A Study of The Equilibrium, Kinetics, and Thermodynamics of Malachite Green Dye Adsorption Onto Lignin

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Research Article

Keywords: Malachite green, water treatment, lignin, kinetic models, isotherm models

Posted Date: October 29th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-1009760/v1

A study of the equilibrium, kinetics, and thermodynamics of malachite green dye adsorption onto lignin

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ABSTRACT

Malachite Green (MG), a cationic synthetic dye is considered hazardous when discharged into the water bodies without any adequate treatment. It can affect the multiple segments of the environment leading to irreversible persistent changes. So, there is a need for remediation with cost-effective method to remove dyes from effluents. Adsorption is one such technique to remove dyes from wastewater and is effective and economical. The present study describes the removal of MG cationic dye from wastewater using eco-friendly and biodegradable lignin extracted from hydrothermally treated rice straw by adsorption process. Functional group analysis and morphological characterisation was done to the extracted lignin after quantification. The maximum percent removal of MG 92 ± 0.2 % was observed from a series of batch experiments at optimum process parameters of: contact time 80 min, initial dye concentration 50 ppm, lignin dosage 0.25g, pH 7, temperature 30^0c and with 100 rpm agitation speed. The adsorption kinetics and isotherms were determined for the experimental data using four kinetic models (pseudo-first-order, second order, pseudo-second-order and intra-particle diffusion model) and two isotherm models (Langmuir and Freundlich). The results suggested that the kinetics data fit to the pseudo-second-order kinetic model with the maximum adsorption capacity 36.7 mg/g and the two isotherm models were applicable for the adsorption of MG onto the lignin. Additionally, the thermodynamic parameters ΔS^o, ΔH^o and ΔG^o were evaluated. Therefore, lignin which is an environmental friendly and low cost carbon material that can be used as an adsorbent for dye removal.

Key words: Malachite green, water treatment, lignin, kinetic models, isotherm models.

INTRODUCTION

In several industries such as cosmetics, leather, textile, printing, pharmaceuticals, food and plastic etc. are using dyes in large quantities to colour their products (Shraddha Khamparia et al.2018, Ravi Vital Kandisa et al.2016). These industries discharge effluents into water bodies containing dye and organic content. Among all dye stuff production, two third of the all dye materials are coming out only from the textile industry (Kamaljit singh et al.2011). The discharged pigments and dyes in wastewater not only causing damage to natural water bodies but also leading to lower rates of photosynthesis as these are preventing the penetration of light through water so that the levels of dissolved oxygen affecting the entire aquatic biota. More over these are highly toxic, poor degradability and potentially carcinogenic, so that they are related to environmental and health hazards (Bruno Lellis et al. 2019, Tahir Rasheeda et al. 2019). Malachite green (MG) is one such dye which is basic and cationic dye has also been considerably used in world wide as a fungicide, bactericide and parasiticide in aquaculture sectors (Shivaji Srivastava et al. 2004). Previous studies showed that, even low concentrations of MG when discharged into water bodies can affect the aquatic life and cause carcinogenic effects on human beings (NirmalaDevi.V et al. 2018). The conventional methods which are electrochemical approaches, oxidation, chemical coagulation, microbial remediation, ion exchange, reverse osmosis and membrane filtration are employed for the removal of discharged dyes from waste water (Rajasulochana.P et al. 2016). As these approaches typically entail high exploitation costs and are incapable of handling massive volumes of effluent, consequently adsorption was chosen as best alternate method to remove the dyes due to its simplicity in design, inexpensive, low matrix effects and has feasibility for several materials to use as adsorbents (Grégorio Crini et al. 2018). Currently, the interest on usage of bio adsorbents is increasing as a substitute for synthetic adsorbents due to its secondary pollution in their preparation (George Z. Kyzas et al. 2014). Lignin is such a sort of low cost adsorbent which is an organic compound and has many biological functions. It is available in abundance after cellulose and most important chemical constituent of renewable lignocellulosic biomass (Karolina Kucharska et al. 2018). Additionally,

lignin has good absorption capacity because of presence of alcohol hydroxyl, phenolic hydroxyl, carboxyl, carbonyl, methyl and aromatic groups, etc.. (Jin Huang, Shiyu Fu et al. 2019). As these functional groups are effective in the removal of dyes and heavy metals from the waste water that were reported by many studies (Jin Huang, et al.2020, Xianzhi Meng, et al.2020). In this work, lignin extracted from hydrothermally treated rice straw was used as an adsorbent to adsorb MG from aqueous media and was evaluated as a function of contact time, initial concentration of dye, adsorbent dosages, pH, temperature and agitation speed. Adsorption data was analyzed on the basis of isotherm, kinetics and adsorption equilibrium data to determine the possible mechanism of MG dye adsorption onto lignin.

MATERIALS & METHODS

Materials

The rice straw was collected directly from the fields. Then the rice straw was sun dried, ground, screened and the fraction was collected above 20-mesh sieve was used in the experiments. Malachite green, sulphuric acid (H_2SO_4), sodium hydroxide (NaOH), ortho phosphoric acid (H_3PO_4) used for separation and extraction of lignin were obtained from Hi-Media, Hyderabad, India. A stock concentration of 1g/L was made with distilled water to prepare fresh working dye solutions.

Methods

Pretreatment of rice straw

Initially, rice straw was hydrothermally treated at 121^{o}C temperature for 45 min in an autoclave for removal of hemicelluloses in the form of monomeric sugars from the liquid fraction. The solid fraction recovered from the treatment was enriched in lignin and cellulose. So, this solid was used to extract lignin for further studies.

Isolation & Extraction of lignin

The solid faction which is cellulo-lignin was treated with 3% NaOH in the ratio of 1:10 (Solid to liquid) and refluxed at a temperature of 80^{o}C for 3h.The black liquor containing dissolved lignin was separated from the solids (cellulose) by filtration and pH of the black liquor was adjusted to pH 3-4 by adding orthophosphoric acid. Further, the precipitated lignin was separated from the black liquor by centrifugation and washed with water until to reach pH 7. The obtained lignin was vacuum dried and stored for further analysisat a temperature of 80^{o}C for 3h.The black liquor containing dissolved lignin was separated from the solids (cellulose) by filtration and pH of the black liquor was adjusted to pH 3-4 by adding orthophosphoric acid. Further, by centrifugation, the precipitated lignin was separated from the black liquor and washed with water until to reach pH 7. The obtained lignin was vacuum dried and stored for further analysis.

