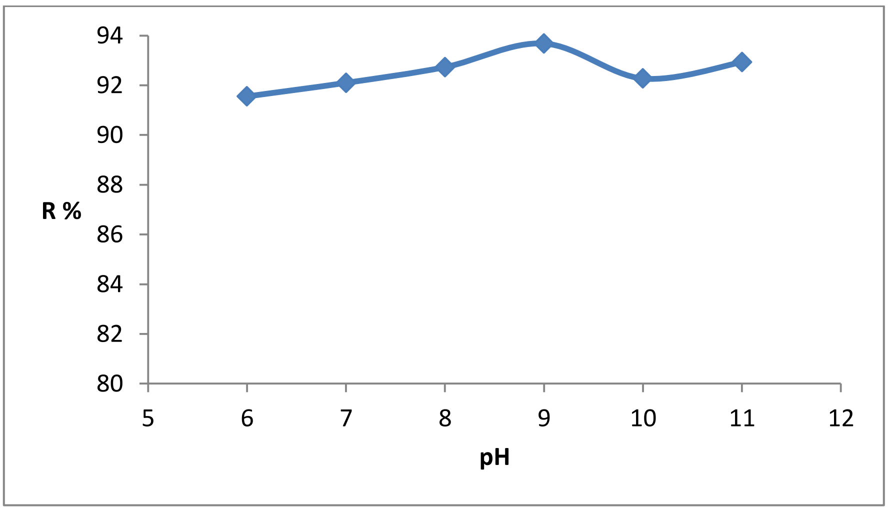


Fig. 2. Effect of pH on the adsorption of Malachite-green die by Azolla filiculoides roots. ($U:5rpm, V:10mg$; C_0: $20ppm$; $M=0.1g$; $pH:6-11$; $T=120\min$).

3.3. Effect of adsorbent dose

The study was carried out to examine the effect of Azolla filiculoides roots does on the cationic dye removal at room temperature. The uptake of dye with change in adsorbent dosage (0.05 – 0.5) g at adsorbate concentration of 20 mg/L and pH 9 is presented in figure3. The results indicated that increase in a dose of Azolla filiculoides roots to 0.1 g lead to increasing in Malachite green (MG) removal percentage. This fact is due to a more available adsorption sites for MG dye. The result indicates that the more dose of Azolla filiculoides roots leads to decrease of MG dye adsorption. Hence, optimum doses were selected to be 0.1 g for the adsorption of MG dye by adsorbent.

4.3. Effect of contact time and initial dye concentration

0.1 g of adsorbent (Azolla filiculoides roots) with 25 m1 of MG dyed solution was kept constant. Batch experiment for initial MG dyed concentration of (5 – 30) mg/L was performed for (5 -120) min and pH 9. In figure 4, the effect of contact time and initial dye concentration on adsorption of MG with Azolla filiculoides roots is presented. Adsorptions of MG dye were rapid in first 40 min and after 40 min amount of MG dye absorbed were constant. During the initial stage of sorption, a large number of vacant surface sites are available for adsorption. After laps of some time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules adsorbed on the solid surface and the bulk phase [23].

5.3. Effect of temperature

The effect of temperature on the adsorption process was studied at 287.15, 297.15, 309.15 and 319 k. 0.1 g of adsorbent was put into the dye solution with concentration of 30 mg/L, pH 9, contact time (40 min) and agitated at 5 rpm. The result in figure 5 that the sorption capacity of MG increased from 7.18 to 7.27 mg/g with temperature increased from 287.15 to 309.15 K. As the temperature increases, rate of diffusion of adsorbent particle increased [24].

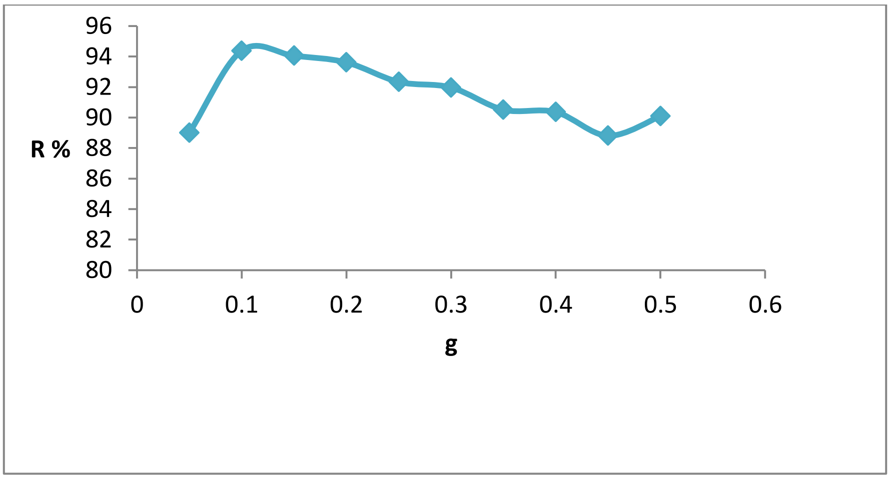


Figure3: Effect of sorbent dosage on sorption of Malachite-Green dies. ($V:25ML$; C_0: $20ppm$; M: 0.05-0.5 g; $pH:9$; $T=120$ min; $U:5rpm$).

