



Tribulus Terrestris Spent Adsorbent Utilized For Dye Removal Of Malachite Green Dye

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Abstract

The agro-based Nutraceutical industrial Tribulus Terrestris Spent (NITTS) an aqueous solution on dye adsorption, the effects of starting dye concentration, pH, temperature, adsorbent dosage, and particle size were investigated. The obtained experimental equilibrium data were examined using Langmuir and Freundlich isotherm models. The adsorption capacity, q_e , had an experimental value of 50 mg g⁻¹. The models used in the kinetics of adsorption investigations suit a pseudo-second order model quite well. The exothermic nature of the adsorption process was demonstrated by the values of thermodynamic parameters such as ΔG^0 , ΔH^0 , and ΔS^0 . The Malachite Green dye (MG) adsorption onto NITTS was demonstrated by the FTIR spectra and SEM pictures. It is discussed whether there was any interaction in the MG-NITTS system. An efficient adsorbent for removing MG dye from an aqueous solution is NITTS.

Keywords

Nutraceutical industrial Tribulus Terrestris Spent, Adsorption, Isotherms, Kinetics

1. Introduction

The widespread use and large-scale production of synthetic dyes are seriously endangering the environment and raising public concerns. Large volumes of wastewater dyeing that contained a sizable amount of leftover dye have resulted in increasingly stringent laws governing the limits of colour discharge (Verma et al., 2012). Tiny amounts of dyes are quite noticeable and unfavourable. Accordingly, it is

absolutely essential that water containing dye be treated before being disposed of in the environment (Fernando et al., 2013; Wang and Xu 2012). It has been demonstrated that the adsorption technique is a desirable and successful method for treating waste water that contains dyes (Fu, F., and Wang, 2011).

Known by several names, including Puncture vine, Gokshur, or Gokharu (Evstatieva and Tchorbanov 2011; Tutin et al., 1968; Gain-pietro Di sanse bastiano et al., 2012), *Tribulus terrestris* L. (Zygophyllaceae) is an annual plant that has long been used in Chinese and Indian medicine to treat a wide range of illnesses. Chemical components that are significant for medicine include alkaloids, steroidal saponins, flavonoids, and flavonol glycosides. According to Saurabh Chhatre et al. (2014), it possesses the following properties: diuretic, aphrodisiac, antidiabetic, absorption boosting, hypolipidemic, cardiogenic, hepatoprotective, anti-inflammatory, analgesic, antispasmodic, anticancer, asthelmintic larvicidal, and anticariogenic. Extracts from the entire plant or fruit, which are used for everything from skin care to regulating human hormones (Gain-pietro). Antibacterial (Oh.H et al., 2011), anti-inflammation (Heidari M et al., 2007), immune-stimulant as well as Di Santo Bastiano et al., 2012; Gauthaman and Ganesan 2008; Huang J et al., 2003; Iacono F et al., 2011).

This study uses Nutraceutical industrial *Tribulus terrestris* waste (NITTS) as a economical biosorbent to test the adsorption of Malachite Green (MG) dye from aqueous solution. In this instance, the material remaining after the primary component(s) is extracted is referred to be wasted. Steps in the process include mechanical, chemical, and thermal ones.

To comprehend the nature of the adsorption, we first optimised the adsorption parameters, including the mass, pH, and effect of the starting concentrations of NITTS. We also assessed the kinetics and equilibrium isotherms.

2. Materials and Methods

The supplier of malachite green was Sigma Aldrich Private Limited in Mumbai, India. Every chemical that was utilised was an analytical-grade reagent. The temperature at which the adsorption studies were conducted was $25 \pm 2^\circ\text{C}$, 300, 400, and 500°C . Figure 1 shows the molecular arrangement of MG.