Functional group analysis and morphological characterisation of alkali treated lignin

The functional group analysis of lignin after extraction was analysed by Fourier-transform infrared spectroscopy (FTIR) (Nicolet iS 5). The dried lignin was mixed with the IR grade KBr to prepare the sample at 2:200 ratios to form a disk. Then the sample was characterized at a resolution of 4 cm^{-1} for 16 scans in the range from 400 to 4000 cm^{-1} region. The control KBr's background spectrum was subtracted from lignin spectrum. The surface morphology of lignin was analyzed and visualized by scanning electron microscopy (SEM).

Batch studies on various effective parameters of adsorption of MG dye on lignin

The effect of various factors i.e. contact time, initial concentration of dye, adsorbent dosages, pH, temperature and agitation speed on percent removal of MG were studied by batch absorption experiments. These experiments were carried out in 250 mL conical flasks by placing them in an orbital shaking incubator with an agitation speed of 100 rpm and at a room temperature of 30^{o}C (except for effect of agitation speed and temperature studies) until equilibrium were reached. The effect of pH was studied over a range of pH 4.0–9.0 by adjusting with 0.1 M HCl or NaOH aqueous solutions. 4 mL of samples were collected at time intervals ranging from 0 to 100 min and were centrifuged at 10000

rpm for 2 min. The residual MG concentration of the supernatant was then determined by using a spectrophotometer (RAY LEIGH, VIS-7220G) equipped with 1.0 cm path length quartz cell.

Equation (1) was used to determine the percentage of dye removal from the sample

$$\% \text{ removal of MG} = \frac{C_0 - C_e}{C_0} \text{ x } 100 \quad \text{----- (1)}$$

Where,

C_0 (mg/L) - Initial MG concentration in the aqueous media,

C_e (mg/L) - Equilibrium MG concentration in the aqueous media

Adsorption Kinetic studies of MG dye onto lignin

Adsorption kinetic experiments were conducted by allowing different concentrations of MG dye to adsorb onto lignin material by placing the solution in an 250ml conical flasks and the solution was agitated in an orbital shaker. The adsorption kinetic profile was studied at various combination of lignin with MG dye concentrations 20,30,40,50 ppm, at various temperatures (30, 35,40, 45 and 50^{o}C), at various residence time of 0 to100 min and agitation speed of 100 rpm in an orbital shaker. 4mL of samples were collected at regular time intervals which were centrifuged at 10000 rpm for 2 min and the residual concentration of MG concentration in the aqueous media was determined by UV spectrophotometer until it reaches to adsorption equilibrium.

The amount of MG dye adsorbed onto lignin (q_e) was calculated using equation (2).

$$q_e = \frac{C_0 - C_e}{M} \text{ x V---------- (2)}$$

Where, q_e (mg/g) - Amount of MG absorbed per unit mass of lignin at equilibrium,

C_0 & C_e (mg/L) are the initial and equilibrium MG concentration in the aqueous media,

V (L) - Volume of MG solution,

M (g) - Weight of lignin as adsorbent.

At various time intervals, the amount of MG adsorbed per unit mass of lignin was estimated using equation (3):

$$q_t = \frac{C_0 - C_t}{M} \text{ x V-------- (3)}$$

Where, q_t (mg/g) is the amount of MG absorbed per unit mass of lignin at time t,

C_0 (mg/L) is the initial MG concentration in the aqueous media,

C_t (mg/L) is the MG concentration at time t in the aqueous media.

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RESULTS & DISCUSSION

Chemical Composition of rice straw and yield of lignin

The composition analysis of rice straw was analyzed according to the National Renewable Energy Laboratory Protocols (NREL-LAPs) (Sluiter, A et al. 2008) which was shown in Table. 1. Initially rice straw was hydrothermally treated under specific conditions followed by alkaline treatment to increase the yield of lignin fractions. The hydrothermal treatment could break the compact and rigid cell wall structure of the plant as well as partial breaking of chemical bonds between hemicelluloses and lignin which resulted in the maximum yield of lignin when extracted with alkali solution. Therefore, hydrothermal treatment of rice straw resulted in the removal of 91% of hemicelluloses into hydrolysate and 85% lignin yield was obtained after treatment of solid residues with NaOH. As a result, the combination of hydrothermal pretreatment followed by alkaline treatment is considered as an effective method for the utilization of lignocellulosic materials efficiently (Xue Chen et al. 2016).

Functional group analysis and morphological characterisation of alkali treated lignin

The FTIR spectrum of alkali treated lignin as shown in Fig.1 provides an overview of its chemical structure. The broadband at 3411 cm^{-1} is assigned to OH stretching. The bands at 2920, 2849 and 1463 cm^{-1} represent C–H antisymmetric and symmetric stretching of CH2 and CH3 groups respectively (Amine Moubarika, et al.2013). The strong bands at 1710 and 1654 cm^{-1}, corresponds to C═O stretching of acetyl and conjugated C–O (Olga Derkacheva et al 2008). The peak at 1511 cm^{-1} is attributed to aromatic skeleton (C=C) vibrations in herbaceous lignin. The bands assigned at 1463 and 1424 cm^{-1} are due to the stretching in the phenol–ether bonds of alkali lignin (Yang Liu, et al.2014) and a weak vibration at 1223 cm^{-1} can be attributed to C-O of guaiacyl ring and C=O stretching. The bands at 1126 cm^{-1} arise from C–H in-plane deformation for S type (Nicole M. Stark et al 2015). Furthermore, the absorption bands attributed at low wave numbers are relevant to the position of substituting groups on the phenyl ring. The morphology of lignin was analyzed by Scanning Electron Microscope analysis at different magnifications. The hierarchical structure of lignin shown in Fig.2 depicts irregular, rough surface and consists of many pores on the surface. As the porosity increases the surface area of lignin also increases. Therefore, more number of adsorption sites are made available per unit area to enhance the rate of adsorption.

Factors affecting adsorption of MG dye onto lignin

The systematic analysis is required to achieve maximum MG adsorption by evaluating the operating conditions. So, the effects of contact time, initial dye concentration, adsorbent dosage, pH, agitation speed and temperature on adsorption process are discussed in detail below.