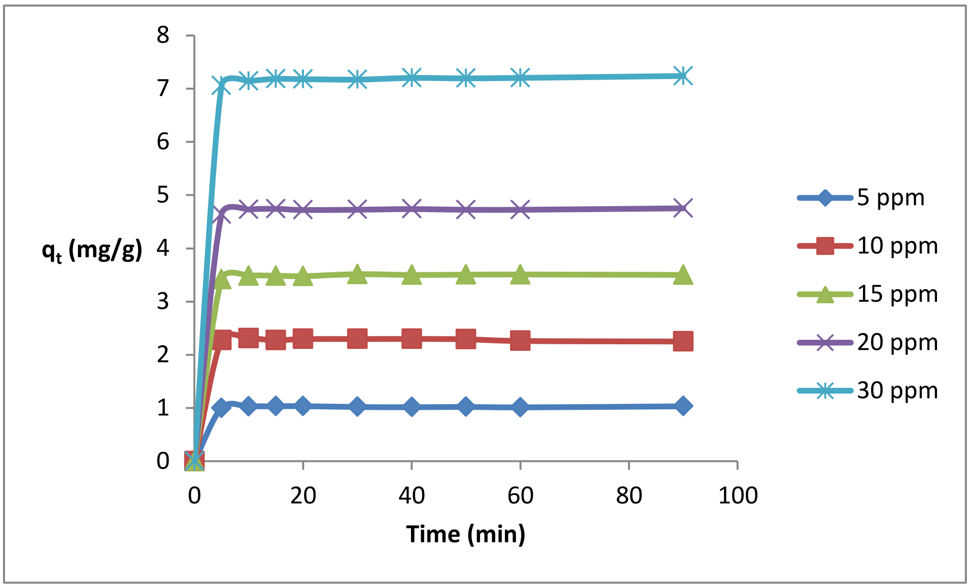


Fig. 4. Effect of initial dyed concentration on sorption MG by Azolla filiculoides.

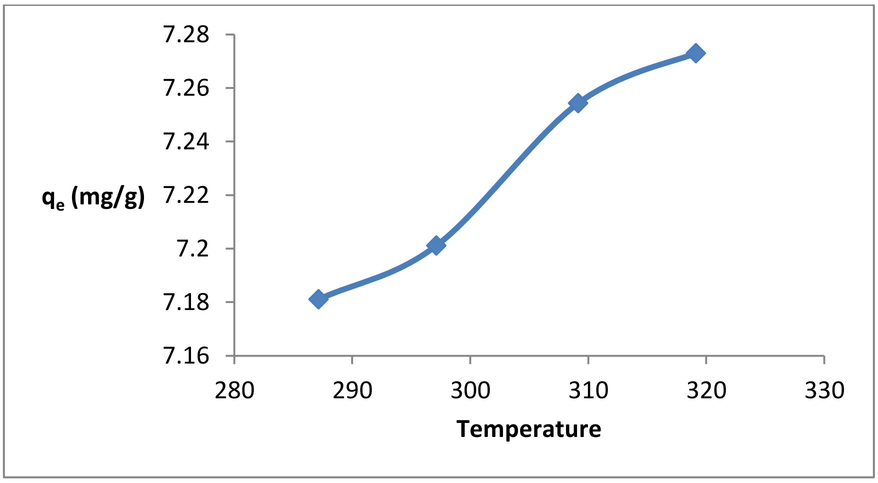


Fig. 5. sorption capacity of Azolla filliculoides on removal of MG dye at a different temperatures. ($V:25ML$; $U:5rpm$; C_0: $30ppm$; $M:0.1g$; $pH:9$; $Time:40\,min$).

6.3. Adsorption kinetics

Adsorption kinetic is an important part of the adsorption study for complete understanding of the adsorption behavior [25]. In this study, the adsorption data were analyzed using three kinetic models, the pseudo- second order, and Elovich and Intra particle diffusion kinetic models.

7.3. Pseudo second order

Kinetic data are further treated with pseudo second- order kinetic model [26]. The pseudo second- order equation after transformation into linear from can be written as eq3:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

where, q_e: Amount of solute adsorbed at equilibrium (mg/g); q_t: amount of solute adsorbed at time (mg/g); k_2: pseudo second- order equilibrium rates constant (g.mg-1. H-1); t: contact time (min).

Additionally, h (mg.g-1.min-1) standard for original adsorption rate which can be defined as $h = K_2 \ q_2$ [27]. The slopes and intercepts of the plot of t/q_t against t in figure 6 were used for calculated K_2 and q_e. From table 2 and 3, it is very obvious to see that kinetics of adsorption MG dyed by Azolla filiculoides roots are better described by pseudo second- order kinetic model rather than Elovich kinetic and Intra-particle diffusion. The pseudo second- order kinetic model has a regression coefficient of R2 as 1 when the initial MG dyed concentration increases from 5 to 30 mg/L, while that of Elovich kinetic and Intra-particle diffusion kinetic models various from 0.07 to 0.83 and 0.03 to 0.71.

