

Termite soil as a potential low-cost adsorbent for the removal of methylene blue and malachite green dyes

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Abstract

The adsorption of methylene blue (MB) and malachite green (MG) from aqueous solution using a termite soil has been studied by batch adsorption technique. The adsorption experiments were carried out under different conditions of initial concentration (5–100 mg/L). The equilibrium data were fitted to Langmuir and Freundlich isotherms and the equilibrium adsorption was best described by the Langmuir isotherm model with maximum monolayer adsorption capacities found to be 338.98 and 327.21 mg/g at 305 K, respectively. Three kinetic models, pseudo-first-order, pseudo-second-order and intraparticle diffusion were employed to describe the adsorption mechanism. The experimental results showed that the pseudo-second-order equation is the best model that describes the adsorption behaviour with the coefficient of correlation $R^2 \geq 0.99$. Fourier transform infra red (FTIR) spectroscopy, X-ray diffraction (XRD), Scanning electron microscopy (SEM), Tunnelling electron microscopy (TEM) studies are evident that the termite soil has an effective adsorbent material. The results suggested that termite soil has high potential to be used as effective adsorbent for MB removal.

Keyword: Termite soil, MB removal, XRD, SEM

1. Introduction

Malachite green (MG), Methylene Blue (MB), tri-phenyl methane dye, has been widely used as a strong anti-bacterial, anti-fungal and anti-parasitical agent in fish farming [1]. MG is also an effective tropical anti-protozoal agent [2]. It is generally used for the dyeing of silk, wool, cotton, leather, jute, etc. [3]. MG is highly cytotoxic to mammalian cells and acts as a tumor enhancing agent [4]. This dye may enter into the food chain and could possibly cause mutagenic, carcinogenic and teratogenic effects on humans [5].

The present day, Waste water contamination is one of the most serious environmental problems. Mainly, the aqueous waste effluent from dye industry causes serious environmental problems. Dyes prevent reoxygenation in waters by inhibiting the penetration of sunlight. This interrupts the biological activity of aquatic organisms. In addition, wastewaters from dyeing and textile industries easily produce toxic trihalomethanes when it is chlorinated. The growing concern about environmental issues has prompted the textile industry to investigate appropriate and environment friendly treatment technologies [6].

Many methods are available for the removal of dyes from industrial effluents. The most widely used are biodegradation [7], flocculation-coagulation [8], chemical oxidation [9] and adsorption. Among these methods, adsorption technique has been proven to be effective and attractive for the treatment of dye-bearing wastewaters [10]. Adsorption is also a comparatively cheap and effective method in the removal of MG and MB dyes. The adsorption characteristics of dyes on various adsorbents, such as activated carbon (AC), agriculture waste, clay, silica, sewage sludge, industrial solid wastes [11] etc. have been extensively investigated.

Termites are often mentioned as an example of ecosystem engineers. They significantly alter the physical, chemical and biological properties of the soil environment [12]. They build organo-mineral structures of different stability such as galleries, casts, sheetings, fungus-comb

chambers and mounds [13]. Termites that form large, stable nest can concentrate the organic materials they collect as forage in the vicinity of the nest, in the form of inedible debris, stored food and waste products.

The present study has been undertaken to evaluate the efficiency of a termite soil adsorbent from soil mound for the removal of Malachite green and Methylene blue dyes from aqueous solutions. In order to design adsorption treatment systems, knowledge of kinetic and mass transfer processes is essential. In this paper, we have reported the applicability of kinetic and mass-transfer models for the adsorption of Methylene blue and Malachite green onto termite soil.

2. Materials and Methods

2.1 Adsorbent

Termite soils were collected from Thennangudi village, Thanjavur district. They were washed with distilled water and dried. Size of the Particles present in the soil is graded with the help of sieves. Major portion of termite soil was found to be below the size of 0.75 mm. Particle size below 0.75 mm was taken for the further study as an adsorbent which is designated as Termite Soil Adsorbent (TSA).

2.2 Characterization techniques

The TSA were characterized by X-ray diffractometer (model: X'PERT PRO PANalytical). The diffraction pattern was recorded in the range of 25°-80° for the adsorbent samples where the monochromatic wavelength of 1.54 Å used. The surface morphology of adsorbent termites soil was inspected using FE-SEM (Hitachi SU6600, Japan). The morphology of the adsorbent material was examined using HRTEM. Sample for HRTEM analysis was prepared by drop coating the termite soil solutions on carbon-coated copper grids at room temperature. The excess termite soil solutions were removed with filter paper. The copper grid was finally dried at room temperature and was subjected to TEM analysis by the instrument Tecnai F20 model operated at an accelerating voltage of 200 kV. The FT-IR spectrum was

recorded in the range of 400-4000 cm^{-1} by using Perkin-Elmer spectrometer.

2.3 Adsorption Dynamic Experiments

Batch Equilibrium method

In order to estimate the adsorption characteristics of TSA for the adsorption of MB and MG, batch sorption studies were carried out. Known weight of adsorbent is added to 50 mL of prepared dye solution of known concentration. The contents were shaken thoroughly using a rotary mechanical shaker with a speed of 200 rpm. The solution was then centrifuged at preset time intervals by keeping all other factors constant.

2.4 Effect of adsorbent dosage of the dye removal

Effect of adsorbent dosage was studied by varying the adsorbent dose from 15 to 75 mg for 100mg/L of 50 mL Methylene Blue and malachite dye solutions. The various dosages consisting of the adsorbent respectively mixed with the dye solution and the mixture was agitated in a mechanical shaker for 100 minutes. The adsorption capacities for different doses were determined by keeping all other factors constant.

2.5 Effect of initial dye concentration on dye adsorption capacity

In order to determine the effect of initial concentration, experiments were conducted with different initial concentration 100,150 and 200 mg/L of the dye solution for different contact time ranging from 5 to 100 min, keeping all other factors constant.

2.6 Adsorption Isotherm Test

The adsorption isotherm is the most extensively employed criterion for representing the equilibrium states of an adsorption system. It can give useful information regarding the adsorbate, the adsorbent, and the adsorption process. Several adsorption isotherm equations have been derived. The theoretical amount of dye adsorbed at equilibrium q_e (mg/g), was calculated by the following mass balance relationship.

$$q_e = (c_o - c_e) \frac{V}{W} \quad \text{--- (1)}$$

Where C_o and C_e (mg/L) are the initial and equilibrium phase concentration of dyes respectively, V the volume of the solution (L) and W is the weight of the TSA (g). In the present study, Langmuir and Freundlich adsorption isotherm models were used to analyse the experimental data.

2.6.1 Langmuir adsorption isotherm

The Langmuir isotherm equation is the first theoretically developed adsorption isotherm and still retains an important position in physisorption as well as chemisorption process. The Langmuir non-linear equation is

$$q_e = q_m \frac{bC_e}{1 + bC_e} \quad \text{--- (2)}$$

Where C_e is the equilibrium concentration (mg/L) and q_e is the amount adsorbed at equilibrium (mg/L), Q_m is constant which reflect a complete monolayer coverage mgg^{-1} , b is adsorption equilibrium constant (Lmg^{-1}) that is related to the apparent energy of sorption. The linearised form of Langmuir isotherm is

$$\frac{C_e}{Q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad \text{--- (3)}$$

The linear plots of C_e/Q_e versus C_e suggest the applicability of Langmuir isotherm. The values of Q_m and b were determined from the slope and intercepts of plot.

2.6.2 Freundlich adsorption isotherm

Freundlich isotherm on the other hand assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage. If q_e is the amount of adsorbate adsorbed per gram of adsorbent, and C_e is the concentration of the adsorbate in solution phase, the Freundlich adsorption 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 isotherm can be derived assuming a logarithmic decrease in the adsorption with the increase in the fraction of occupied sites and is commonly given the following non-linear equation.

$$q_e = k_f c_e^{1/n} \quad \text{--- (4)}$$

Where k_f is defined as distribution co-efficient and represents the quantity of dye absorbed onto

adsorbent for unit equilibrium concentration. C_e is the equilibrium concentration of the dye solution. n indicates the adsorption intensity. Line arised logarithmic form of the Freundlich equation is given below.

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \text{ --- (5)}$$

The applicability of the Freundlich adsorption isotherm was analysed using the experimental data by plotting $\log q_e$ versus $\log C_e$.

2.6.3 Temkin adsorption isotherm

Of the two isotherms considered so far (Langmuir and Freundlich), the Freundlich isotherm is likely to be more widely obeyed than the Langmuir isotherm because the heat of adsorption normally falls with increasing surface coverage. This effect is only allowed in the Freundlich isotherm, because it involves a term n that allows for heterogeneity of the solid surface. Temkin and Pyzhev considered the effects of indirect adsorbate/adsorbate interactions on adsorption isotherms and assumed that the free energy of adsorption is a function of the surface coverage. The Temkin isotherm is represented as,

$$q_e = \frac{RT}{bT} (\ln A_T + \ln C_e) \text{ ---- (6)}$$

Equation 3.22 can be expressed in its linear form as:

$$q_e = B \ln A_T + B \ln C_e \text{ (7)}$$

where C_e ($\mu\text{g/L}$) is concentration of the adsorbate at equilibrium,

q_e ($\mu\text{g/g}$) is the amount of adsorbate adsorbed at equilibrium,

$RT/bT = B$ where T is absolute temperature (K), R is the ideal gas constant (8.314 J/mol.K) and A_T and bT are constants.