Effect of Contact Time

The effect of contact time for a period of 120 min on the percentage removal of MG dye was shown in Fig.3 at fixed adsorbent dosage (0.1g) and at an initial MG concentration of 30ppm under same operating conditions i.e. at temperature 30^{o}C, pH 7 and agitation speed of 100 rpm. Initially, the rate of percentage removal of MG was rapidly increased within 10 min due to adsorption of MG molecule onto the adsorbent's exterior surface as well as the existence of more number of binding sites on the adsorbent. Therefore, almost 70% of adsorption was observed within 10 min. From there on the absorption rate was slowdown as the binding sites gets saturated with the dye. After 80 min equilibrium was attained i.e there was no increment in MG adsorption rate with increase of residence time, which represents the attainment of adsorbent's maximum adsorption capacity (Gamal O. El-Sayed, et al.2014, Bharathi. K.S et al. 2013). Similar findings were recently reported by Gebreslassie.Y.T et al. for malachite green adsorption on Ficus cartia leaves (Gebreslassie.Y.T. 2020).

Effect of initial concentration of dye

The adsorption rate with respect to different initial concentration of MG (i.e 20, 30,40, 50 ppm) onto the fixed lignin dosage (0.1g) were observed for a time period of 100 min as shown in Fig.4. The fast adsorption equilibrium was observed with lower initial MG concentration which was slow down by increasing the MG concentration. This is because , active sites of lignin were hindered by the increased dye concentration in the aqueous phase where as in case of lower concentration of dye only monolayer of dye was formed on the surface of the lignin causing quick adsorption equilibrium. The similar pattern of decrease in percentage removal of MG with high concentrations of dye was seen in the studies of Senthil Kumar. P et al (2010) and Bhaskar.A et al (2014) . From this result, 50 ppm was chosen as initial dye concentration for next experiment to find the suitable adsorbent dosage.

Effect of adsorbent dosage

The effect of different adsorbent dosages (0.1g, 0.15g, 0.2 g, 0.25g) on the fixed initial MG concentration (50 ppm) was shown in Fig.5. The adsorption rate of MG onto the lignin was increased with increased adsorbent dosage. Because there are many active sites available on the lignin surface for adsorption of MG (Ghaedi. M et al. 2011). The percent removal of MG was increased from 77% to 92% with the increased lignin dosage from 0.1g to 0.25g. In accordance

with the result obtained, lignin dosage was chosen as 0.25g with the same initial concentration of dye for the next experiment.

Effect of pH

Fig.6 describes the effect of pH on percentage removal of malachite green on lignin. The adsorption rate of MG was increased from 76% to 95% with increase of pH from 4 to 9. It is clear that the pH of the solution had a considerable impact on adsorption of MG. At low pH, the functional groups present in lignin i.e. hydroxyl groups in aliphatic chain and aromatic phenolics are being protonated so that the lower adsorption rate was observed (Hengky Harmita et al. 2009). Moreover, when the pH is low, more positively charged surfaces are available which causes electrostatic repulsion between MG dye and lignin resulting in a lower adsorption rate. On the other hand, the adsorption rate of MG was increased at high pH. This is because of deprotonation of protonated phenolic and aliphatic hydroxyl gruops of lignin in the solution where the proton availability is less and also due to an electrostatic attraction between the positively charged surfaces of malachite green and negatively charged binding sites of lignin which enhanced the rate of adsorption of malachite green onto the lignin (Yong Qian et al 2011, Yufang Tang et al 2015). Equally the ion exchange mechanism between phenolic hydroxyl group, aliphatic hydroxyl contents of lignin and malachite green would enhance the percent removal of malachite green. Therefore the adsorption rate was increased with increase of pH. But at pH greater than 8, the colour reduction of MG was also observed. Similar trend was seen in Binod kumar et al (2015) study on adsorption of malachite green on rice husk.

Effect of Agitation Speed

The impact of agitation speed from 0 to 250 rpm at constant adsorbent dosage of 0.25g and at temperature 30^0C was shown in Fig.7.The adsorption rate of MG onto lignin was increased as the agitation speed increases up to 200 rpm. This is because as the agitation speed increases, the movement of dye molecules on to the adsorbent surface increases which means that by increasing rpm, there is improvement in mass transfer between the dye and adsorbate and also the dye molecules exerts kinetic velocity so that the boundary layer effect gets reduced (Muinde. V.M, et al. 2017). Thus the adsorption rate increases with increased rpm. But when the agitation speed exceeds 200 rpm the decrease in adsorption rate was observed. This is due to when agitation speed increases beyond 200 rpm, the dye molecules impelled by force towards the centre and generates excess centripetal force which results like repulsion between the dye molecules (Kamal Sukla Baidya et al. 2020). So, desorption starts as the centripetal force exceeds the binding force. Therefore the maximum percentage removal of MG was obtained at 200 rpm.

Effect of temperature

Batch experiments were conducted at different temperatures 30,35,40,45 and 50^0C with fixed lignin dosage (0.25g), initial dye concentration (50 ppm), pH 7 and at 100 rpm. The effect of temperature on adsorption rate was shown in Fig.8 and it was observed that with the increase of temperature, the percentage removal of MG also increased. This is because, availability of active sites on the surface and rate of opening of pore volume of the adsorbent increases with temperature. Moreover, the viscosity of dye suspension decreases with rise in temperature, allowing more adsorbate to diffuse across the outer boundary layer and through the internal pores of the adsorbent. In addition to that, the dye molecules exerts kinetic energy as temperature rises which result in enhancement of adsorption rate. The obtained results are in agreement with the studies of Daneshva et al (2007) and Rais Ahmad et al (2010) on adsorption of MG by microalgae Cosmarium SP and treated ginger waste respectively. Therefore, the adsorption process at different temperatures indicates that it is an endothermic process and further substantiated in isotherm models. However, when the temperature was raised to 50^oC the adsorption rate has decreased from 94% to72%. The MG dye molecules exert kinetic energy at higher temperatures, thereby resulting in a reduction in boundary layer thickness and thus leading to a greater tendency for dye molecules to outrun to the aqueous solution from lignin surface. So, a significant reduction in adsorption rate was observed at elevated temperatures (Michael Horsfall Jnr et al.2005).

Adsorption kinetics

The adsorption potency of malachite green dye onto the lignin was evaluated by adsorption kinetic study. The adsorption kinetic studies are useful in representing the correlations between solid- liquid contact time, the adsorption

rate on initial dye concentration and diffusion across an interface. Based on the experimental adsorption data, pseudo-first order kinetic model, second order kinetic model, a pseudo-second order kinetic model and an intraparticle diffusion model were applied to investigate the adsorption kinetic data (Yufang Tang,et al.2015, Labidi et al.2016).

