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Original Research Article

Equilibrium Modelling, Thermodynamic and Kinetic Studies on the Bio Sorption of Malachite Green Dye by a Low Cost Effective Adenanthera Pavonina Leaves Activated Carbon

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Abstract

The aim of the current work is to investigate the applicability of raw Adenanthera Pavonina Leaves Activated Carbon (APLAC) for the removal of Malachite Green (MG) in aqueous solution. The adsorption of Malachite Green (MG) on APLAC adsorbent was studied as a function of APLAC dose (0.2–1g), initial concentration (10–70mg/L), pH 4–9 solutions, and a varying contact time(30-150)minutes and temperature(298-328)K. The effect of these parameters on the adsorption capacity was investigated using a batch process. The experimental data were fitted to Langmuir, Temkin and Freundlich adsorption models and were found to coincide Freundlich adsorption isotherm. Kinetic data were fitted to the pseudo-first-order and pseudo second-order models, and were found to follow pseudo- second-order kinetic model. The Characterization of the APLAC adsorbent was achieved by FT-IR, UV and SEM techniques. This study reveals that APLAC is eco benign and has a very good dye uptake property and can be best used as low cost and effective adsorbent in removing the environmentally polluting dyes.

Keywords: Adenanthera Pavonina Leaves Activated Carbon; Batch Process; Adsorption; Isotherms; Kinetics; Equilibrium; Bio sorption.

INTRODUCTION

One of the lethal environmental issues is the discharge of industrial dyes in freshwater source which in turn affects the quality of water and makes it unfit for domestic and ecological uses. Discharge of wastewater from textile, paper, printing, and pharmaceutical industries contains colored effluent. The presence of these substances in streams or rivers beyond the permissible limits has been reported to cause potential health risks to public and aquatic environment [1]. To curb this havoc many modern-day technologies were adapted to remove the dyes from industrial discharge before letting it in freshwater source. One such technique is adsorption, which has very good results in dye uptake from industrial effluents. Recent trends of studies reveal that activated carbon has a very good effect as adsorbent due its magnanimous adsorbing capacity and its availability. In addition to this Activated carbon (AC) adsorption has been identified by United States Environmental Protection Agency (EPA) as one of the best available technologies [2, 3] for embarking adsorption. This is precisely due to their vast specific surface area, large pore volume and the presence of many surfaces' functional groups [4]. Activated carbon substances are complex porous structures with associated energetic as well as chemical in homogeneities. Their structural heterogeneity is a result of existence of micro pores, mesopores and macropores of different sizes and shapes, since it has high surface area its adsorption capacities are large such that it can effectively adsorb dye pollutants [5, 6]. In this study Adenanthera Pavonina Leaves Activated Carbon was used as a cost effective and successful adsorbent to remove malachite green dye from the aqueous solution.

MATERIAL AND METHODS

Materials

Malachite green (MG) dye has chemical formula $C_{23}H_{25}N_2Cl$ (molecular weight = 364.92, λ max = 617nm) Fig 1. Analytical reagent was used without any further purification in addition to deionised water, Sodium hydroxide (NaOH) hydrochloric acid (HCl) and ethanol (C_2H_5OH).

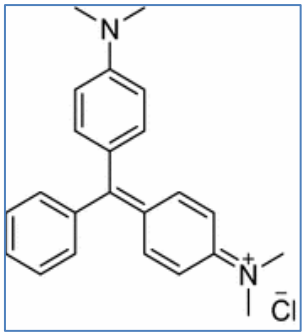

Fig-1: Structure of Malachite Green

Preparation of adsorbent

The (APL) Adenanthera Pavonina was used as an adsorbent were collected from Chennai. The unwanted materials like impurities, soils, dust etc., were removed by extensively washed in running tap water for removing. It was followed by washing with distilled water. The washed material was dried under sun light for ten days, it was ground in mixer. This ground powder was oven dried a 50°C for 24hrs. The APL powder weighed accurately in beaker than soak with 1:1 H_2SO_4 poured in beaker soak for 2 days then washed with distilled water pH level attain neutral. Then transferred to beaker dried in muffle furnace at 450°C for 3hrs dried well we get coal (black color powdered) obtained. It's called an activated carbon. Then used for further analysis.