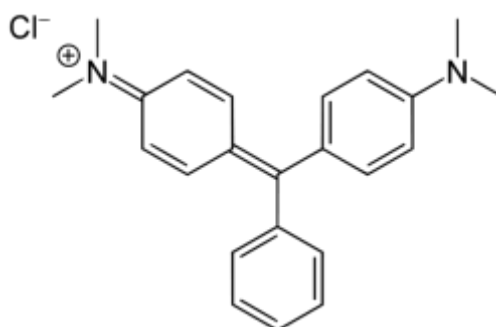


Fig. 1 Molecular arrangement of Malachite green

3. Results and Characterisation

3.1. Characterization of adsorbent by FTIR

3.1.1. FTIR characterization of MG adsorbed on to NITTS

Figure 2 illustrates how FTIR spectroscopy investigates the relationship between NITTS and MG. The NITTS FTIR Spectra show the vibrational frequency of the functional groups in the adsorbent. The following vibration patterns are found in alkanes: 3344 cm^{-1} for O-H stretching vibrations, $1038\text{--}1028\text{ cm}^{-1}$ for carboxylic acid C-O stretching vibrations, $605\text{--}612\text{ cm}^{-1}$ for C-Cl stretching vibrations, $662\text{--}674\text{ cm}^{-1}$ for C=C cis alkene bending vibrations, 1609 cm^{-1} for N-H bending vibrations, and 1422 cm^{-1} for C-H bending vibrations. After adsorption, the FTIR of MG-NITTS reveals functional groups. There are C-Cl stretching vibrations at 581 cm^{-1} , $1366\text{--}1435\text{ cm}^{-1}$ C-H bending vibrations, 900 cm^{-1} C=C bending vibrations, and 2971 cm^{-1} C-H stretching vibrations, 1739 cm^{-1} C=O stretching vibrations, and $1217\text{--}1229\text{ cm}^{-1}$ C-O stretching vibrations. C-Cl stretching vibrations at 581 cm^{-1} , C-H bending vibrations at $1366\text{--}1435\text{ cm}^{-1}$, and C=C bending vibrations at 900 cm^{-1} are present.