8.3. Elovich kinetic

Elovich equation is also used successfully to describe second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not purpose any definite mechanism for adsorbate –adsorbent [28]. The Elovich model equation is generally expressed as (4):

$$\frac{dq_t}{dt} = \alpha e^{(-\beta q_t)} \quad (4)$$

where α is the initial adsorption rate (mg. g-1.min-1) and β is the desorption constant (g.mg-1) during experiment. The Elovich equation could be simplified by assuming αβ≫ t and applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Eq (5). It becomes [29].

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln t \quad (5)$$

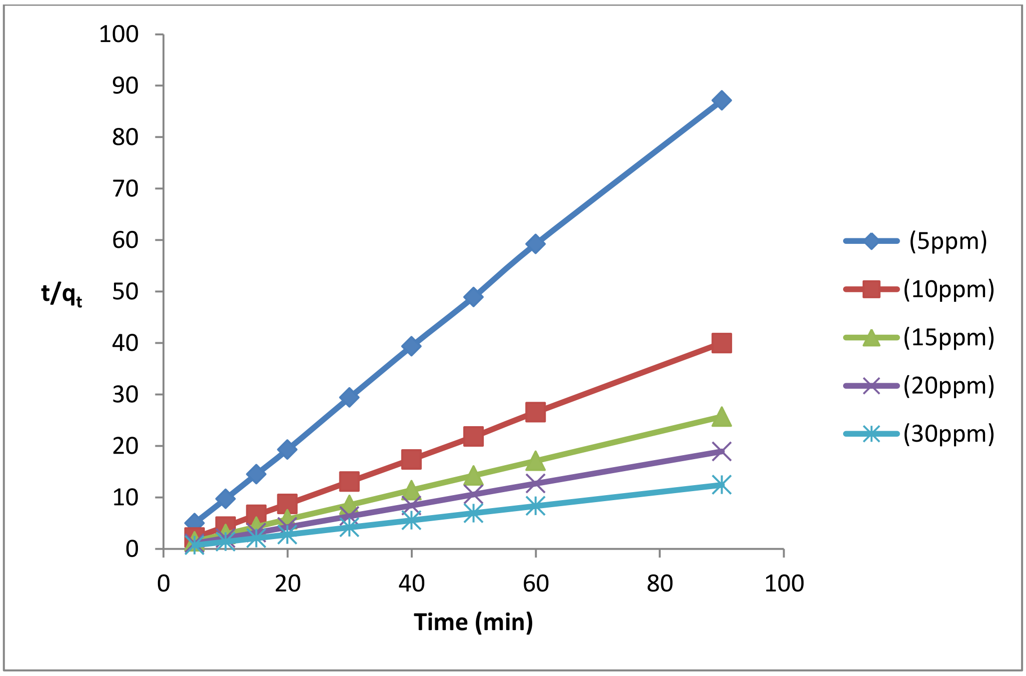


Fig. 6. Pseudo second- order model of kinetic' curves.

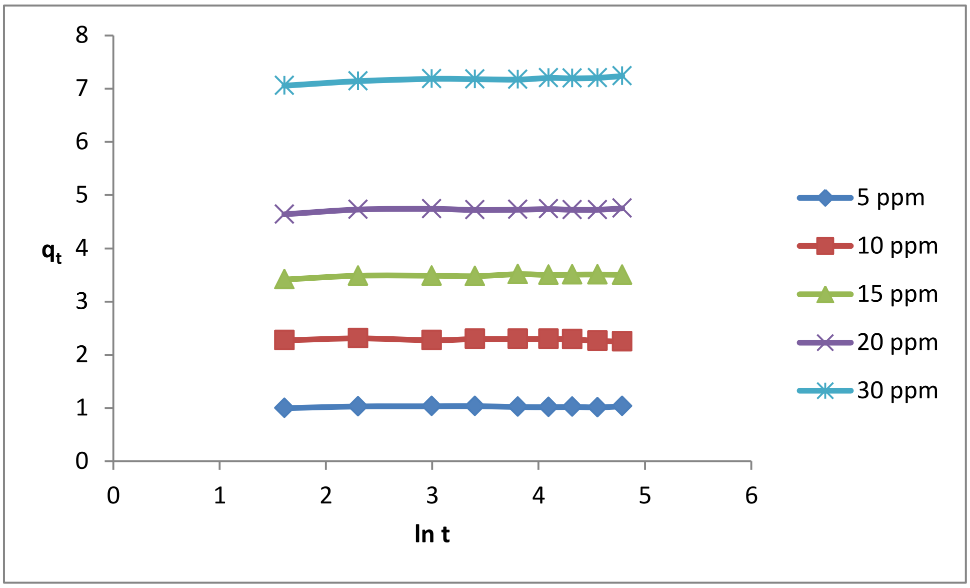


Fig. 7. Elovich kinetics for MG dye adsorption on Azolla fililculoides roots.