The kinetic equations for Pseudo- first order, pseudo-second order and second order kinetic models are represented below:

$$\ln(q_e - q_t) = lnq_e + k_1 t/2.303 \text{------ (4)}$$

$$t/q_t = 1/(k_2 q_e)^2 + t/q_e \text{ ------ (5)}$$

$$\frac{1}{q_e - q_t} = k_3 t + \alpha \quad \text{------ (6)}$$

Where k_1(min^{-1}) - Rate constant for Pseudo- first order,
k_2 ((g (mg min) $^{-1}$) - Rate constant for pseudo-second order,
k_3 (g (mg $min)^{-1}$) - Rate constant for second order and
α - The intercept (g mg^{-1}).

The graphs for kinetic models are represented in Fig.9 (A, B and C) by plotting ln (q_e - q_t) versus t, t/qt versus t and 1/(q_e-q_t) versus t for pseudo- first order, pseudo-second order and second order kinetic models respectively. In Figure 9, the slope and intercept of the plots were used to calculate equilibrium adsorption capacity (qe) and equilibrium adsorption rate constants (k_1, k_2, k_3) as well as from the plots the correlation coefficient R^2 for each kinetic model was also determined. But from Fig.9 (c) the correlation coefficient R^2 for second order kinetic model at different dye concentrations were found to be very low (0.33 to 0.71), which means that the experimental data did not fit and this model was ineffective for the adsorption of MG onto the lignin, whereas the correlation coefficient R^2 for Pseudo- first order and pseudo-second-order kinetic model in Fig.9 (A&B) were high as compared to second order kinetic model. The computed values of correlation coefficient R^2, rate constants, q_e calculated from kinetic models and q_e from experimental data were tabulated in Table.2. Inferred from correlation coefficient R^2, pseudo-second order kinetic model was well fitted than Pseudo- first order kinetic model with the experimental data. Furthermore, the values of q_e calculated from pseudo-second-order kinetic model were similar to the values of q_e obtained from experimental evaluation whereas q_e from Pseudo- first order rate equation was varied largely with experimental q_e. Hence, these results confirm the logical deduction of the pseudo-second order kinetic model and its application to the adsorption of malachite green onto the lignin. This result also suggests that the mechanism involved within the adsorption process is by chemisorptions. But, initially a fast adsorption was occurred within 10 min, which also be due to physisorption or ion exchange between MG dye molecules and at the surface of lignin. Therefore, the actual process is influenced by a minimum of two mechanisms. The same two step adsorption mechanism was observed in the studies of Nethaji et al (2010) and Imran Ali et al (2010) on adsorption of MG dye using activated carbon which is derived from palm flower biomass and on mesoporous carbon material.

The Weber and Morris equation described below by equation (7) which explains the rate limiting steps of the adsorption process and can be applied to analyze the impact of the contribution of the intra-particle diffusion mechanism (Kushwaha, A.K et al.2014).

$$q_t = k_i t^{0.5} + C \text{------- (7)}$$

Where k_i (mg/g/$min^{0.5}$) - Intra particle diffusion rate constant
C (mg/g) - Boundary layer thickness

Fig.9 (d) shows the plots of q_t vs $t^{0.5}$ for different dye concentrations. The calculated rate constant K_i from the slope of linear plots, correlation coefficients R^2 and the intercept C values were tabulated in Table.2. The linear lines in the plot did not pass through the origin which indicates that intraparticle diffusion is not the only rate-limiting factor in the adsorption process, boundary layer diffusion also contributes to this phenomenon. The increasing values of K_i and C with respect to dye concentration also indicate the increased effect of boundary layer effect.

Adsorption isotherm studies

An adsorption isotherm provides a basis for understanding the interactions between adsorbates and adsorbents in the adsorption process. The three most common isotherm models i.e. Langmuir, Freundlich, and Temkin isotherm models were compared in this study to determine the suitable isotherm model for equilibrium curve at different temperatures.

Langmuir isotherm model

According to the Langmuir isotherm, a monolayer adsorption takes place on a special surface that has a finite number of binding sites with the strategy of homogeneous adsorption and assumed that there is no transmigration between the molecules that have been adsorbed on the surface of adsorbent. Langmuir's linear equation can be written as follows (T.L. Silva,et al.2016):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m} * \frac{1}{c_e}$$

Where, q_m (mg/g) - Monomolecular layer's maximum adsorption capacity
b (mg/L) - Langmuir isotherm constant .

In addition to this, Weber and Chakravorti defined an equilibrium parameter R_L which is dimensionless and also known as separation factor to describe the characteristic property of Langmuir isotherms as below (Ahmad, M. A.et al.2011):

$$R_L = \frac{1}{1 + bc_e}$$

The R_L value describes the type of adsorption isotherm type and nature of the adsorption process is involved. It specifies whether adsorption is unfavourable if R_L is greater than 1, linear if R_L is equal to 1, favourable if R_L is between zero and 1 or irreversible if R_L is equal to zero.

The plot of $1/q_e$ vs $1/C_e$ was drawn at various temperatures as shown in Fig.10 (a). The parameters in the Langmuir linear equation derived from slope and intercept of the plot as well as the correlation coefficients (R^2) and the separation factor (R_L) were shown in Table.3. The high R^2 values from Table.3 suggest that the Langmuir adsorption isotherm model was well fitted for the adsorption process. Furthermore, the dimensionless constant R_L values were substantially lower than 1.0 at four different temperatures also confirming the suitability of Langmuir isotherm towards adsorption of MG onto lignin. These results suggesting that MG adsorption onto lignin was likely monolayer and that active site distribution on the adsorbent was homogenous.

Freundlich adsorption isotherm

The Freundlich isotherm model can also be used to explain the experimental data. It is an empirical statement based on the assumption of multilayer adsorption at the surface by considering interactions with a heterogeneous surface among the molecules that have been adsorbed. The logarithmic form of Freundlich isotherm model can be expressed as follows:

$$\ln q_e = \ln qK_F + \left(\frac{1}{n}\right) \ln c_e$$

Where K_F - Freundlich isotherm constant
n - Heterogeneity factor, a dimensionless constant.