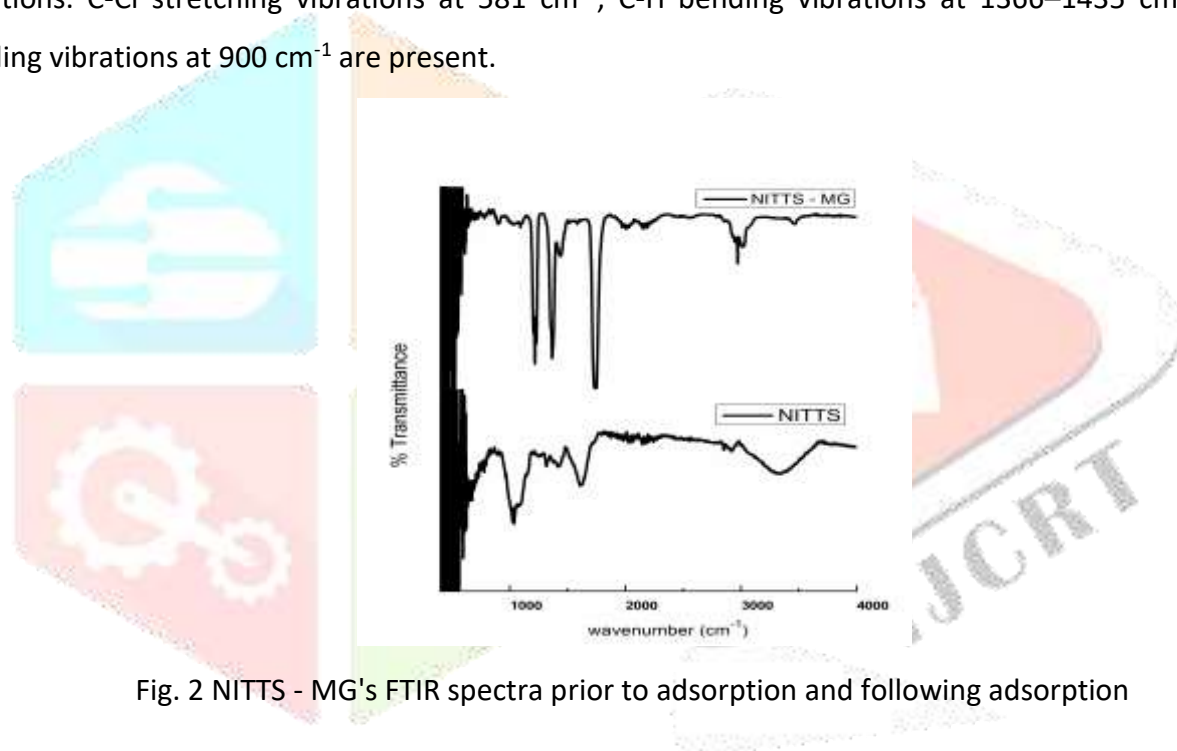


Fig. 2 NITTS - MG's FTIR spectra prior to adsorption and following adsorption

3.2. Surface Characterisation

3.2.1. Scanning Electron Microscope

The NITTS's pliable and elastic configuration was revealed via SEM examination. This assembly facilitates better dye absorption. An SEM image of MG NITTS prior to adsorption is shown in Figure 3a. After adsorption, the NITTS SEM image is seen in Figure 3b. The porous structure indicates that there is adsorption of NITTS with MG.

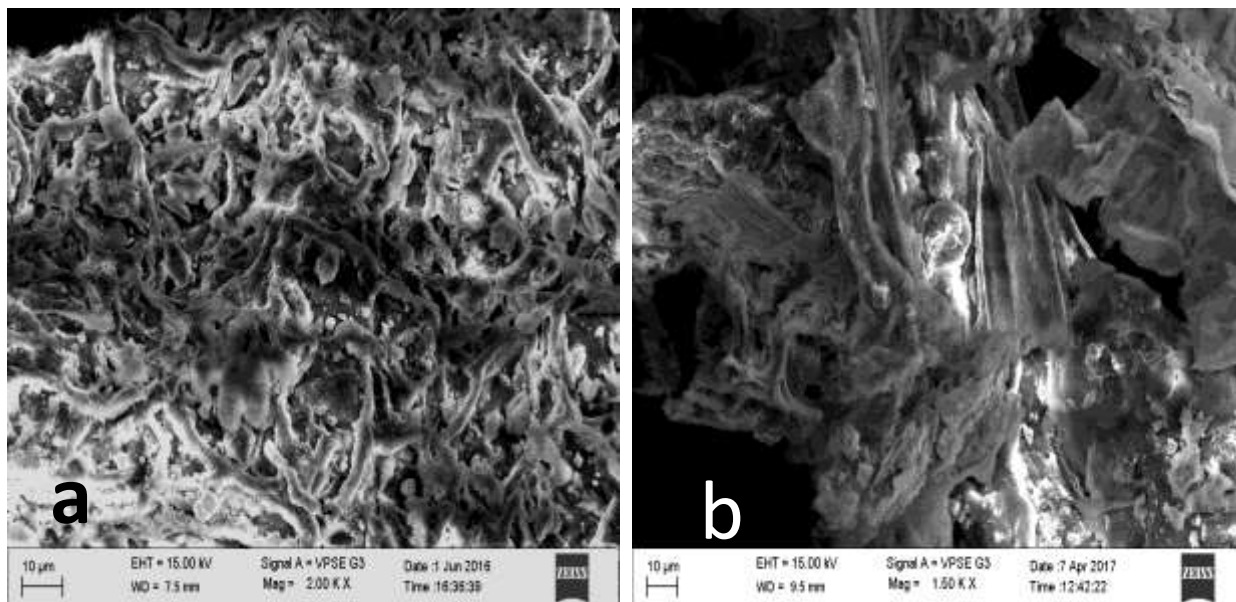


Fig. 3: a. SEM image of NITTS before adsorption b. NITTS with MG after adsorption

3.3. Effect of Initial Dye Concentration

The dye absorption of NITTS amplified from 19 to 60 mg g⁻¹ as the dye concentration enlarged from 25 to 200 mg L⁻¹. The concentration gradient's driving power increases, which results in the initial dye concentration. Adsorption happened quickly at first on the surfaces; later, the dye molecules most likely penetrated the interior surface's pores, which is a slower process. Higher concentrations of MG resulted in greater adsorption, which after equilibrium time remained nearly constant (Figure 4).