Preparation of adsorbate

The synthetic dye Malachite Green (MG) were purchased from Kevin laboratories in Chennai. A stock solution of (1000mg/L) was prepared by dissolving 1.0 g of dye distilled water. Distilled water was used for preparing all the solution and reagents.

Batch adsorption experiment

The experiment was carried out by the batch adsorption method. The removal of dyes was studied various temperature (298K,308K,318K,328k) using the batch technique to investigate the effect of operational parameters such as pH, initial dye concentration, adsorbent dosage, contact time, and solution temperature. The isotherm study was carried out with different initial dye concentration of dyes from 10 to 70mg/L constant and carefully arranged in the orbital shaker and agitation at 150rpm speed for 30 minutes. The adsorbent dosage was checked from 0.2 to 1.0g for better adsorption. The kinetic study was done by varying time from 30 to 150 minutes, for the thermodynamic study temperature from 298 to 328K. The APLAC solution was separated by centrifugation at 2000rpm for 10 minutes. Residual concentration of dye was determined UV-visible spectrophotometer at respective wavelength. The percentage of dye removal from solution was calculated following

The percentage of MG adsorbed was determine based on the following formula

$$\% = \frac{(Co - Ce)}{Co} X\ 100 \qquad \text{eq. (1)}$$

The maximum MG uptake q_e (in mg g^{-1}) was calculated as shown below

$$qe = \frac{(Co - Ce)V}{M} \qquad \text{eq. (2)}$$

Where C_o and C_e are initial and final MG concentration of in mg 1^{-1}, respectively M is the amount of APLAC (in g) and V is the volume of MG solution.

RESULTS AND DISCUSSION

Ftir- fourier transform infrared spectroscopy

The FTIR spectrum of APLAC before and after adsorption Fig 2 & 2.1 of MG dye were analysed to determine the vibrational frequency changes in their functional groups of APL before adsorption in various peaks at 400-4000cm^{-1}, Changes in the vibrational and rotational movements of the molecule shows the detection of functional groups which have specific vibration frequency. For example, C=O, NH_2, -OH etc. Before adsorption of MG dye 3393.14cm^{-1} from O-H Carbohydrates groups, 2921.63cm^{-1} O-H from alcohols, 1654.62 cm^{-1} -NH_2 from amines, C-O str from amino acids, 1160.94cm^{-1} C-O str from aromatic compounds, 1007.62cm^{-1} O-H def from ketone, 765.60 cm^{-1} alkyl halides, 575.64 cm^{-1} aryl halides, 523.57 cm^{-1} -NO_2 Aryl nitro compounds.

After adsorption of MG dye, it was found that most of the functional groups the adsorbent were affected after the dye uptake process. This is judged from shifts in the position of some of the functional groups that moved at lower frequency or higher frequency or band intensity before and after MG adsorption includes 3428.81cm^{-1} from O-H Carbohydrates groups, 2919.7cm^{-1} O-H str from carboxylic groups, 1655.59 cm^{-1} from amines, 1159.97 cm^{-1} C-O str from alcohols, 997.01cm^{-1} C-H $_{def}$ from aldehyde, 853.34cm^{-1} N-H def from amines, 763.67 cm^{-1} alkyl halides, 516.82 cm^{-1} from aryl halides halogen groups respectively indicates involving of these groups for MG binding to APL.

SEM – Scanning Electron Microscope

The SEM images of the APLAC sample Fig 3 revealed a great number of the pores in nanometre size, which were formed during the carbonization and activation process. Pore system and excellent pore morphology observed by SEM. From the SEM images it is confirmed that the particle having size in 27.96 nanometre as calculated by Image J programme. Such porosity should definitely provide APLAC with high adsorption capacity towards MG.