A plot of q_e versus $\ln C_e$ enables the determination of constants A_T and B . The constant B is related to the heat of adsorption and A_T is the equilibrium binding constant ($\text{L}/\mu\text{g}$) corresponding to the maximum binding energy.

2.6.4 Dubinin–Radushkevich (D–R) adsorption isotherm

The Dubinin and Radushkevich (D–R) isotherm is more general than the Langmuir isotherm, because it does not assume a homogeneous surface or constant adsorption potential. The linear form of Dubinin–Radushkevich (D–R) equation is

$$\ln q_e = \ln q_{max} - \frac{1}{2E^2} \times RT \ln \left[1 + \frac{1}{C_e} \right]^2 \text{ --- (8)}$$

where E is the mean free energy of adsorption per mole of the adsorbate; q_e , q_{max} , C_e , T and R are same as defined in previous equations. If the magnitude of E is in between 8 and 16 kJ/mol, the adsorption process is supposed to proceed via chemisorption, while for values of $E < 8$ kJ/mol, the adsorption process is of physical nature [14,15].

2.7 Adsorption kinetic modeling

The study of adsorption kinetics is most significant as it provides valuable insights into the reaction pathways and the mechanism of the reactions followed so far. Further, it describes the solute uptake rate which in turn controls the residence time of adsorbate at the solid–liquid interface [16]. Adsorption kinetics is also an important physicochemical study for the evaluation of the basic traits of a good adsorbent. In order to estimate the adsorption kinetics it is essential to allow the experimental system to reach equilibrium [17]. Generally, two equilibrium kinetic models used for adsorption study are pseudo first–order and pseudo second–order equations developed by Lagergren (1898) and Ho and McKay (2000) [18,19,20], respectively.

Several steps control the mechanism of adsorption process such as chemical reaction, diffusion control and mass transfer. The kinetics of dye adsorption onto TSA is required for selection of optimum operating conditions for the full-scale batch process. The kinetic parameters which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes.

Thus the kinetics of Methylene Blue onto TSA was analyzed using pseudo first order, pseudo

second order and intra-particle diffusion kinetic models.

2.8 Test for kinetics models

Best fitting kinetic model for a system can be determined by using the statistical tool percentage of sum of error squares (SSE). This can be evaluated by the following formula; the sum of error squares is given as follows;

$$SSE (\%) = \sqrt{\sum[(q_e)_{exp} - (q_e)_{cal}]^2 / N}$$

Where N is the number of data points, $(q_e)_{exp}$ is the experimental q_e and $(q_e)_{cal}$ is the calculated q_e .

2.8.1 Pseudo first order equation

The adsorption kinetic data were described by the Lagergren pseudo first order model which the earliest known equation is describing the adsorption rate based on the adsorption capacity. The linear form of equation is generally expressed as follows.

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

The rate constant k_1 and theoretical q_e can be determined from slope and intercept of the plot respectively.

2.8.2 Pseudo second order equation

The adsorption kinetic may be described by the pseudo second order model. The integrated and linearised Eq.(9) for the boundary conditions $q_t = 0$ at $t = 0$ equation is given below.

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad \text{--- (9)}$$

If the second order kinetics is applicable then the plot of t/q_t versus t should show a linear relationship.

2.8.3 The intra-particle diffusion model

The adsorbate species are most probably transported from the bulk of the solution into the solid phase through film diffusion followed by intra-particle diffusion process which is often the rate limiting step in many adsorption processes, especially in a rapidly stirred batch reactor. So the intra-particle diffusion is another kinetic model should be used to study the rate of dye adsorption onto TSA. The intra-particle diffusion model is commonly expressed by Webber Morris equation as given below.

$$q_t = k_{dif} t^{1/2} + C \quad \text{--- (10)}$$

Where C = the intercept

k_{dif} = The intra-particle rate constant in (mg/g/min)

q_t = Quantity adsorption at the time

The values of q_t were found to be linearly correlated with values of $t_{1/2}$ and pore diffusion rate constant k_{diff} directly evaluated from the slope of the regression line.

3. Results and discussion

3.1 Effect of adsorbent Dose.

The effect of different dosage of adsorbent on adsorption can be inferred from Table 1 and Fig.1 As the amount of adsorbent increases from 15 to 75 mg for 50 ml of 100 mg/L dye solution, the percentage removal of dye found to increase from 64.64% to 82.5%. Moreover, the percentage removal of malachite green dye was found to increase from 52.21 % to 75.65 %. The increase in adsorption with increase in dosage may be attributed to increased adsorbent surface with the availability of more adsorption sites. From that results, termite soil has been adsorbed more percentage of methylene blue dye than malachite green dye. 50 mg of adsorbent is chosen for further studies.

The effect of contact time on the percentage removal of dye is shown under various other fixed operating conditions. The experimental results of adsorption of dye on TSA for various concentrations of dye solutions (100, 150, 200 mg/L) with contact time at 305 K were presented in Table 2 and depicted in Fig. 2. It is observed that the percentage removal increased rapidly with an increase in contact time. After 80 minutes no noticeable change in the percentage removal was observed. Equilibrium was established in 40 to 80 min for all the studied concentrations.

3.3. Effect of initial concentrations

The study on the effect of initial concentration showed that the percentage of the removal of dyes decreased with the increase of initial concentrations of adsorbate solution as given in Table 3 and shown in Fig. 3. The percentage removal of MB dye at the equilibrium was found to decrease from 77.24 to 58.96 and 76.53

to 56.21 as the initial concentration of MB and MG dyes increased from 100 mg/L to 200 mg/L. This is because the ratio of available adsorbent surface to the concentration of solute decreases with the increase of initial concentration and hence the percentage of removal decreases with the increase of initial concentration. However the amount of dye adsorbed on the unit mass of the adsorbent increased with an increase in the initial concentration of the adsorbate solutions.

3.4 Adsorption Isotherm

The values of the constants of the two isotherms, namely, Freundlich and Langmuir, have been given in the table below (Table 4 & 5). The values for Freundlich and Langmuir isotherm ranges between 0.98-0.99 and 0.99 respectively, for the adsorption of methylene blue and malachite green. It is clearly noticeable that Freundlich model is better fit in the adsorption isotherm model (Fig.3,4 & 5,6). This shows that adsorption of the dye follows heterogeneous coverage which has overlapping layers.

3.5 Adsorption kinetics

The adsorption capacity as well as the percent removal is time-dependent. The process reaches to equilibrium after a definite time. Furthermore, the process at equilibrium depends on initial concentration of dye which is correlated with time. In this work, for all concentrations of dye, the malachite green adsorption reaches equilibrium only at 2 hours or 100 minutes. Also we need to study the kinetics of reaction for which the experimental data were fit into kinetic models

The pseudo-first-order (table 6 & 8) as well as the pseudo-second-order (table 7 & 9) models were analysed to study methylene blue and malachite green adsorption onto termite soil sample. The pseudo first order kinetics and second order kinetics adsorption for the linear expression of methylene blue were explained in, figure 7 & 8 and malachite green were explained in figure 9 & 10 respectively. The best-fit model was determined based on the values of correlation coefficient. Our experimental results tend to follow the pseudo

second-order model better (Fig 8 & 10). It was observed from Table 7 & 9 that methylene blue and Malachite green adsorption on termite soil followed pseudo 2nd order kinetics. R^2 values are 0.99 – 1.00.

3.6 Intraparticles diffusion method

The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intraparticle diffusion plot. Previous studies by various researchers showed that the plot of Q_t versus $t^{0.5}$ represents multi linearity, which characterizes the two or more steps involved in the sorption process. According to Weber and Morris, an intraparticle diffusion coefficient K_p is defined by the equation:

$$K_p = Q/t^{0.5} + C$$

Thus the K_p (mg/g min^{0.5}) value can be obtained from the slope of the plot of Q_t (mg/g) versus $t^{0.5}$ for Methylene blue and Malachite green. From figure 11 and 12, it was noted that the sorption process tends to be followed by two phases. The two phases in the intraparticle diffusion plot suggest that the sorption process proceeds by surface sorption and intraparticle diffusion [125,126]. The initial curved portion of the plot indicates a boundary layer effect while the second linear portion is due to intraparticle or pore diffusion. The slope of the second linear portion of the plot has been defined as the intraparticle diffusion parameter K_p (mg/g min^{0.5}). On the other hand, the intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate limiting step. The calculated intra-particle diffusion coefficient K_p values was given in the table 10 and 11 for methylene blue and malachite green respectively.