9.3. Intra-particle diffusion

The adsorbate species are most probably transported the bulk of the solution into the solid phase through an intra –particle diffusion process, which is often the rate-limiting in many adsorption processes. The possibility of intra-particle diffusion is explored by using the intra-particle diffusion model [26]. The intra - particle diffusion model was expressed by (6):

$$q_t = k_{id} t^{0.5} \quad (6)$$

Where k_{id} (mg.g-1.min-0.5) is intra-particle diffusion rate constant [27]. In figure 8 shown the R^2 amount determined from the slop and intercept of the plot of q_t against $t^{0.5}$.

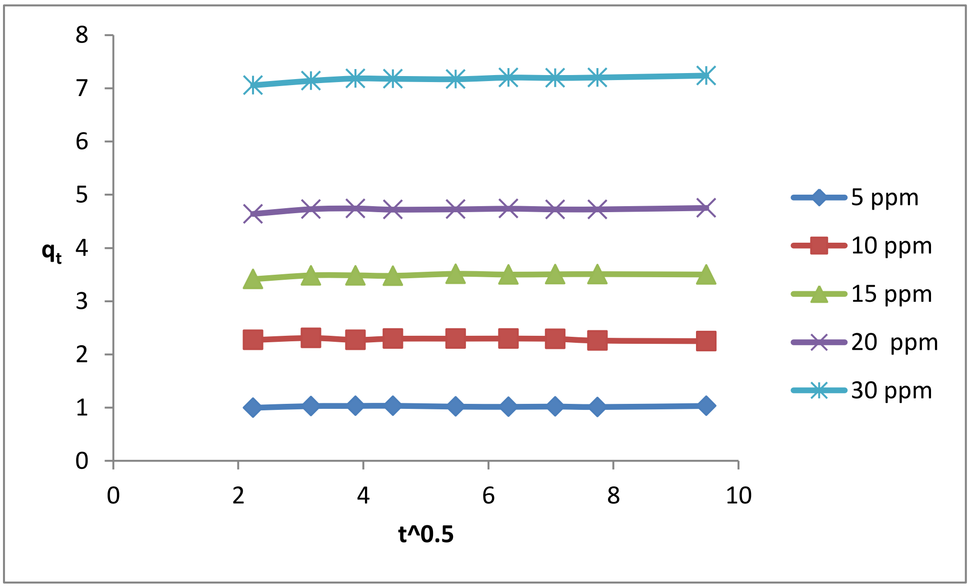


Fig. 8. Intra-particle kinetics for MG dye by adsorbent.

Table 2. Rate constant of the kinetic model (Pseudo-order rate constants)

Mg/L (C_0)	Qe (EXP) Mg/g)(	$Q_{e\,(Cal)}$ Mg/g)(	R^2	K^2	$1/Q_e$
5	1.025	0.9734	0.9998	-8.27814	1.0273
10	2.2675	2.6602	0.9999	0.06278	0.37559
15	3.305	0.2850	1	152.1815	3.5083
20	4.720	0.21062	1	-201.454	4.7478
30	7.2	7.2411	1	0.7251	0.1381

Table 3. The values R^2 of Elovich and Intra-particle diffusion models

$C_0(Mg/L)$	**(Elovich)** R^2	R^2 **(Intra-particle diffusion)**
5	0.0702	0.0356
10	0.0921	0.2242
15	0.6781	0.4925
20	0.4782	0.3599
30	0.832	0.7161

10.3. Adsorption isotherm

The main factors that play a role for the dye –adsorbent interactions are charge and structure of dye, adsorbent surface properties, hydrophobic and hydrophilic nature, hydrogen bonding, electrostatic interaction, steric effect, and van deer wall forces et [30]. The equilibrium experimental data for MG dye on Azolla filiculoides roots compared using three isotherm models namely, Langmuir, Freundlich and Temkin. Figure 9 shows the relationship between equilibrium uptake (q_e) and equilibrium C_e of Malachite Green onto Azolla filiculoides roots. The results shown that, with the increase in initial MG dye, q_e increased.

10.3.1 Freundlich isotherm

The freundlich equation was employed for the adsorption of MG dye using Azolla filiculoides. The equation is stated as follows (7):

$$q_e = k_f C_e^{1/n} \tag{7}$$

Where n and k_f $[mg/g(L/mg)n]$ are both the Freundlich constants given an indication of adsorption intensity and capacity, respectively [31]. The Freundlich isotherm can be given in the linear form by the following equation (8):

$$\ln q_e = \ln k + 1/n \ln C_e \tag{8}$$

Where k (L/mg) and n are the Freundlich constants [32]. The values of Freundlich parameters were calculated from the slope and intercept of the Freundlich plot of Lnq_e of against Lnc_e given in figure 10 and table 4.