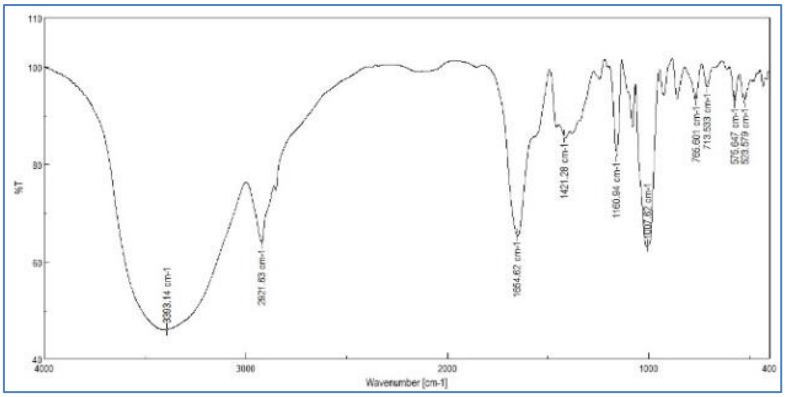

Fig-2: FTIR spectrum for before adsorption on APLAC

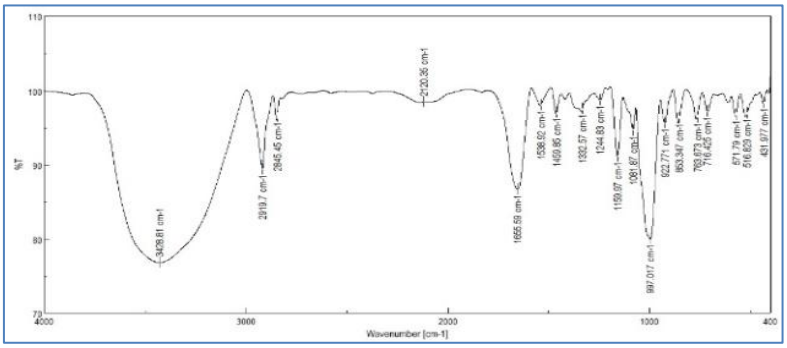

Fig-2.1: FTIR spectrum for after adsorption on APLAC

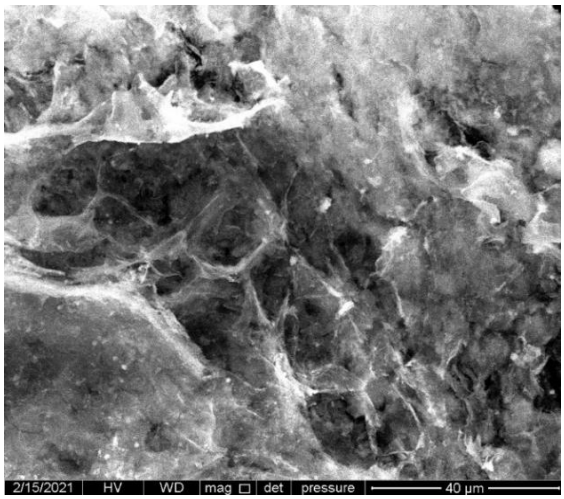

Fig-3: The SEM images of APLAC

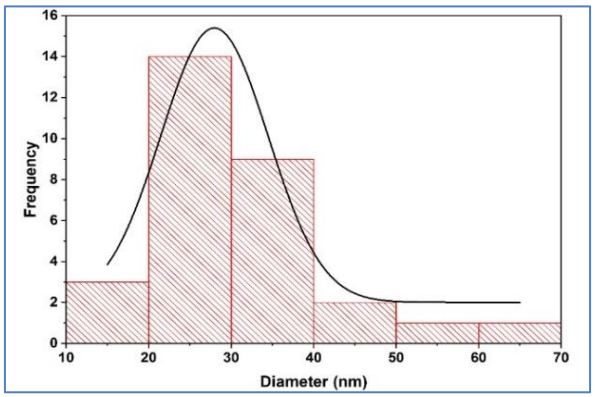

Fig-3.1: Histogram of APTA

Effect of Adsorption process parameters on the removal of MG

Effect of initial dye concentration of MG

The inference of the initial concentration of MG in the solution on the rate of adsorption on APLAC was investigated. The Experimental parameter was carried out with fixed adsorbent dosage, optimal pH and stably maintained temperature. The percentage removal increased with an increase in initial dye concentration. The dye concentration is increased from 10 to 70mg/L. Maximum adsorption of 89.86% was recorded for (50mg/l) and then the percentage removal was constant till the adsorption attains the equilibrium. This could be attributed to the increase in the driving force from higher concentration which enhances the sorption process- Fig (5).