3.7 Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye. If the adsorbed dyes can be desorbed using neutral pH water, then the attachment of the dye of the adsorbent is by weak bonds. If sulphuric acid or alkaline water desorb the dye then the adsorption is by ion exchange. If organic acids like acetic acid can desorb the dye, then the dye has held by the

adsorbent through chemisorption. The effect of various reagents used for desorption studies indicate that hydrochloric acid is a better reagent for desorption, because we could get more than 73% removal of adsorbed dye. The reversibility of adsorbed dye in mineral acid or base is in agreement with the pH dependent results obtained (Figure 13). The desorption of methylene blue and Malachite green dyes by mineral acids and alkaline medium indicates that the dyes were adsorbed onto the activated carbon through by physisorption mechanisms [21,22,23].

3.8 Evidences for adsorption

3.8.1 IR spectral studies

The IR spectra of the raw termite soil and after adsorption of the dyes methylene blue and malachite green have been shown in Figure 14. It could be seen that the slight reduction of stretching vibration adsorption bands. This clearly indicates the adsorption of dye on the adsorbent by physical forces [24, 25].

3.8.2 X-ray diffraction studies

The XRD diagrams of activated termite soil and MG, MB adsorbed termite soil have been shown in Figure 15. The intense main peak shows the presence of highly organized crystalline structure of raw termite soil [26, 27], after the adsorption of dye, the intensity of the highly organized peaks are slightly diminished. This has attributed to the adsorption of MG and MB on the upper layer of the crystalline structure of the termite surface by means of physisorption.

3.8.3 ZETA POTENTIAL:

It indicates the surface potential of material and it was -42.4 mV, -40.2 mV for methylene blue and malachite green dye adsorbed termite soil respectively, which shows that the surface of the termite soil is negatively charged (figure 16). The negative charges on the surface increases the adsorption as methylene blue and malachite green are a cationic dye. Zeta potential in the range of 40-60 shows stability of material as high zeta potential indicates that flocculation of materials don't take place

3.8.4 SEM studies

The SEM diagrams of raw termite soil and dyes-adsorbed termite soil have shown in Figures 17a & 17b & 17c respectively. Figure 17a shows the presence rough and porous structure of raw termite soil. Favourable morphology change in the figure 17b and 17c shown that after treatment with dye indicates that the adsorption of the malachite green and Methylene Blue on the surface of the termite soil by means of physisorption [26, 27].

3.8.5 TEM studies

The TEM diagrams of methylene blue and malachite green dye-adsorbed termite soil have shown in Figures 18 & 19 respectively. The bright spots, shows the presence of tiny holes on the crystalline structure of termite soil, after treatment with dye the bright spots became black shows the adsorption of the methylene blue and malachite green on the surface of the termite soil by means of physisorption [26, 27].

Conclusion

Termite soil has been proven to be an effective low-cost adsorbent for the removal of MB and MG via adsorption from aqueous solution. The equilibrium data were analyzed using the Langmuir and Freundlich isotherm models. The adsorption equilibrium was best described by the Langmuir isotherm model with maximum monolayer adsorption capacities found to be 33.98 and 327.21 mg/g at 305 K. Kinetics of the adsorption over termite soil was also observed and it was found that the process proceeds via pseudo-second-order kinetics. Intraparticle diffusion model was applied to interpret the adsorption mechanism. A comparison of the adsorption capacity of termite soil with different adsorbents previously used for the adsorption of MB and MG reveals that termite soil is remarkably effective for this purpose. FTIR, XRD, SEM, TEM, Zeta potential studies are evident that the termite soil has an effective adsorbent material.

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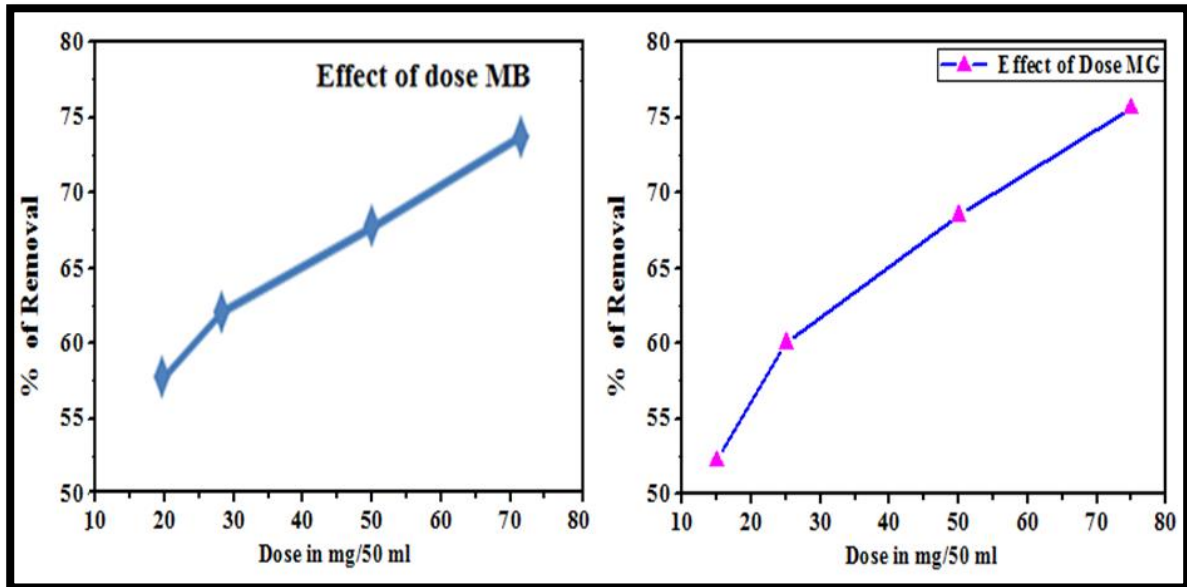


Fig.1 Effect of adsorbent dosage on the removal of Methylene blue and Malachite green

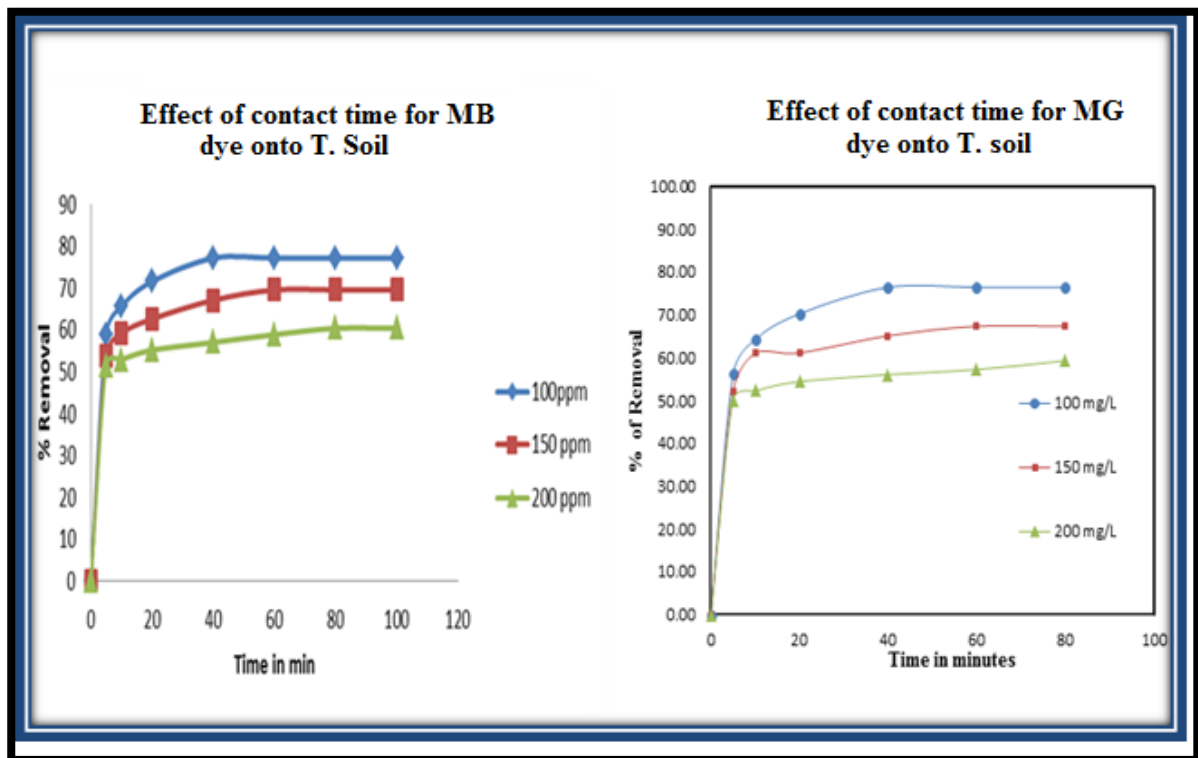


Fig. 2 Effect of contact time on adsorption of Methylene blue and Malachite green