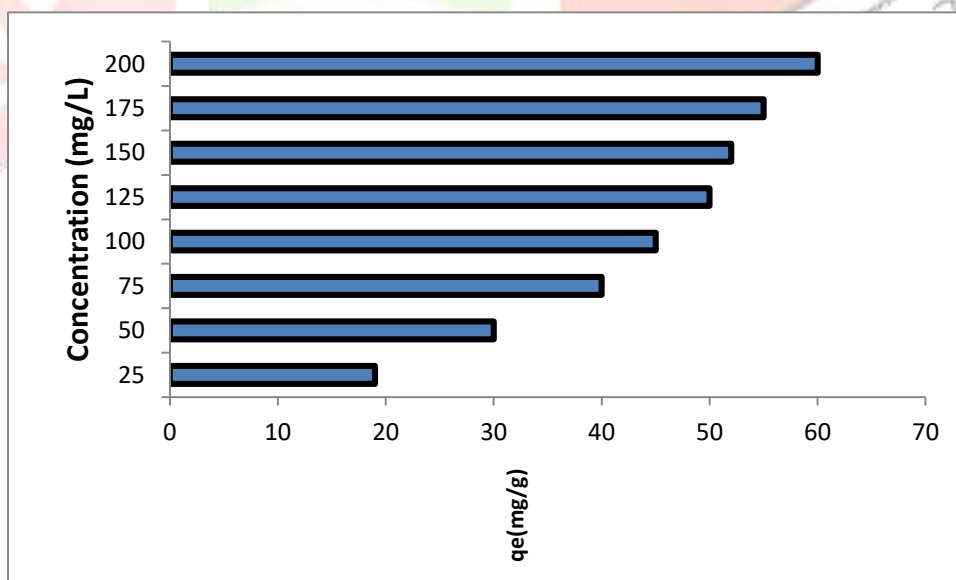


Fig. 4 Effect of initial dye concentration on adsorption of MG

3.4. Effect of pH

One of the most crucial elements in the adsorption process is the pH. By affecting the ionic forms of dye and the surface characteristics of the adsorbent, it regulates the adsorption capacity. The highest adsorption capacity of MG was in an acidic environment, and the adsorption capacity of NITTS increased somewhat as the pH of the solution increased. In an acidic pH, an excess of H^+ ions competes with the cations of the dye for adsorption sites. The repulsion between the positively charged dye and the adsorbent surface decreases as the surface charge density rises in the solution pH. As shown in Figure 5, this leads to enhanced adsorption.

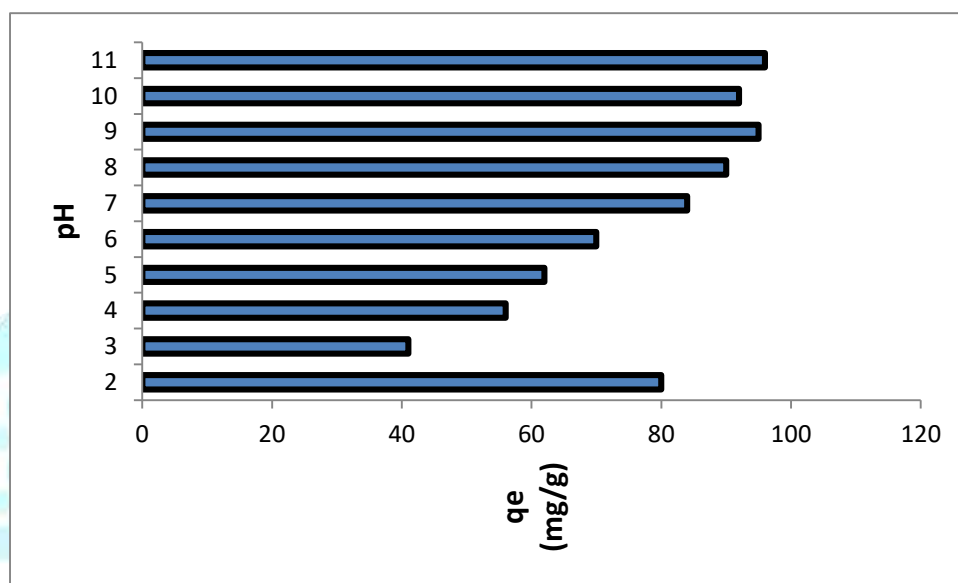


Fig. 5 Effect of pH on adsorption at 100 mg L^{-1} concentration of MG

3.5. Effect of temperature

The temperature was examined at three different temperatures: 30°C , 40°C , and 50°C . Figure 6 displays the findings. It is noticed that the adsorption capacity rises somewhat with temperature, suggesting that the method is exothermic in nature. The higher rate of adsorbate intra-particle diffusion and the increased mobility of dye molecules with rising kinetic energy may be the causes of the temperature-dependent increase in adsorption. A greater interaction between the adsorbent and adsorbate could be the cause of the small increase in dye removal observed with temperature rise.