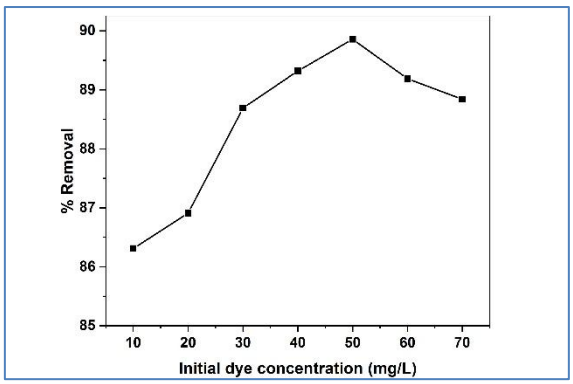

Fig-4: Effect of Initial MG dye concentration on the adsorption of APLAC

Effect of adsorbent dosage

Adsorbent dosage also plays a predominant role in the Adsorption process. Because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent dosage was studied on the dye removal. The other parameters such as pH, temperature and contact time were fixed. The amount of MG dye adsorbed gets decreased with increase in adsorbent dosage. The maximum sorption was obtained at 0.2g. Generally, the percentage of MG dye removal increases with increasing amount of adsorbent. But however, the amount of dye adsorbed into APLAC decreased when adsorbent dose was increased from 0.2g to 1.0g, since the percentage of porosity increases with increase in adsorbent dosage. The amount of MG dye adsorbed decreased from 92.02 to 88.29% is shown in fig 6.

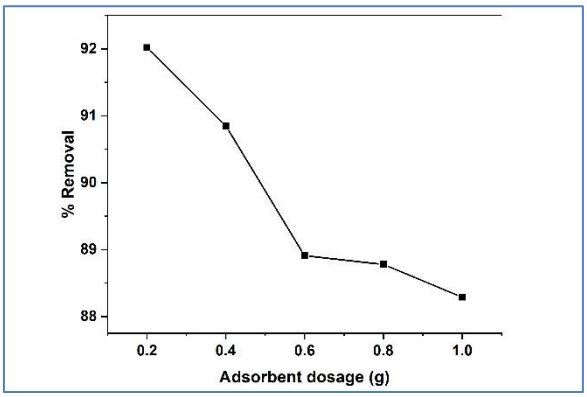

Fig-5: Effect of adsorbent dose on removal of MG

Effect of pH study

The initial pH plays an important role in surface binding sites of the adsorbent and the whole adsorption process. The effect of pH on malachite green adsorption on APLAC was studied. The other experimental parameters such as adsorbent dosage, Initial dye concentration contact time and temperature were fixed as constant. The pH of the solution is altered from 4-9, the maximum dye adsorption of APLAC is obtained by 92.07% at pH 7 Fig 7. At lower pH (4-6) adsorption was unfavourable for malachite green adsorption by APLAC. Since initial pH of the test solution decreases, the number of negatively charged adsorbent sites decreased and positively charged sites increased which did not favour the adsorption of positively charged dye cation due to electrostatic repulsion [7]. Therefore, Adsorption of MG dye is highly favoured at pH 6, since electrostatic force of attraction between basic MG dyes in less acidic solution exists.