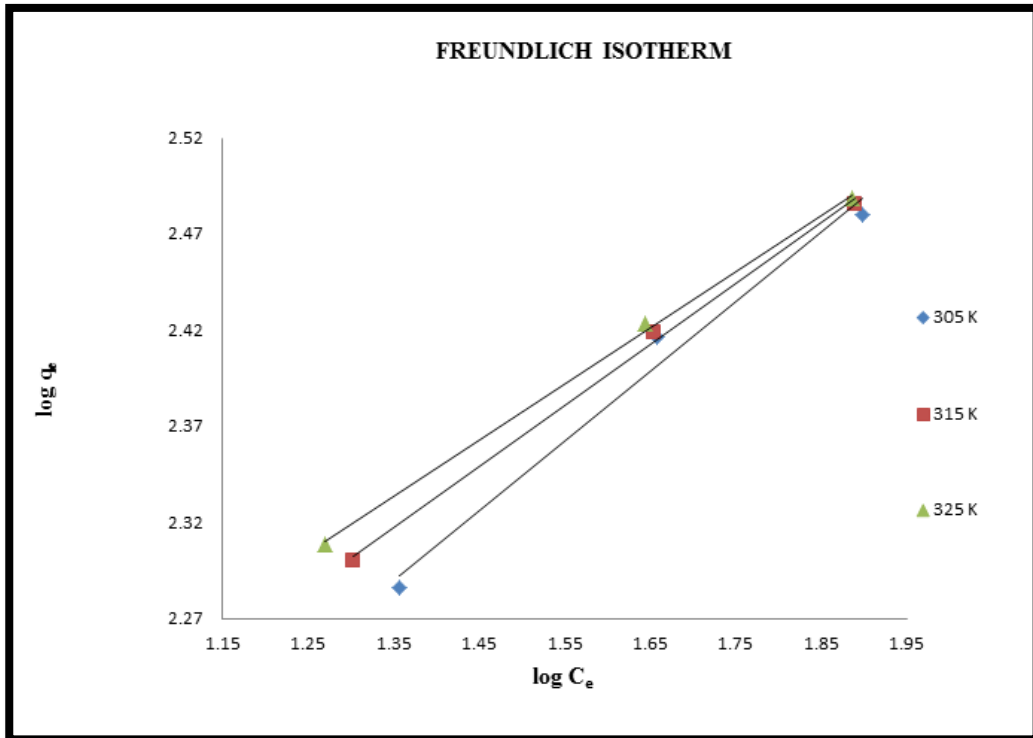


Fig. 3 Freundlich adsorption isotherm for methylene blue adsorption (linear)

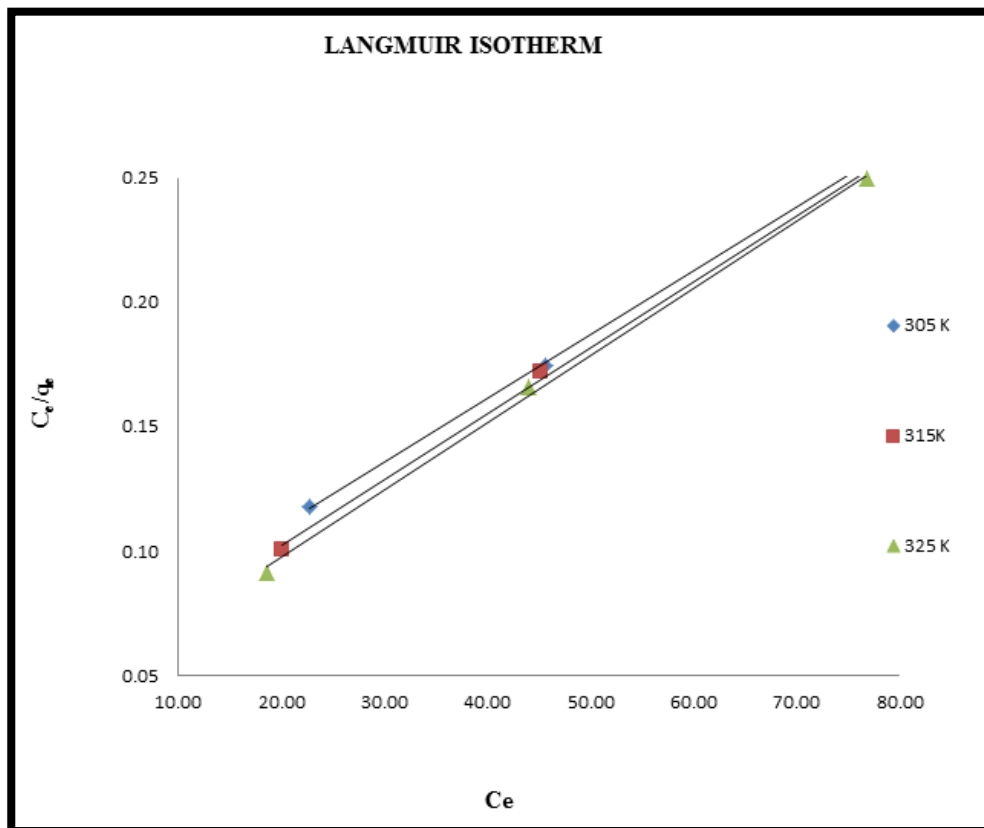


Fig. 4 Langmuir adsorption isotherm for methylene blue adsorption (linear)

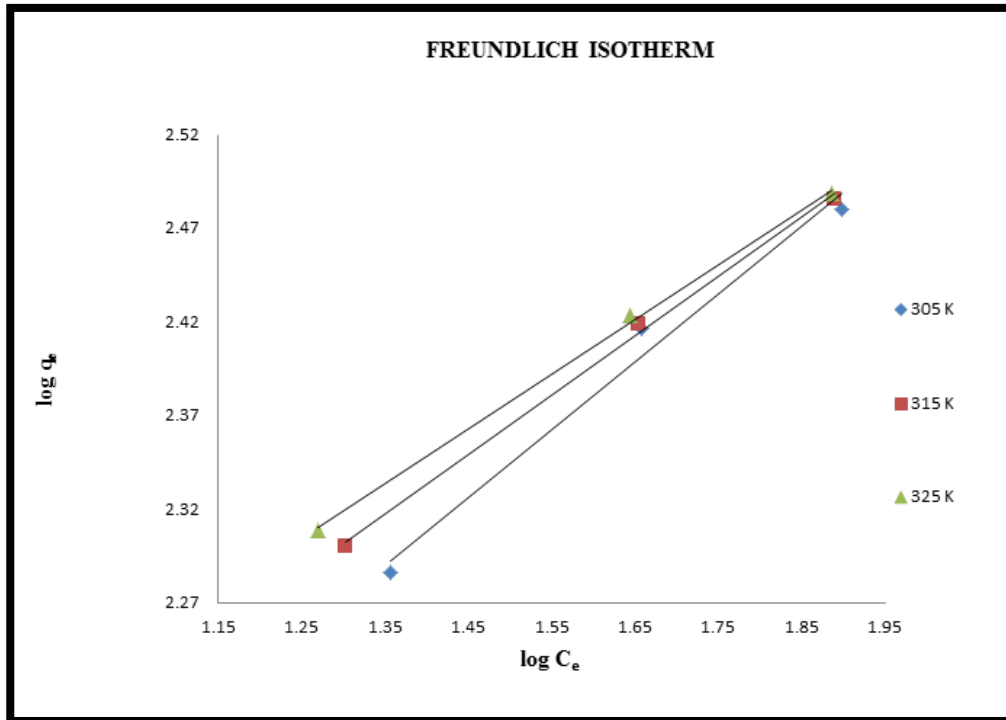


Fig. 5 Freundlich adsorption isotherm for malachite green adsorption (linear)

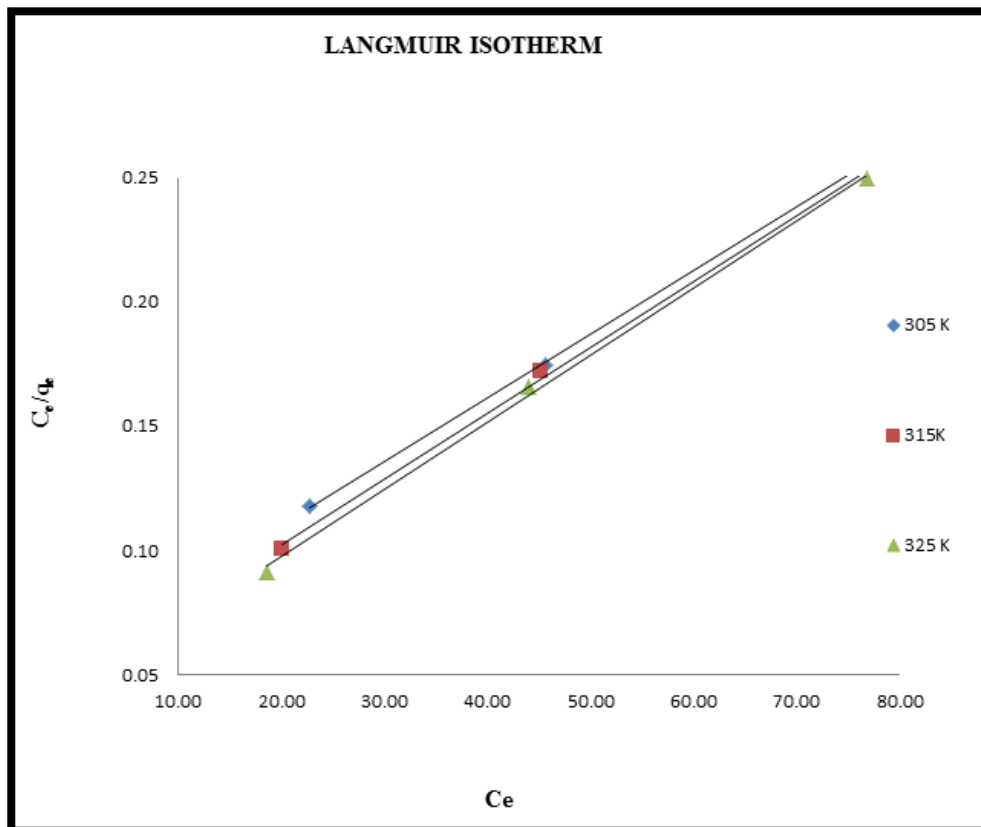


Fig. 6 Langmuir adsorption isotherm for malachite green adsorption (linear)