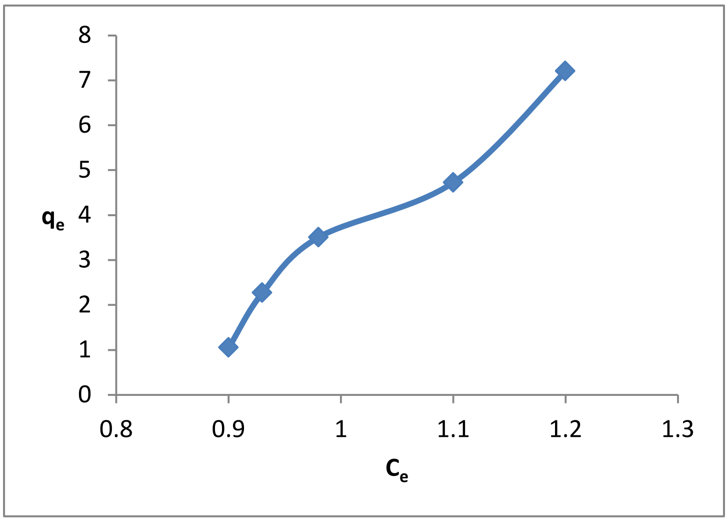


Fig. 9. Adsorption isotherms for MG dye on Azolla filiculoides roots.

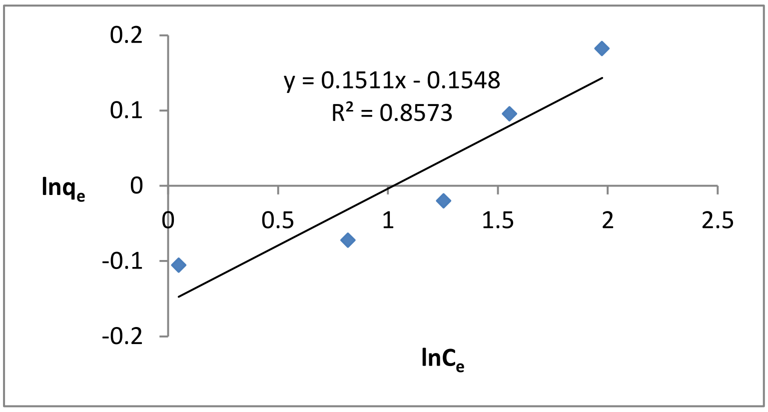


Fig. 10. Freundlich plot for sorption of MG dyed onto Azolla filiculoides roots.

10.3.2. Langmuir isotherm

Langmuir isotherm assumes that all binding sites have equal affinity for the sorbate, resulting in the formation of the monolayer of adsorbed molecules [33]. The Langmuir isotherm is expressed as (9):

$$1/q_e = 1/q_m + 1/bq_m \times 1/C_e \quad (9)$$

where b is the constant that increases with increasing molecular size, q_m is the amount adsorbed to form a complete monolayer on the surface ($mg.g^{-1}$), C_e is the concentration remaining in solution (mgL^{-1}) [34]. The q_m and b values calculated from the sol and intercept of the plot of in $1/q_e$ against $1/C_e$ (figure 11) and (table 6).

10.3.3. BET isotherm

In Figure 12, adsorption and desorption isotherms, Azolla filiculoides roots are shown. Both isotherms type II according to IUPAC classification. Type II isotherms are characteristic of systems containing microspores because they exhibit a strong interaction between adsorbate and adsorbent, which results in a steep rise in the isotherm under low partial pressures [35]. The results of the plots (BET, BJH plots are given in Tables 4 and 5 and figures 12-14).

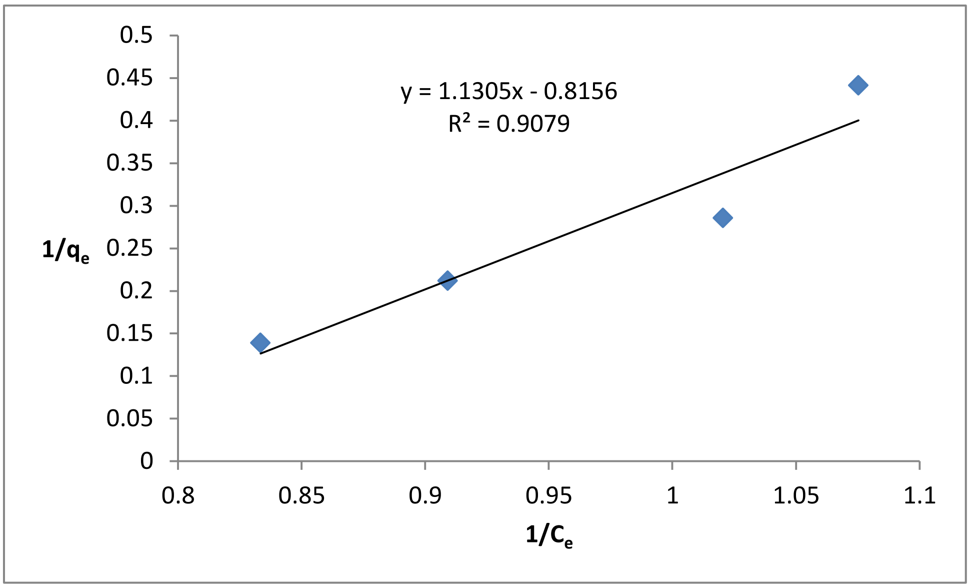


Fig. 11. Langmuir plot for sorption of MG dyed onto Azolla filiculoides roots.