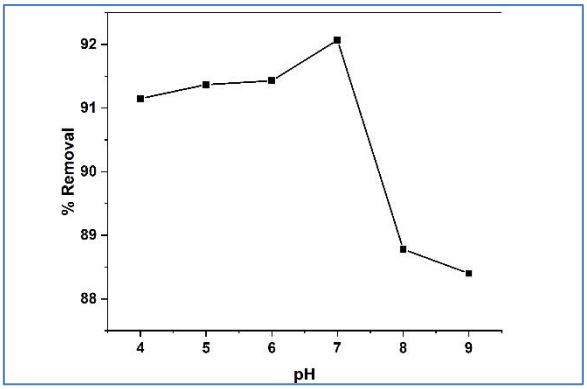

Fig-6: Effect pH on the adsorption of MG onto APLAC

Effect of contact time

Equilibrium time is one of the most important parameters in the design of economical waste treatment system and its effect on the adsorption of MG on APLAC is presented Fig 7. These experiments have been carried out at variation time of contact (30-150 minutes). After every contact time, one sample was removed and filtered immediately and the filtrate was analysed. The results show that the maximum adsorption is obtained 92.27% at contact time 60 minutes. The adsorption of dye initially increases with increasing contact time and then the percentage removal gradually decreases with increasing contact time. The time taken to reach the equilibrium was 60 minutes for APLAC.

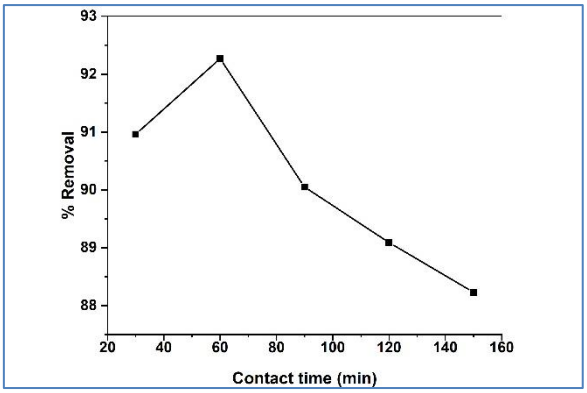

Fig-7: Effect of contact time adsorption for the MG onto APLAC

Effect of temperature

The temperature can affect adsorption rate. In this study the Effect of temperature on MG adsorption was investigated is the range of 293-328 K Fig 8.

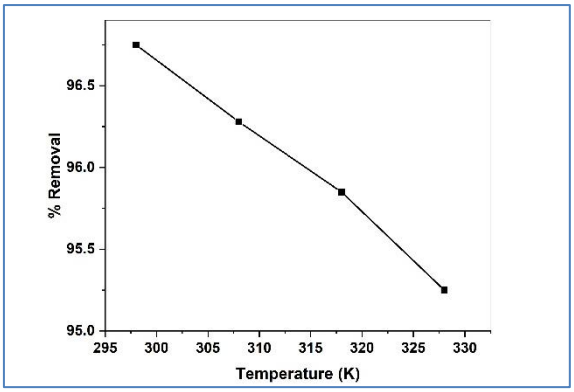

Fig-8: Effect of temperature on the adsorption of MG onto APLAC

The adsorption of dye decreased when increase of temperature. The percentage removal decreased 96.25 to 95.25%. The maximum amount of dye adsorbed was 96.25% at 298k. The decrease dye adsorption at higher temperature was to the weakening supportive for between active site on the adsorbent and adsorbate [8]. A sharp reduction after 298 K decrease in surface activity at higher temperature. Thereafter, IT indicates that the adsorption process is exothermic and MG dye adsorption onto APLAC occurred mainly by physical adsorption [9].

Adsorption isotherm

Adsorption isotherm are important in predictive modelling the Procedures for designing the adsorption system, because the adsorption Capacity of a quantitative of adsorbent could be describe, and it helps in Making the selection of appropriate adsorbent and determination of Adsorbent dosage feasible [10]. Several isotherm models are available. Adsorption isotherms obtained in this work were fitted using the Langmuir, Freundlich and Temkin models. Their correlation with our adsorption process was judged by the values of correlation coefficient (R^2).

The Langmuir models assume monolayer adsorption on a Homogenous surface with all active sites being equivalent and with the same energy. The Langmuir model also assumes dynamic equivalent and no Interaction between [11].

$$\frac{1}{qe} = \frac{1}{qmKlCe} + \frac{1}{qm} \qquad \text{eq. (4)}$$

Where qe is the amount of adsorbed dye at the Equilibrium (in mg g^{-1}), K (L mg^{-1}) and qm (mg g^{-1}) are Langmuir Constant related to energy adsorption and maximum adsorption Capacity respectively. A graph of 1/qe against 1/ce results in a Straight line with a slope of (1/qm K_L) and intercept (1/qm).