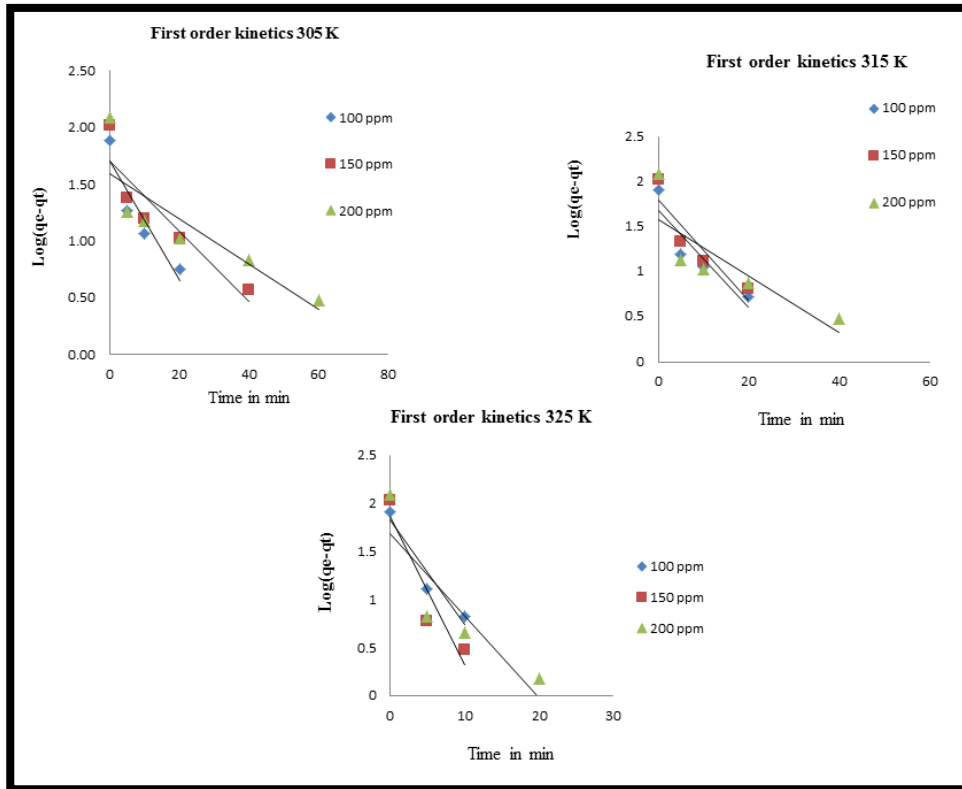


Fig. 7 Pseudo first order kinetics for the adsorption of methylene blue

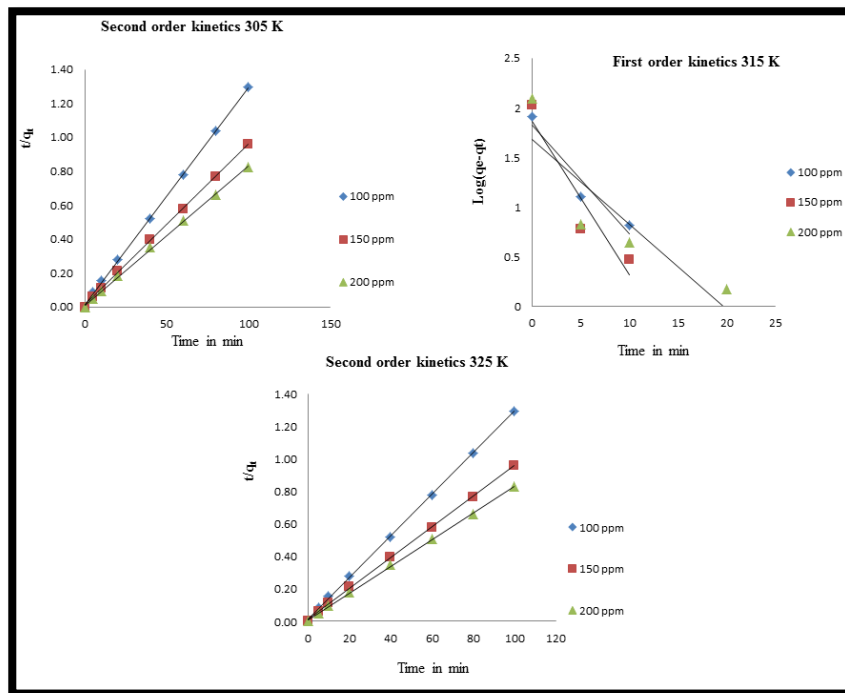


Fig. 8 Pseudo second order kinetics for the adsorption of methylene blue

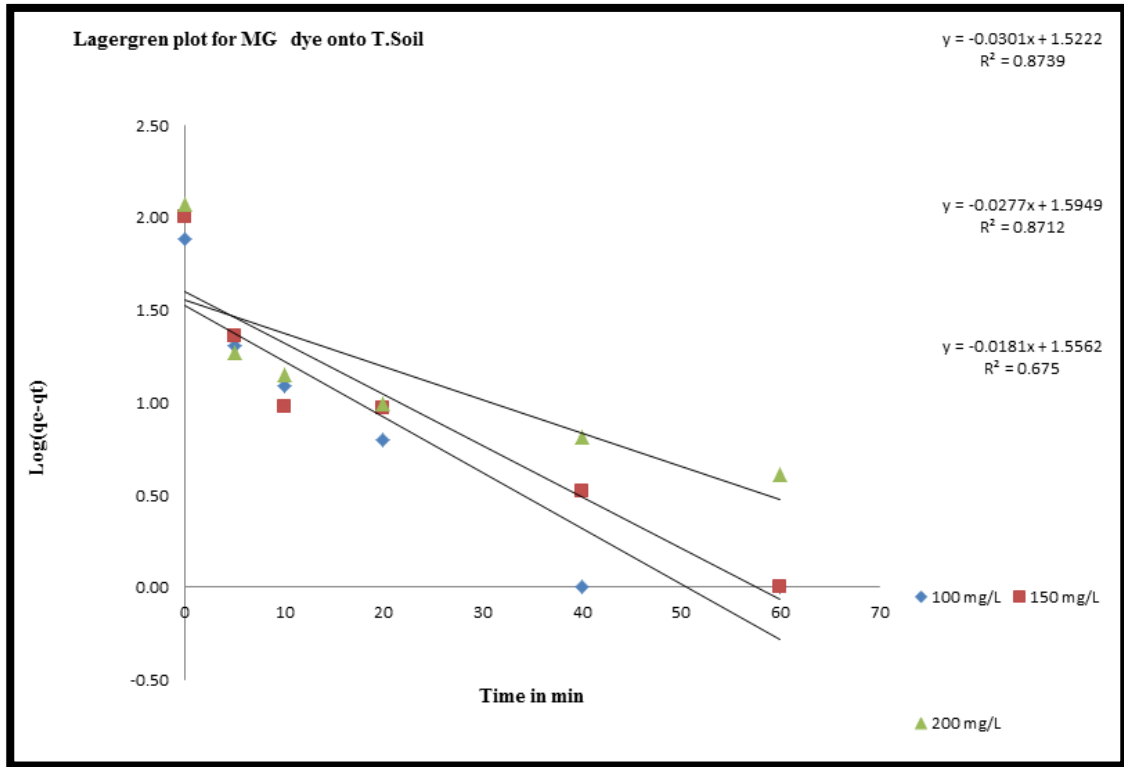


Fig. 9 Pseudofirst order kinetics for the adsorption of malachite green

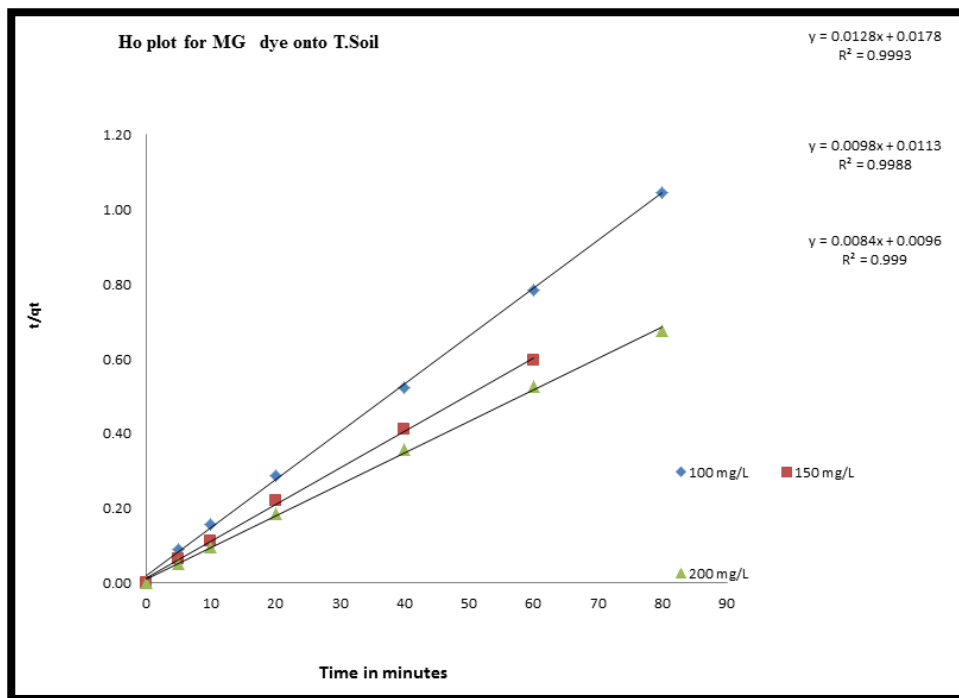


Fig. 10 Pseudo second order kinetics for the adsorption of malachite green