The n value indicates the degree of adsorption process favourability. A favourable adsorption is indicated when the value of $n > 1$, whereas a cooperative adsorption is indicated by a value of $n < 1$.

The plot of ln q_e vs ln C_e at various temperatures was shown in Fig.10 (b). The Freundlich constants, K_F and n values were determined from the intercept and slope of the plot ln q_e and ln C_e, and the correlation coefficients (R^2) were shown in Table.3. The value of heterogeneity factor (n) in the Freundlich model was calculated at varying temperatures where the values obtained were more than 1, which indicates a favourable absorption of MG onto lignin. Langmuir and Freundlich isotherm models both appear to agree very well with experimental results, indicating the possibility of monolayer and heterogeneous conditions may exist on the surface of the lignin (Yan Li et al. 2017).

Thermodynamic parameters

Generally, the thermodynamic analysis of an adsorption reaction is commonly assessed using parameters like Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0). We can compute the value of Gibbs free energy of adsorption from equation (11). The Van't Hoff equation (12) can be used to estimate the values of ΔS^0 and ΔH^0 (Rajeev Kumar et al.2014).

$$\Delta G^0 = -RT\ln K_L \text{--------- (11)}$$

Where K_L is the distribution coefficient and can be estimated by using the equation (12)

$$K_L = q_e/c_e \text{ -------- (12)}$$

T - Absolute temperature in Kelvin
R - Gas constant (8.314 J K^{-1} mol^{-1}).

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \text{ -------- (13)}$$

Fig.11 shows the plot of ln K_L vs 1/T. The slope and intercept of the linear line generated by plotting ln K_L against 1/T were used to derive the values of ΔH^0 and ΔS^0, whereas the values of ΔG^0 were determined using equation 11. These thermodynamic parameters such as ΔG^0, ΔS^0 and ΔH^0 were shown in Table 4. The positive values of ΔH^0 and ΔS^0 results confirms that lignin and dye adsorption interaction are endothermic in nature as well as that randomness and disorder increase was at solid-liquid interfaces only (Yufang Tang,et al.2015). The fact that the adsorption of MG onto lignin was spontaneous and was supported by the values of ΔG^0 ranging between -20 and 0 kJ mol^{-1} which indicating that the physisorption mechanism dominates in the adsorption process (Sivarajasekar.N, et al. 2014).

CONCLUSIONS

Lignin from pretreated rice straw was used for the adsorption of cationic dye malachite green in an aqueous solution. The characterization of lignin with FTIR and SEM indicated the functional groups and porous structure are suitable for the adsorption process. From the batch studies of adsorption, it can be concluded that the maximum dye removal of 92± 0.2 % has been achieved with optimum pH of 7, at temperature 30^0C, at agitation speed of 100 rpm and with 0.25 g of lignin dosage. According to the experimental results obtained for adsorption process, the suitable isotherm models were both Freundlich isotherm model and Langmuir adsorption isotherm model and it follows a pseudo-second-order kinetic model with the maximum adsorption capacity of malachite green onto lignin was 36.7mg/g at optimum conditions. The positive ΔH^0 and ΔS^0 values, as well as the negative ΔG^0 values, indicate that the adsorption of MG onto the lignin is endothermic, random and spontaneous. Therefore, lignin as an adsorbent is an alternative to the synthetic adsorbent and cost-effective material for the removal of cationic malachite green dye from wastewater.

Conflicts of interest: The authors declare no conflict of interest.

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Components	Rice straw (%wt)
Lignin	16.8
Cellulose	40.1
Hemicellulose	22.9

Table.1 Composition of rice straw by NREL-LAPs method

C_o (mg/L)	q_e cal (mg/g)	Pseudo first order			Pseudo second order			Intraparticle diffusion		
		q_e	K_1	R^2	q_e	K_2	R^2	K_i	C	R^2
20	35	4.56	0.064	0.85	35.7	0.134	0.99	0.342	31.24	0.79
30	50.8	16.411	0.099	0.91	52.63	0.089	0.99	0.923	41.48	0.94
40	70.2	16.29	0.0621	0.72	71.2	0.077	0.99	1.255	54.42	0.911
50	81	31.78	0.094	0.92	83.3	0.06	0.99	1.986	58.65	0.96

Table.2. The kinetic parameter from the adsorption kinetic models

Temperature (^oC)	Langmuir isotherm				Freundlich isotherm		
	q_m (mg/g)	b	R^2	R_L	K_F	n	R^2
30	90.91	0.155	0.99	0.11	1.011	1.78	0.988
35	100	0.141	0.97	0.124	1.02	1.74	0.94
40	125	0.114	0.98	0.148	0.989	1.49	0.99
45	100	0.172	0.99	0.103	1.05	1.69	0.99

Table.3. Isotherm parameters for the adsorption of MG onto lignin

Dye concentration (PPM)	ΔG^0 (KJ/mol) at temperature (K)				ΔH^0 (KJ/mol)	ΔS^0 (J/mol/K)
	303	308	313	318		
40	-5.65	-5.82	-6.14	-6.55	12.72	60.44
50	-5.20	-5.48	-5.71	-6.24	15.10	66.90
60	-5.06	-5.54	-5.68	-5.92	11.43	54.73
70	-4.56	-4.78	-5.41	-5.58	17.76	73.62