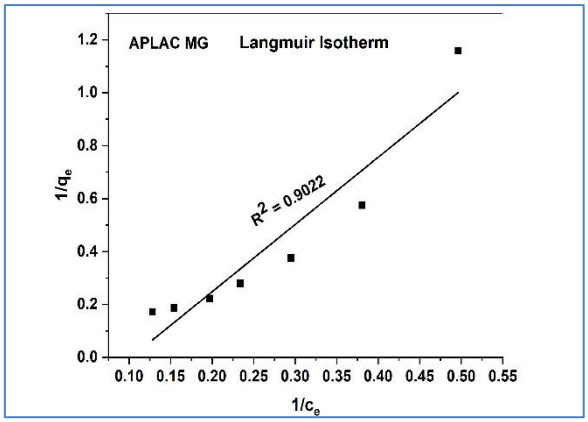

Fig-9. 1: Langmuir isotherm plot for the adsorption of MG onto APLAC

The Freundlich model is described by a formula assuming heterogeneous multilayer adsorption on heterogeneous Surfaces. The Freundlich model also assumes interaction between the Adsorbates and that adsorption capacity increases with the analyte Concentration. The formula describing the Freundlich model is shown [12].

$$\log q_e = \log K_F + 1/n \log C_e \qquad \text{eq. (5)}$$

Where K_F is the reaction constant reflecting adsorption Capacity (in 1 mg-1), and 1/n indicates dimensionless exponent of the Freundlich model to show adsorption intensity (it is calculated from the slope and intercept of log qe versus log Ce plot).

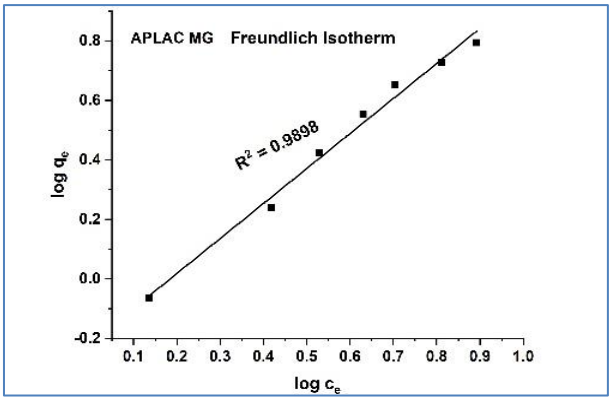

Fig-9.2: Freundlich isotherm plot for adsorption of MG onto APLAC

The Temkin isotherm model assumes that the Adsorption energy decrease linearly with the surface coverage due to adsorbent-adsorbate interaction. The linear form of Temkin Isotherm model is described as follows [13].

$$q_e = \frac{RT}{BT} \ln KT + \frac{RT}{BT} ce \qquad \text{eq. (6)}$$

Where BT is the Temkin constant related to the heat of sorption (KJ/mol), KT is the equilibrium binding constant Corresponding to the maximum binding energy (L/g), T is the Absolute temperature(K) and R is the gas constant (8.314 X 10^{-3} KJ/mol K). The Langmuir, Temkin and Freundlich Isotherms for our adsorption experiments displays Fig 9.3.