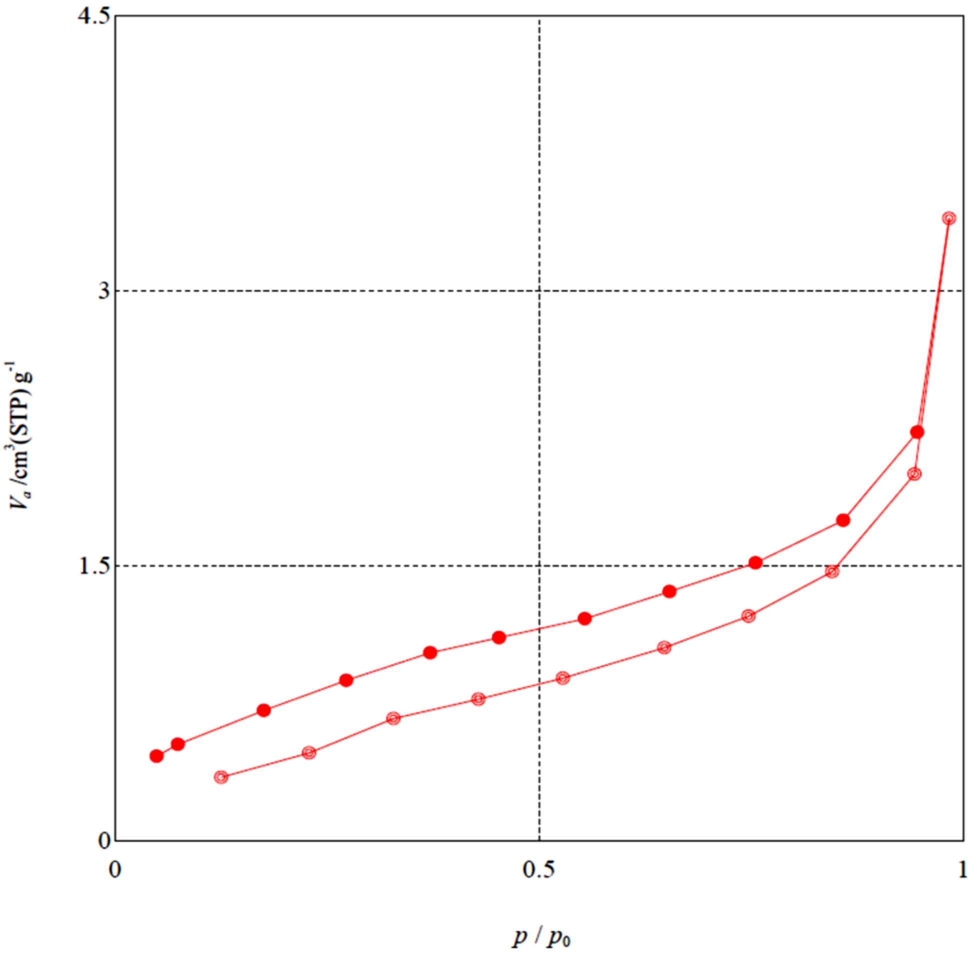


Fig. 12. Adsorption/ desorption isotherm (Adsorbate: N_2, adsorbent: Azolla filiculoides roots, adsorption temperature: 77 k).