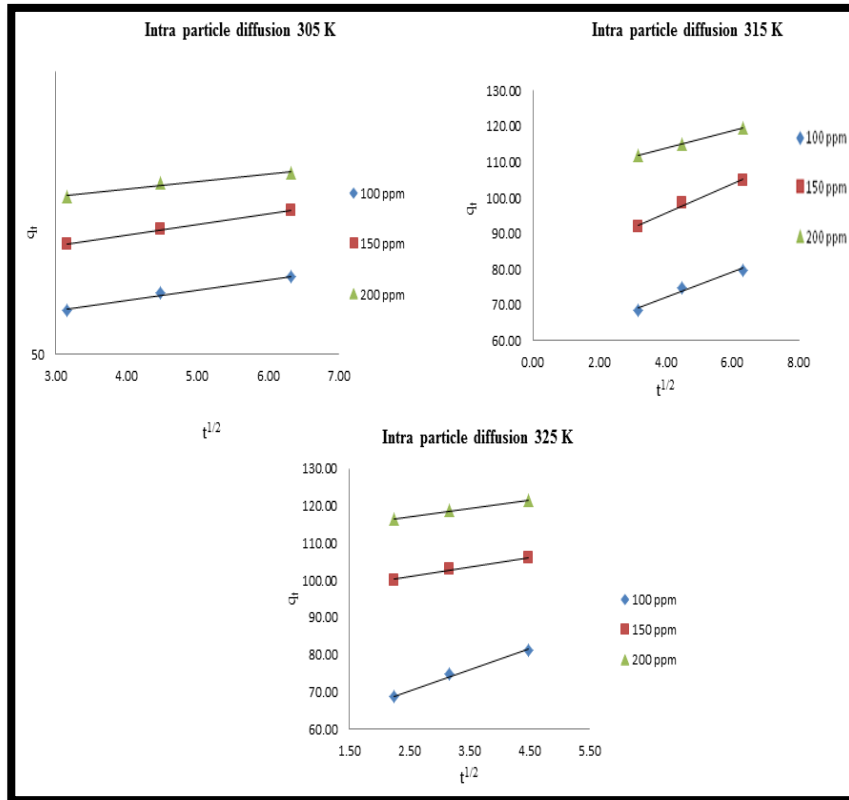


Fig. 11 Intra particle diffusion model for the adsorption of methylene blue

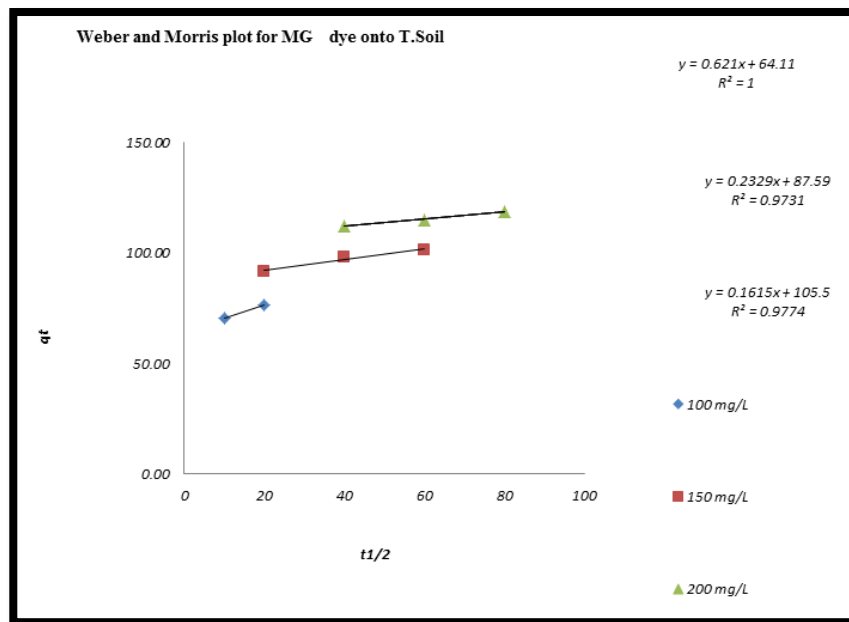


Fig. 12 Intra particle diffusion model for the adsorption of malachite green

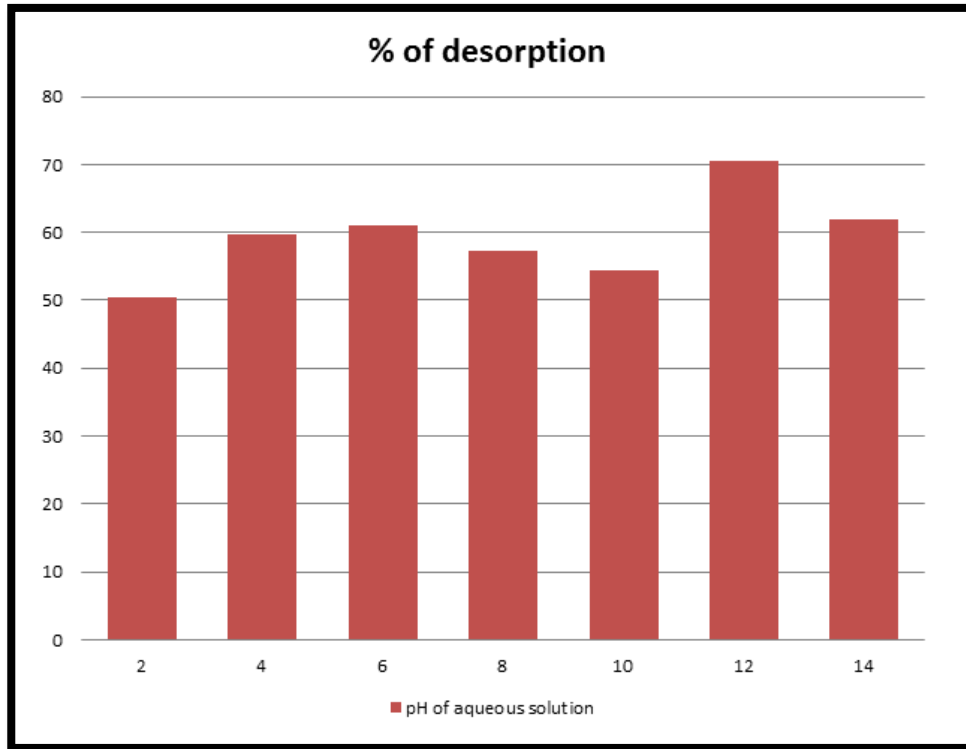


Fig. 13 Desorption studies of methylene blue and malachite green dyes

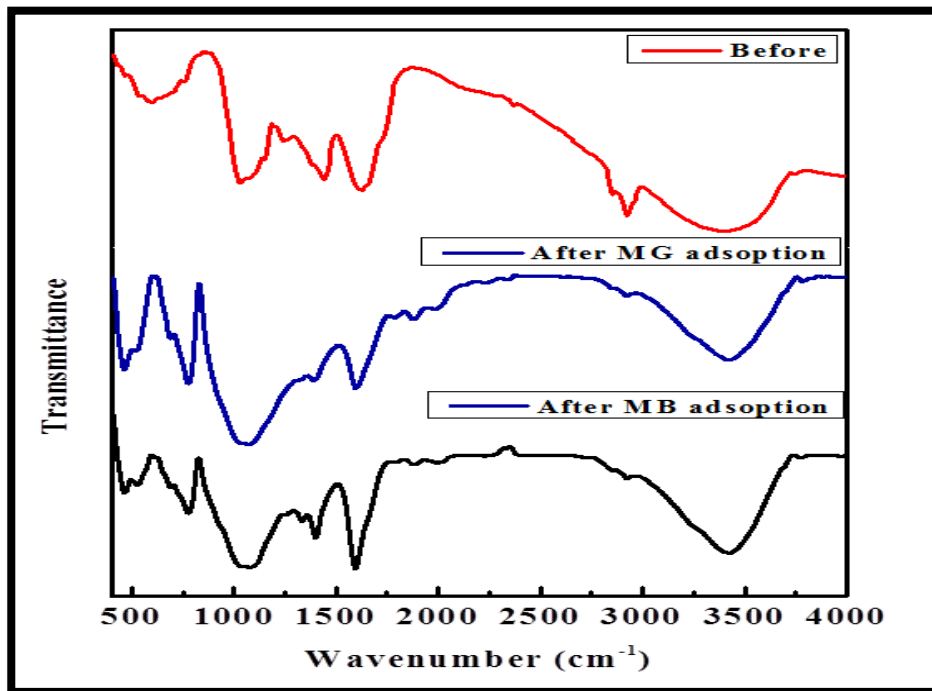


Fig. 14 FTIR spectrum of before and after methylene blue and malachite adsorbed termite soil