Table.4. Thermodynamic parameters for the adsorption of MG onto lignin

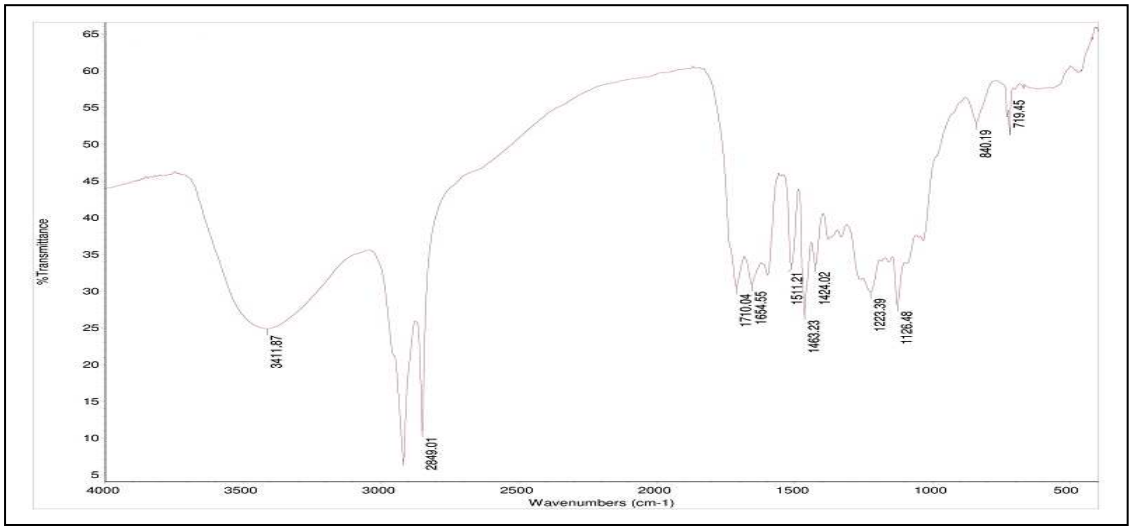

Fig.1 FTIR spectra of alkali lignin

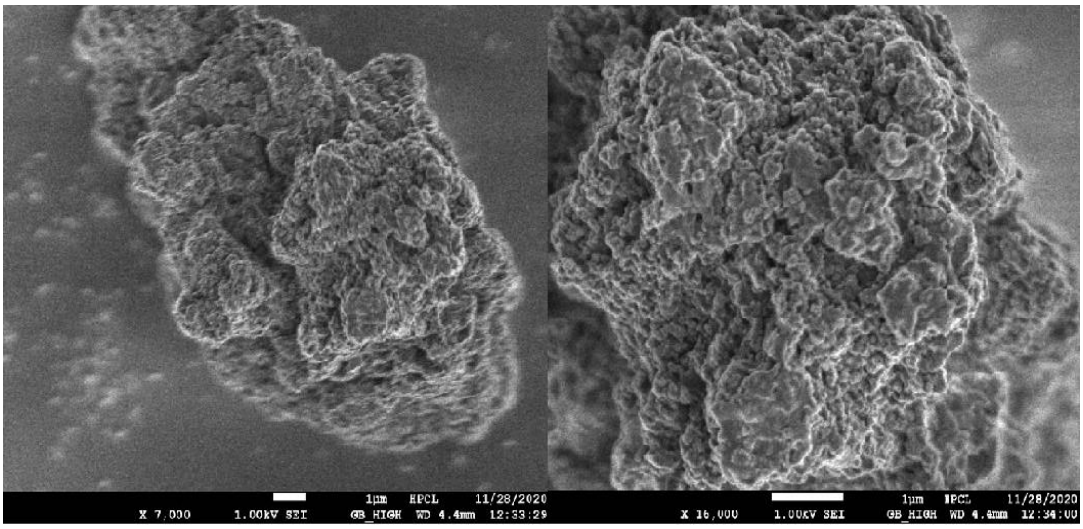

Fig.2 SEM images of alkali treated lignin at magnifications 7000 X, 16000X

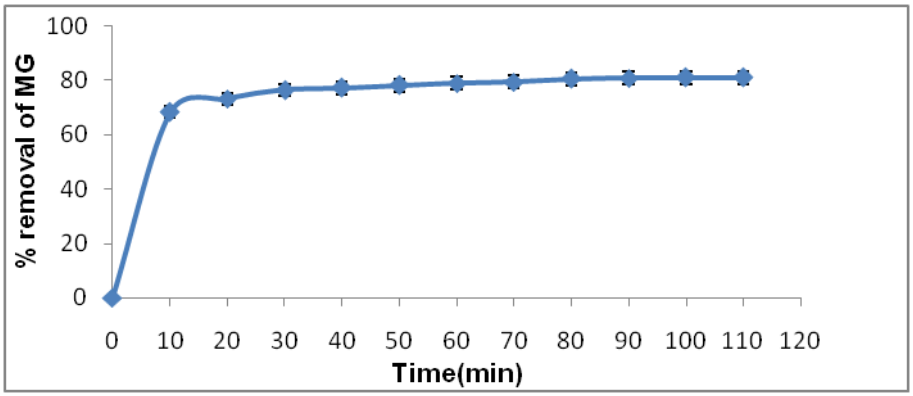

Fig.3 Effect of time on Percentage removal of MG