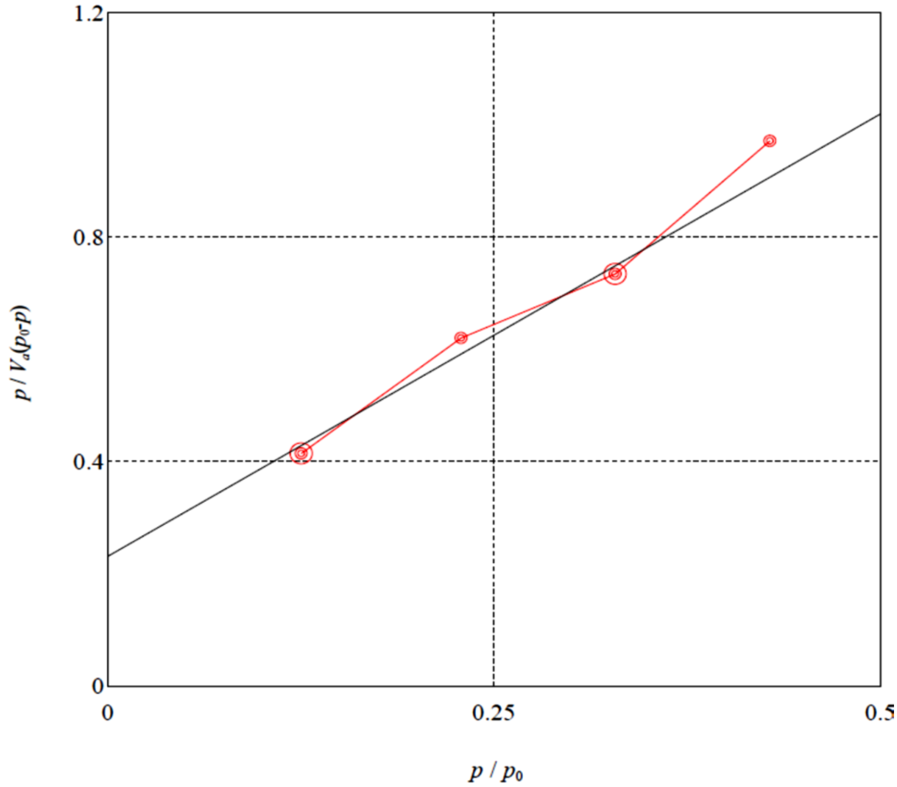


Fig. 13. BET- Plot (Adsorbate: N2, adsorbent: Azolla filiculoides roots, adsorption temperature: 77 K).

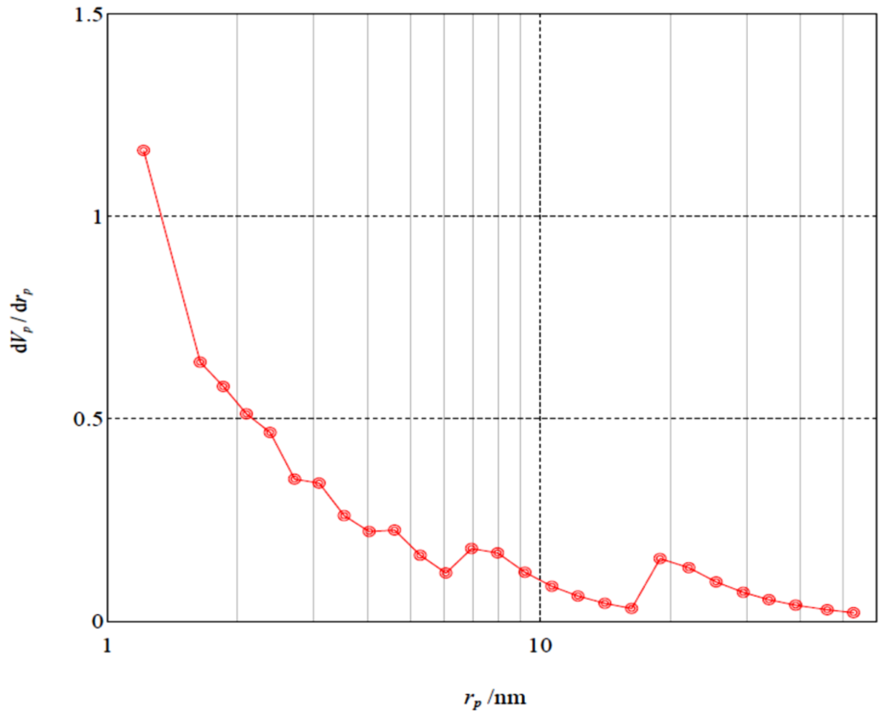


Fig. 14. BJH- Plot (Adsorbate: N2, adsorbent: Azolla filiculoides roots, adsorption temperature: 77 K).

Table 4. Data from BET-plot by Azolla filiculoides roots

Sample: Azolla filiculoides roots	V_m $[cm^3 g^{-1}]$	C **(constant)**	**Mean pore diameter** (nm)	**Total pore volume** $(p/p_0 = 0.983)$ $[cm^3 g^{-1}]$	a_s **,BET** $[m^2 g^{-1}]$
	0.5531	7.8189	8.7170	5.2460E-03	2.4073E+00

Table 5. BJH-plot

BJH< 2 nm (Microspores)		
V_p $[cm^3 g^{-1}]$	a_p $[m^2 g^{-1}]$	$r_{p,peak}$ **(Area)**
5.4608E-03	2.6208	1.21 nm

10.3.4. Temkin isotherm

The Temkin model proposes into account the effects of the interaction of the adsorbate and the adsorbing species [31]. The Temkin isotherm is given as (9):

$$q_e = B \ln A + B \ln C \tag{9}$$

where A ($1/g$) is the equilibrium binding constant, corresponding to the maximum binding energy and constant B is related to heat of adsorption. A linear plot of q_e against LnC_e, enables the determination of the constant's B and A from the slope and intercepts [24]. The results of the plots are given in Table 6 and figure 15.

Table 6 reveals that R^2 values of Freundlich, Langmuir and Temkin isotherm are o.8573, 0.9079 and 0.9665, respectively. From the observation based of R^2, it can be seen that the Temkin model fits better than the Freundlich and Langmuir models.

4. Thermodynamic study

In order to explicate the feasibility and spontaneous nature of MG uptake studies, the thermodynamic parameters have been evaluated using Vant Hoff's equation (10)

$$\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{10}$$

ΔH° and ΔS° were calculated the slope and intercept of van't Hoff plot of LnK_b against $1/T$, where ΔH°, Enthalpy and ΔS° Entropy change (fig 16 and table7. supporting information) [21].