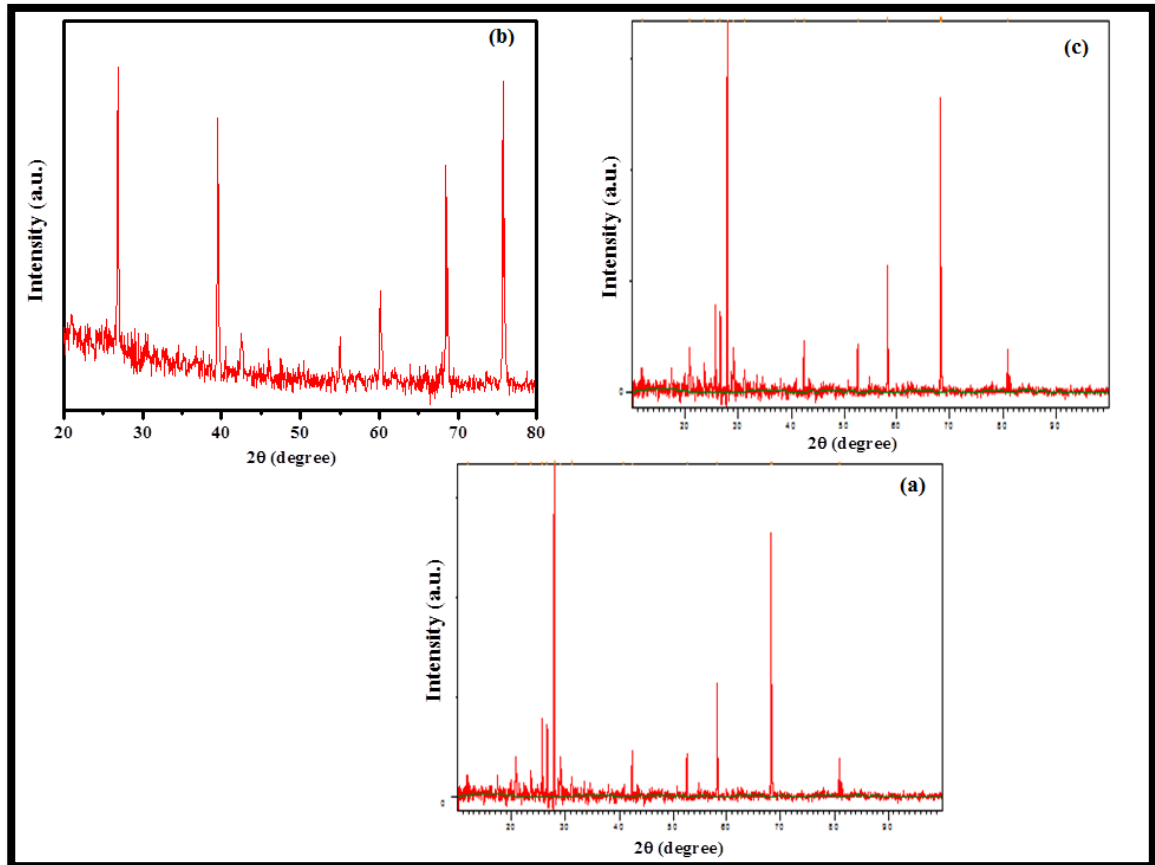


Fig. 15 XRD results of (a) pure termite soil, (b) methylene blue adsorbed termite soil, (c) malachite green adsorbed termite soil

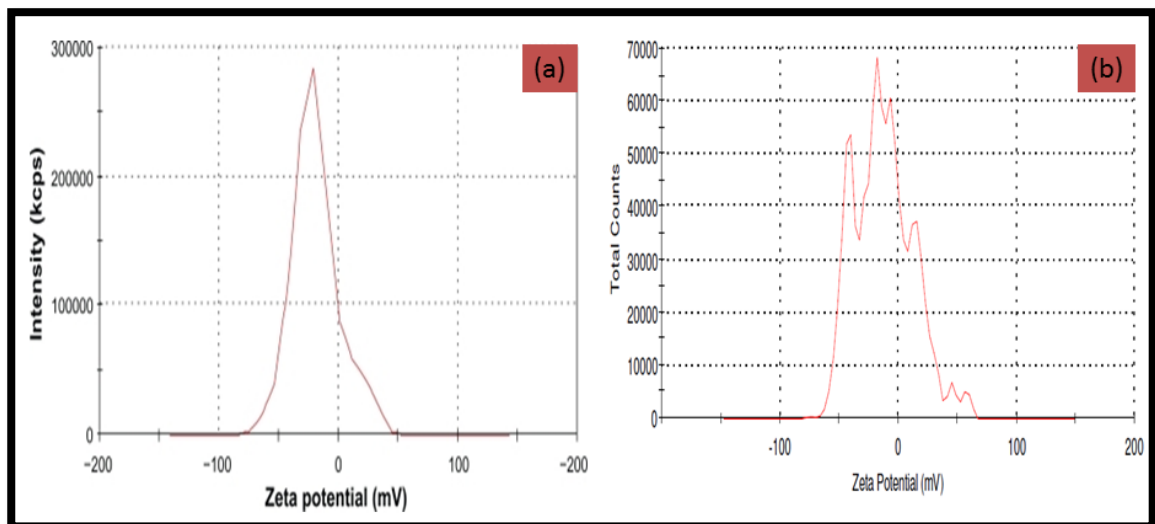


Fig. 16 Zeta potential results of (a) methylene blue adsorbed termite soil and (b) malachite green dye adsorbed termite soil

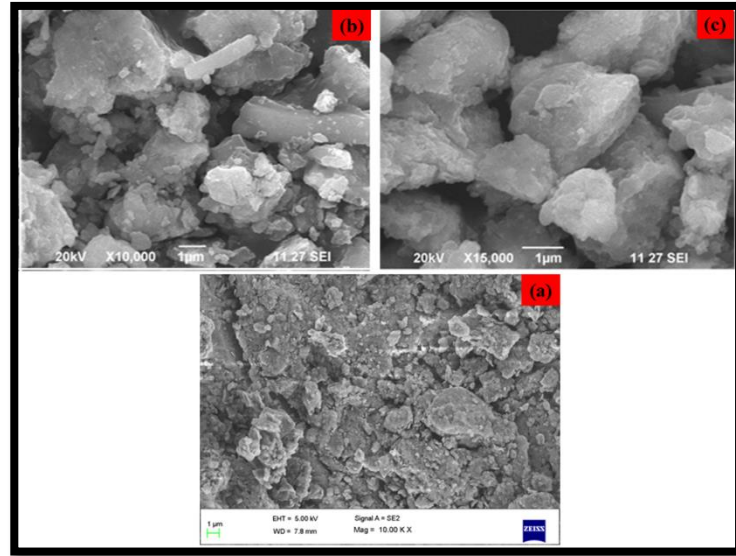


Fig. 17 SEM images of (a) pure termite soil, (b) methylene blue adsorbed termite soil, (c) malachite green adsorbed termite soil/