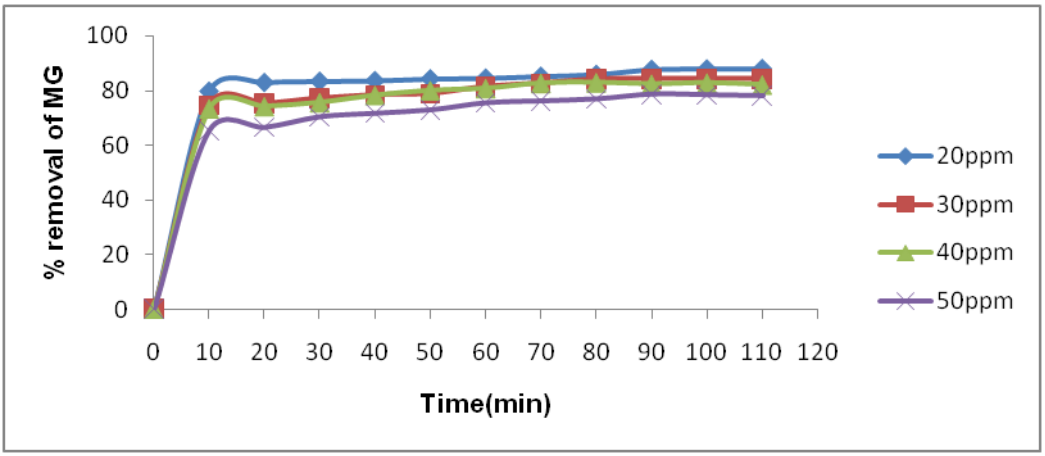

Fig.4 Effect of initial MG concentration on percentage removal of dye

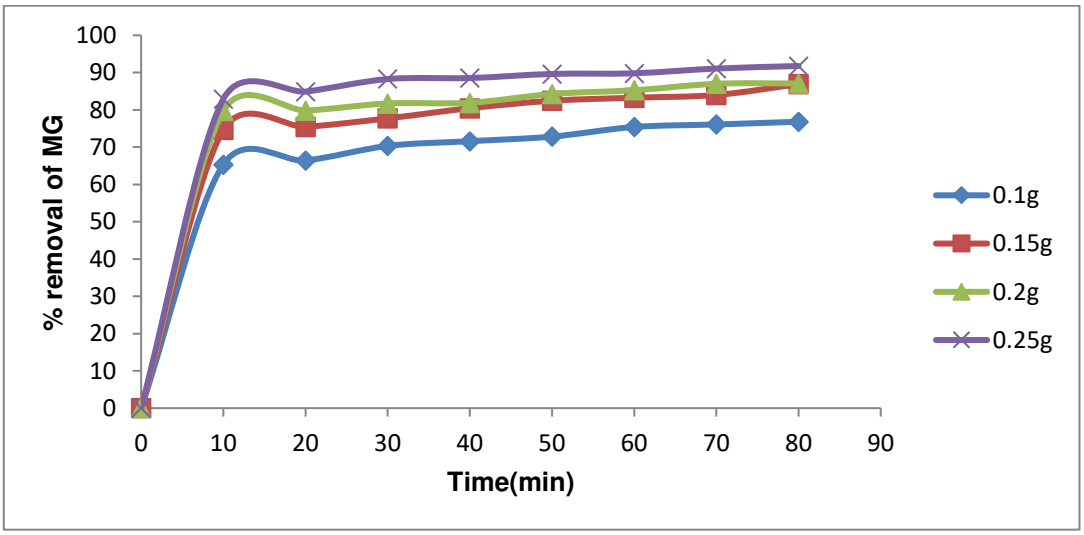

Fig.5 Effect of different dosage of lignin on MG removal

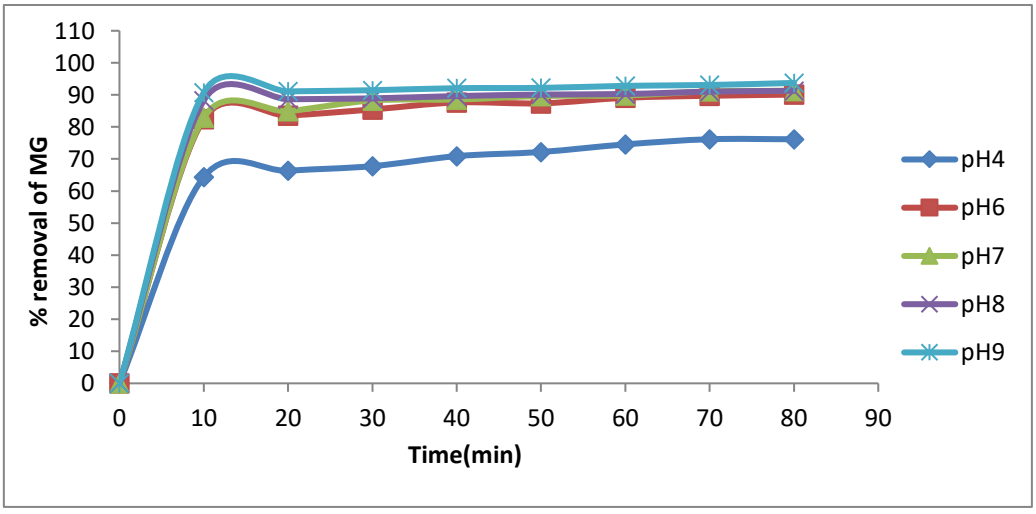

Fig.6 Effect of pH on percent removal of malachite

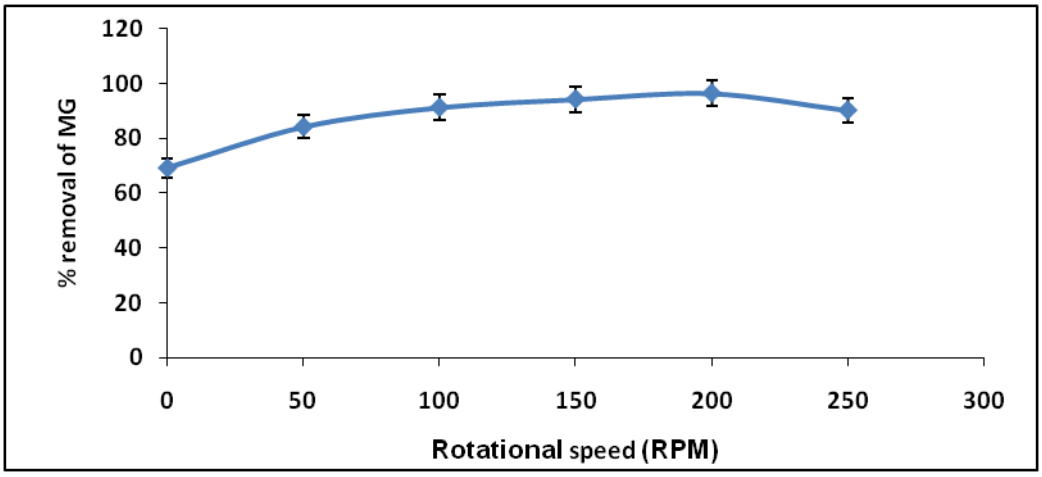

Fig.7 Effect of rotational speed on percent removal of malachite green