The Gibbs energy determined by equals (11) to (12):

$$\Delta G^0 = -RT \ln k_c \tag{11}$$

$$k_c = \frac{C_{Ae}}{C_e} \tag{12}$$

where R(8.314 J.mol-1. K-1) is the ideal gas constant, $T(K)$, K_c is the equilibrium constant [27].

As can be seen from table7, the positive value of change in enthalpy shows that the adsorption MG dyed onto Azolla filiculoides roots is endothermic. Also, the negative value of ΔG° indicated that the adsorption MG dye was thermodynamically spontaneous.

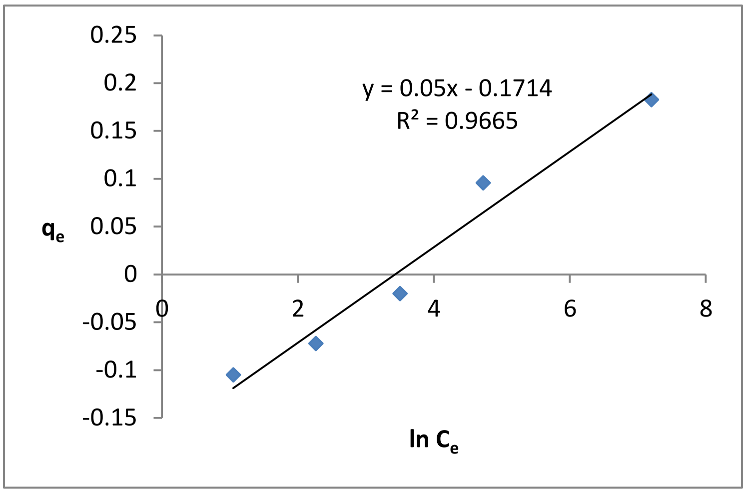


Figure 15: Temkin plot for sorption of MG dyed onto Azolla filiculoides roots.

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Table 6: Isotherm parameter for adsorption MG dyed onto Azolla filiculoides roots

Isotherm	Parameter	Values
Langmuir	q_m (mg/g)	-1.22609
	b (L/mg)	-0.72145
	R^2	0.9079
Freundlich	K_f	o.8565
	$1/n$	0.1511
	R^2	0.8573
Temkin	B	0.05
	A	0.03245
	R^2	0.9665

Table 7. Thermodynamic parameters for 30 mg/L of MG dye onto o.1 g adsorbent

Temperature (K)	K_c	ΔG° (kJ/mol)	ΔH° (kJ/mole)	ΔS° (J/mol. K)
278.15	22.51351	-7.43453	+8.94253	0.05686
297.15	24.09615	-7.86127		
309.15	29.52632	-8.70109		
319.15	32.03797	-9.19917		

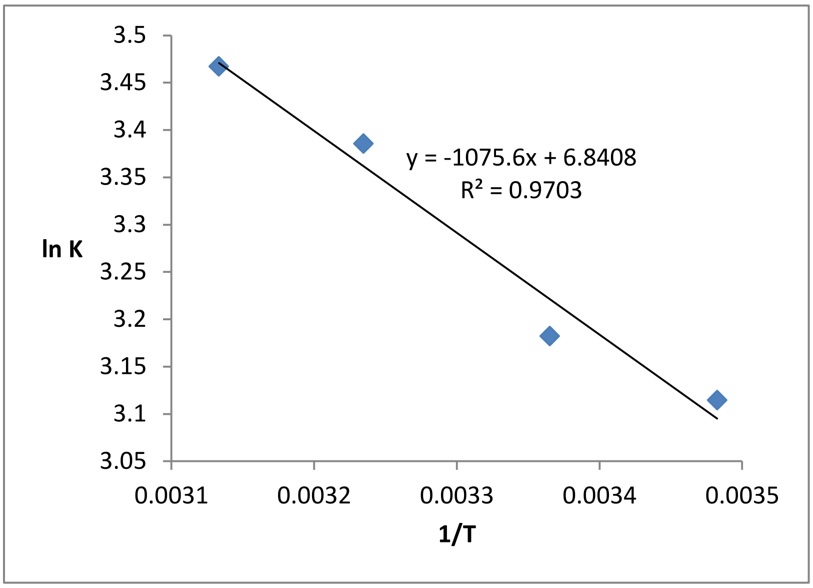

Fig. 16. van't Hoff plot for sorption of MG dyed onto Azolla filiculoides roots.

CONCLUSION

The results showed he Azolla filiculoides roots can bused as an effective and inexpensive adsorbent for removal of Malachite-Green dye adsorption. Four isotherms, Langmuir, BET, Freundlich and Temkin were used to the equilibrium data and the results showed that the Temkin isotherm is best. Adsorption and desorption isotherms (BET) Azolla filiculoides roots are investigated. Both isotherms are type II according to IUPAC classification. Type II isotherms are characteristic of systems containing micro pores. The kinetic of MG dye onto Azolla filiculoides roots were best fitted to pseudo second-order model. The negative ΔG° value of adsorption of Malachite Green dye onto Azolla filiculoides roots indicates that the process spontaneous.

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