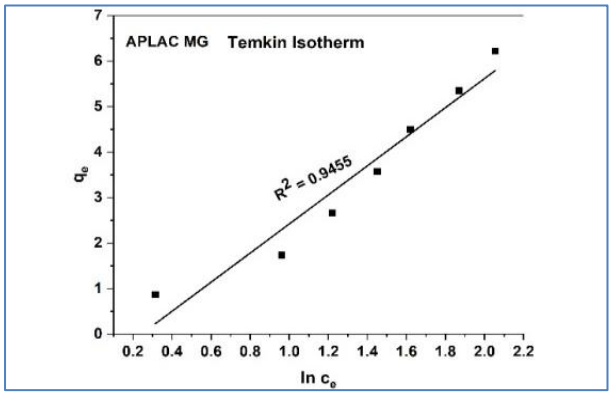

Fig-9.3: Temkin isotherm plot for the adsorption of MG onto APLAC

The Freundlich isotherm model well fitted and good Agreement with the experimental data better than the Langmuir and Temkin models (table 1). The result is also confirmed by the high R^2 value for the Freundlich model (0.9898) compared with the Langmuir (0.9025) and Temkin (0.9455) isotherm models. Therefore, the adsorption of MG on APLAC occurs as surface that is homogeneous in adsorption affinity.

Adsorption Kinetic studies

The pseudo-first order and pseudo-second-order Model were used to investigate the adsorption kineties of the MG dye on APLAC.

Pseudo-first-order model

The pseudo-first—order rate model of Lagergren(s) is based on solid capacity and generally expressed as follows Log (q_e-q_t) = logq_e – K_1/2. 303.t eq. (7)

Where q_e is the amount of solute adsorbed at equilibrium per unit Weight of adsorbed (mg/g), q_t is the amount of solute adsorption at any time (mg/g), K is the adsorption constant. This expression is the most popular form of the pseudo first order kineties model. K_1 Values at different initial MG concentration were calculated from the plots of ln(qe-qt) vs t. Constant K_1 and correlation coefficient (R^2) were calculated and summarized table (2).

The correlation coefficient (R^2) value obtained was relatively hence, this model has very poor correlation coefficients ($R^{2)}$ the best fit data.

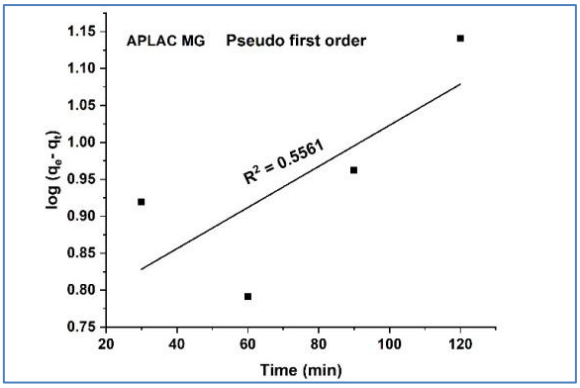

Fig-10.1: Pseudo-first-order kinetic model plot for adsorption of MG onto APLAC

PSEUDO-SECOND-ORDER MODEL

The kineties data were analysed using the pseudo –second-order model which can be expressed as follows

$t/qt = 1/K_2q_e^2 + t/q_e$ eq. (8)

The plot of 1/qt vs t should give a linear relationship from which q_e and K_2 can be determined from the slope and intercept of the plot.

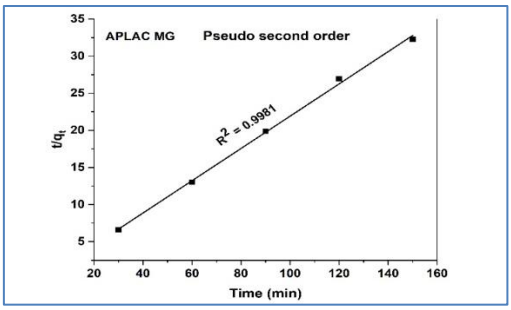

Fig-10.2: Pseudo-second order kinetic model for adsorption of the MG onto APLAC

The K_2 and q_e determines from the model along with the Corresponding correlation coefficients R^2 values are presented in table (2). Based on the given data the adsorption of MG dye perfectly followed the Pseudo-second-order kineties model.