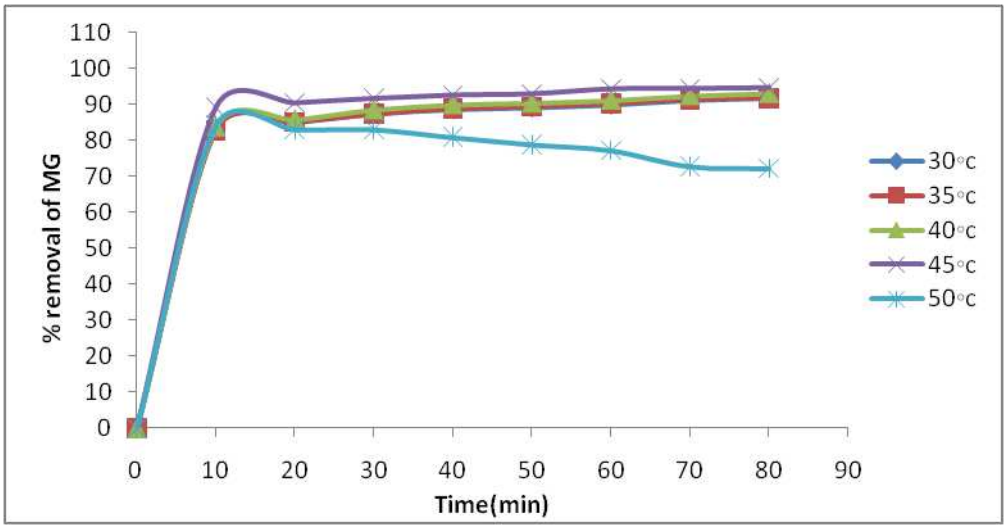

Fig.8 Effect of temperature on percent removal of malachite green

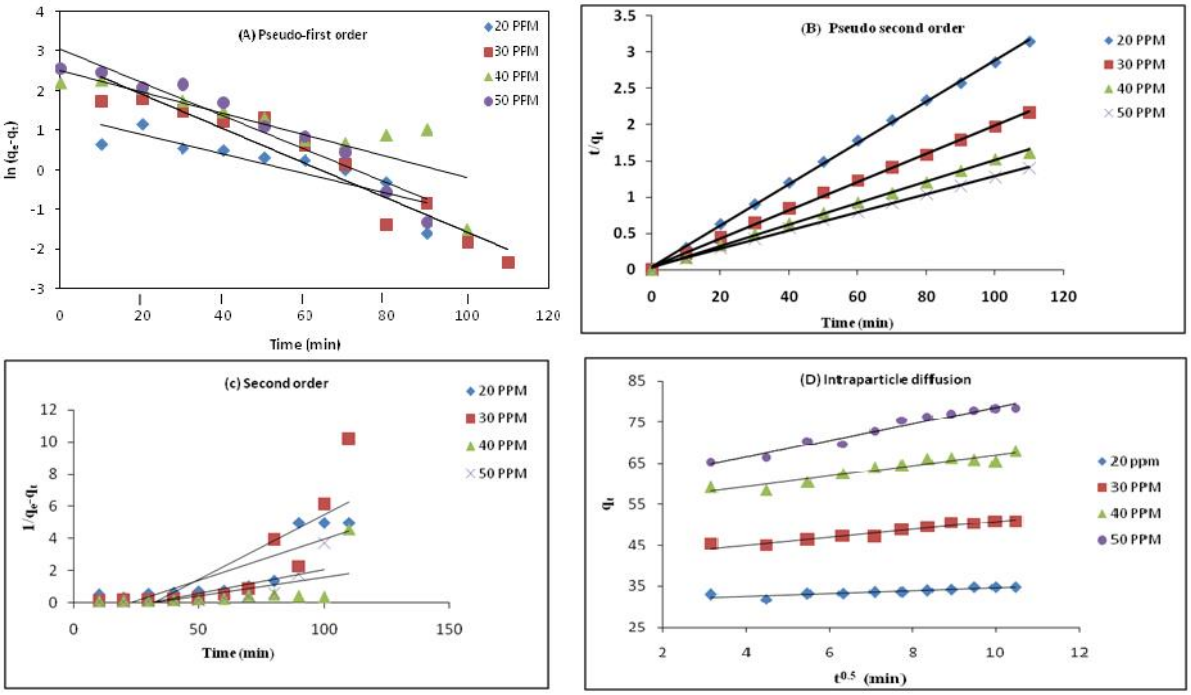

Fig.9. The kinetic models for adsorption of MG onto lignin

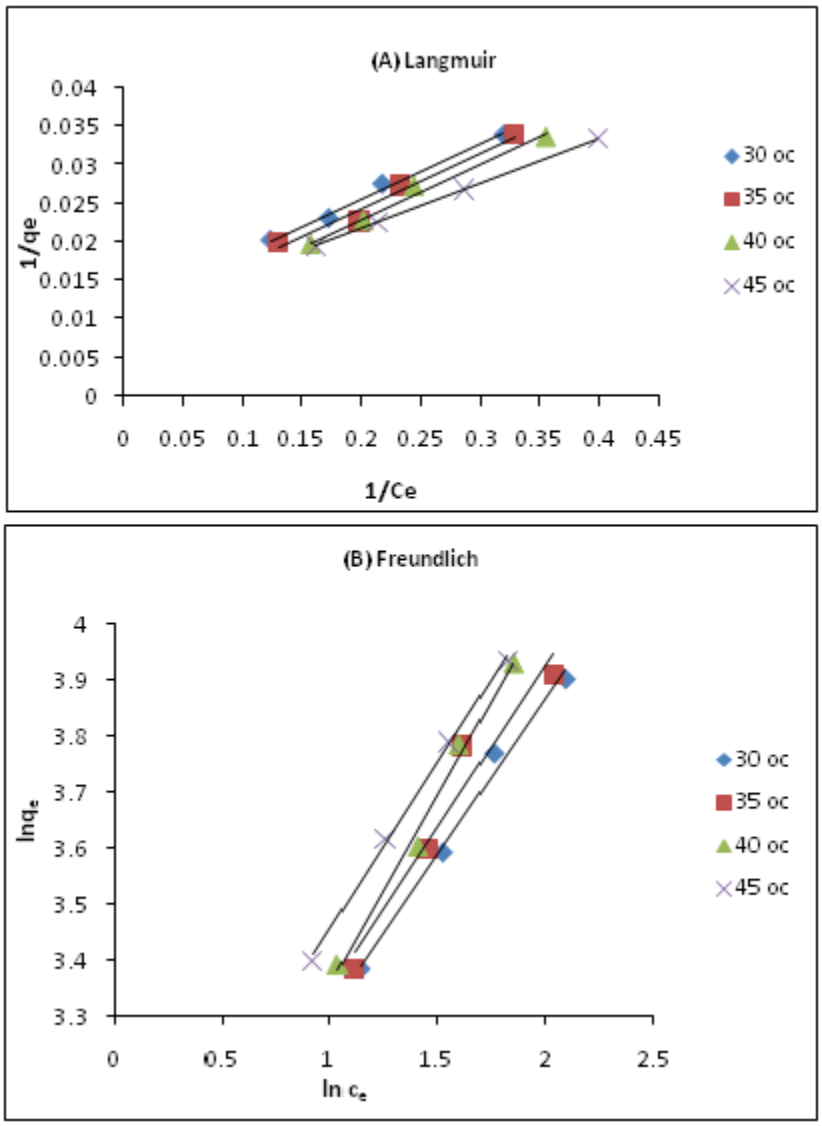

Fig.10 The isotherm models for adsorption of MG onto lignin

Figures

Figure 1

Figure 11