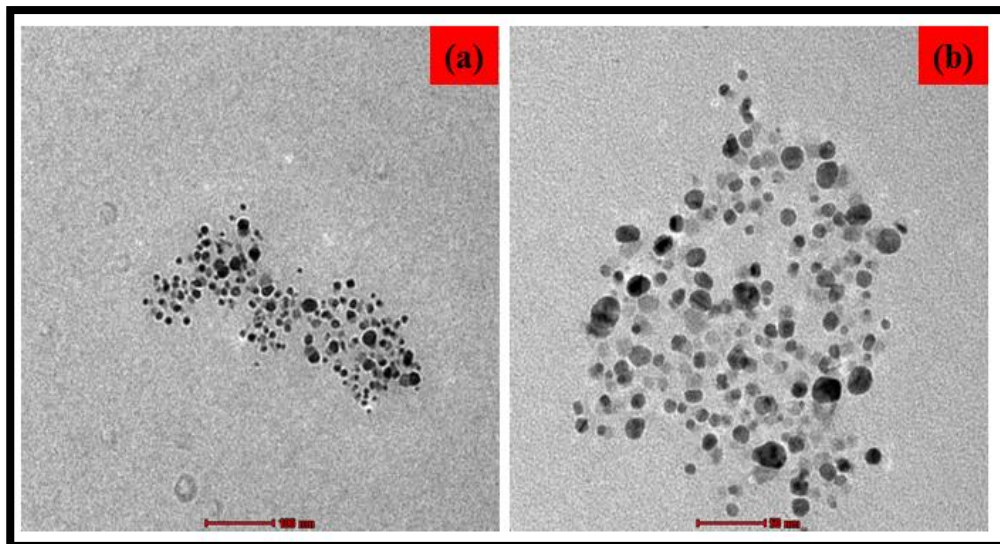


Fig. 18 TEM images methylene blue adsorbed termite soil

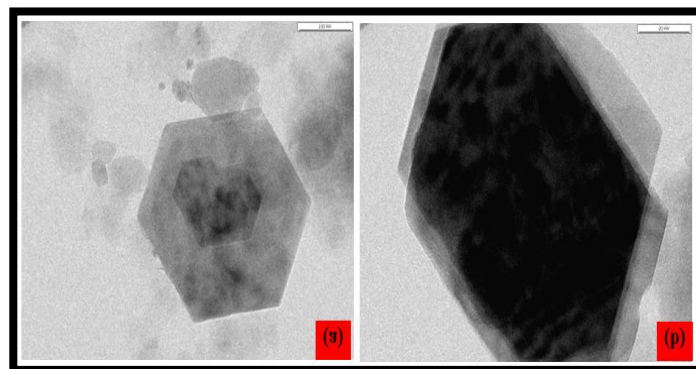


Fig. 19 TEM images of malachite green adsorbed termite soil

Adsorbent Dosage (mg / 50ml)	% of Methylene Blue dye Removal	% of Melachite Green dye Removal
15	64.64	52.21
25	72.38	60.02
50	77.24	68.51
75	82.50	75.65

Table.1 Effect of adsorbent dosage on the removal of Methylene blue and Malachite green

Time in minutes	% of Methylene Blue dye Removals			% of Malachite Green dye Removal		
	100 mg/L	150 mg/L	200 mg/L	100 mg/L	150 mg/L	200 mg/L
0	0.00	0.00	0.00	0.00	0.00	0.00
5	58.96	53.73	51.49	56.21	52.13	50.14
10	65.67	59.20	52.99	64.31	61.10	58.32
20	71.64	62.69	55.22	70.32	61.20	54.47
40	77.24	67.16	57.09	76.53	65.20	56.12
60	77.24	69.63	58.96	76.53	67.41	57.31
80	77.24	69.63	60.45	76.53	67.41	59.35
100	77.24	69.63	60.45	76.53	67.41	59.35

Table.2 Effect of contact time on adsorption of Methylene blue and Malachite green

Time in minutes	% of Methylene Blue dye Removal			% of Malachite Green dye Removal		
	100 mg/L	150 mg/L	200 mg/L	100 mg/L	150 mg/L	200 mg/L
0	0	0	0	0	0	0
5	58.96	80.59	102.98	56.21	78.30	101.32
10	65.67	88.80	105.97	64.31	70.10	103.21
20	71.64	94.02	110.44	70.32	88.31	108.43
40	77.24	100.74	114.17	76.53	96.56	111.36
60	77.24	104.44	117.91	76.53	102.31	115.21
80	77.24	104.44	120.89	76.53	102.31	118.29
100	77.24	104.44	120.89	76.53	102.31	118.29

Table.3 Effect of initial concentration on adsorption of Methylene blue and Malachite green

Langmuir Isotherm						Freundlich Isotherm			
Temperature (K)	Q_m (mg/g)	B (L/mg)	R_L			R^2	n	k_f (mg/g)	R^2
			100 mg/L	150 mg/L	200 mg/L				
305	338.98	0.0500	0.17	0.14	0.14	0.999	2.76	60.117	0.983
315	344.82	0.0591	0.12	0.11	0.10	0.998	3.14	77.090	0.998
325	344.82	0.0674	0.09	0.09	0.09	0.998	3.40	86.297	0.998

Table. 4 Langmuir and Freundlich adsorption isotherm constant for methylene blue adsorption

Langmuir Isotherm						Freundlich Isotherm			
Temperature (K)	Q _m (mg/g)	b (L/mg)	R _L			R ²	n	k _f (mg/g)	R ²
			100 mg/L	150 mg/L	200 mg/L				
305	327.21	0.0301	0.18	0.15	0.15	0.999	2.13	58.20	0.981
315	334.30	0.0482	0.13	0.12	0.11	0.995	3.14	77.090	0.995
325	344.82	0.0674	0.09	0.09	0.09	0.995	3.40	86.297	0.995

Table. 5 Langmuir and Freundlich adsorption isotherm constant for malachite green adsorption

Conc. (mg/g)	Temp. (K)	First order Kinetics				
		k ₁ (1/min)	q _{e(cal)} (mg/g)	q _{e(exp)} (mg/g)	R ²	SSE %
100	305	0.0461	48.42	77.24	0.872	9.60
	315	0.1221	50.12	79.85	0.843	9.91
	325	0.1958	168.27	81.34	0.927	28.97
150	305	0.0691	49.66	104.44	0.837	18.26
	315	0.1290	63.97	104.85	0.855	13.62
	325	0.2510	187.50	105.97	0.889	27.17
200	305	0.1198	53.73	120.89	0.737	22.38
	315	0.1300	58.73	122.39	0.694	21.22
	325	0.3362	120.50	123.13	0.790	0.87

Table. 6 Pseudo first order kinetics constant of methylene blue adsorption for linear expression

Conc. (mg/g)	Temp. (K)	Second Order Kinetic Parameters				
		$k_2 \times 10^{-4}$ (g/mg.min)	$q_{e(\text{exp})}$ (mg/g)	$q_{e(\text{cal})}$ (mg/g)	R^2	SSE %
100	305	0.006	77.24	83.33	0.999	2.03
	315	0.009	79.85	83.33	0.999	1.16
	325	0.029	81.34	83.33	0.999	0.66
150	305	0.007	104.44	111.11	0.999	2.22
	315	0.011	104.85	111.11	0.999	2.09
	325	0.081	105.97	111.11	1.000	1.71
200	305	0.009	120.89	125.00	0.999	1.37
	315	0.014	122.39	125.00	0.999	0.87
	325	0.064	123.13	125.00	1.000	0.62

Table. 7 Pseudo second order kinetics constant of methylene blue adsorption for linear expression

Conc. (mg/g)	Temp. (K)	First order Kinetics				
		k_1 (1/min)	$q_{e(\text{cal})}$ (mg/g)	$q_{e(\text{exp})}$ (mg/g)	R^2	SSE %
100	305	0.0421	46.32	75.14	0.865	9.58
	315	0.1101	48.41	77.31	0.832	9.83
	325	0.1921	150.31	80.38	0.914	28.38
150	305	0.0621	39.54	96.30	0.817	18.16
	315	0.1132	54.31	96.21	0.849	13.21
	325	0.2521	176.30	98.30	0.879	27.11
200	305	0.1091	52.71	118.21	0.721	22.14
	315	0.1293	57.52	120.34	0.672	21.03
	325	0.3358	112.5	120.14	0.785	0.82

Table. 8 Pseudo first order kinetics constant of malachite green adsorption for linear expression

Conc. (mg/g)	Temp. (K)	Second Order Kinetic Parameters				
		$k_2 \times 10^{-4}$ (g/mg.min)	$q_{e(\text{exp})}$ (mg/g)	$q_{e(\text{cal})}$ (mg/g)	R^2	SSE %
100	305	0.005	76.31	82.21	0.999	2.01
	315	0.008	78.65	82.21	0.999	1.09
	325	0.025	80.20	82.21	0.999	0.61
150	305	0.005	102.24	109.31	0.999	2.11
	315	0.010	102.24	109.31	0.999	2.05
	325	0.079	103.81	109.31	1.000	1.51
200	305	0.009	118.21	123.00	0.999	1.31
	315	0.013	120.31	123.00	0.999	0.85
	325	0.054	121.20	123.00	1.000	0.60

Table. 9 Pseudo second order kinetics constant of malachite green adsorption for linear expression

Conc. (mg/g)	Temp. (K)	Intra Particle Diffusion	
		k_p (mg/g.min)	R^2
100	305	2.33	0.986
	315	2.36	0.981
	325	2.56	0.995
150	305	2.64	0.999
	315	3.49	0.986
	325	3.62	0.990
200	305	3.77	0.977
	315	4.08	0.999
	325	5.63	0.999

Table. 10 Intraparticle diffusion constant values for methylene blue adsorption

Conc. (mg/g)	Temp. (K)	Intra Particle Diffusion	
		k_p (mg/g.min)	R^2
100	305	2.29	0.985
	315	2.31	0.980
	325	2.51	0.992
150	305	2.61	0.997
	315	3.29	0.985
	325	3.59	0.990
200	305	3.69	0.969
	315	4.01	0.999
	325	5.59	0.999

Table. 11 Intraparticle diffusion constant values for methylene blue adsorption