Adsorption thermodynamic

Thermodynamic parameters are important in adsorption Studies, they provide a better understanding of the effect of temperature on the adsorption process. They include standard enthalpy change (ΔH^O), Standard entropy change (ΔS^O) and standard free energy change (ΔG^O). The Values can be calculated by using the following equations

$\Delta G^O = -RT\ln K$ Eq. 9

$\Delta G^o = \Delta H^o - T\Delta S^o$

$\log K = \Delta S^o/2.303R - \Delta H^o/2.303RT$ Eq.10

Where R is the universal gas constant (8.314J $mol^{-1}k^{-1}$), T is the absolute temperature (k) and K is the equilibrium constant. Plots of lnk vs 1/T should be a straight line as shown in fig (11). The thermodynamic parameters are tabulated in table (3). The negative values (ΔH^o) obtained in the adsorption of MG dye onto APLAC signify that the adsorption process was exothermic in nature. The positive values of (ΔS^o) indicate that increase in randomness Occurred at solid – solution interface during the adsorption process. This indirectly shows the affinity of adsorbent toward dye molecule [14]. The (ΔG^o) values were negative at all temperature Studied, inferring that the adsorption was spontaneous in nature. Since the Values of (ΔG^o) decreased with increasing temperature. It suggests that at higher temperature the driving force was less resulting in lower adsorption update [15].

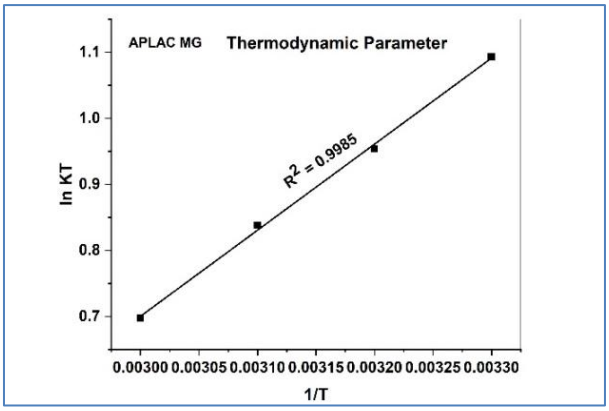

Fig-11: Thermodynamic parameter plot for the adsorption of MG onto APLAC

Table-1: Isotherm parameters for removal of MG adsorption onto APLAC

Adsorption Isotherm	Parameters	values
Freundlich Isotherm	K_F (mg/g)	0.6061
	1/n	1.1764
	n	0.8500
	R^2	**0.9898**
Langmuir Isotherm	K_L (mg^{-1})	0.1023
	q_m (mg/g)	3.8476
	R^2	0.9022
Temkin Isotherm	K_T (mol/g)	0.7843
	B_T (mol/kJ)	3.1951
	R^2	0.9455

Table-2: Adsorption Kinetic Model for MG Adsorbing by APLAC

Kinetic Model	Parameter	Results
Pseudo 1st Order	K_1 (min^{-1})	0.0064
	q_e (mg/g)	5.5564
	R^2	0.5561
Pseudo 2nd Order	h (mg. g^{-1} min^{-1})	6.1462
	q_e (mg/g)	0.1627
	R^2	0.9981

Table-3: Thermodynamics Parameter

Temperature (K)	ΔG^o (J. Mol^{-1})	ΔH^o (KJ. Mol^{-1})	ΔS^o (J. Mol^{-1}. K^{-1})	R^2
298	-2.7087	-24.9468	61.4336	0.9985
308	-2.4418			
318	-2.2166			
328	-1.9018			

CONCLUSION

Based on the results shown, APLAC can be used as a very efficient and cheap adsorbent for the removal of dyes from waste water. The adsorption of MG dye was examined at different experimental conditions like initial dye concentration, dosage, pH, contact time and temperature respectively. More overall result shows that the Freundlich adsorption isotherm model best fits than the Langmuir and Temkin isotherm model. Kinetic study reveals that the adsorption reaction follows pseudo second order kinetic model. The thermodynamic results predict the negative value of ΔG^o which indicates that the adsorption processes of MG dye onto APLAC surface are spontaneous and

thermodynamically more favourable. The negative value of ΔH^o indicates that the nature of the adsorption process is exothermic and the positive value of ΔS^o suggests increasing randomness at the adsorbent solution interface during the adsorption process. Further it can be concluded that APL are abundant in our country, further it can be used for the removal of MG dye from industrial waste water. The future work is going to be based on dye removal using green synthesized nano activated carbon.

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