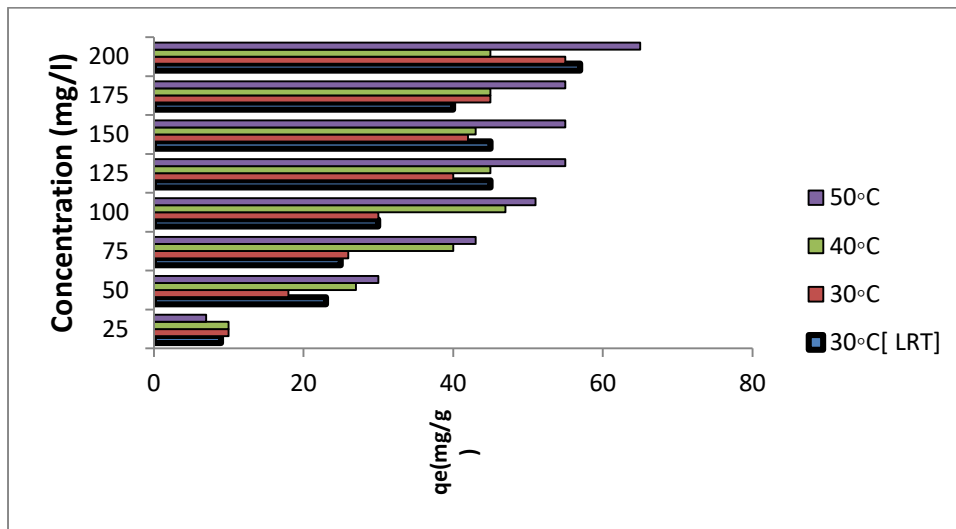


Fig. 6 Effect of temperature on adsorption of MG

3.6. Adsorption Isotherms

The Langmuir (Figure 7) and Freundlich (Figure 8) adsorption isotherm on the MG-NITTS device displays the monolayer adsorption phenomenon. Table 1 provides a list of Langmuir parameters. The experimental data fits the model MG-NITTS adsorption with a straight line, and the good correlation coefficient (R^2) suggests that the Langmuir adsorption isotherms at 40°C are most applicable.

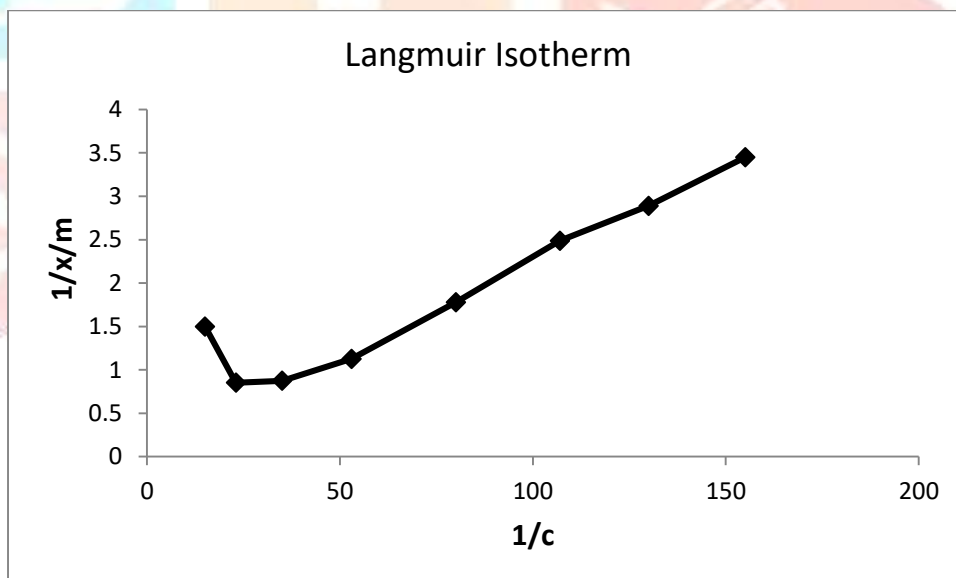


Fig. 7 Langmuir adsorption isotherm for MG adsorption on NITTS

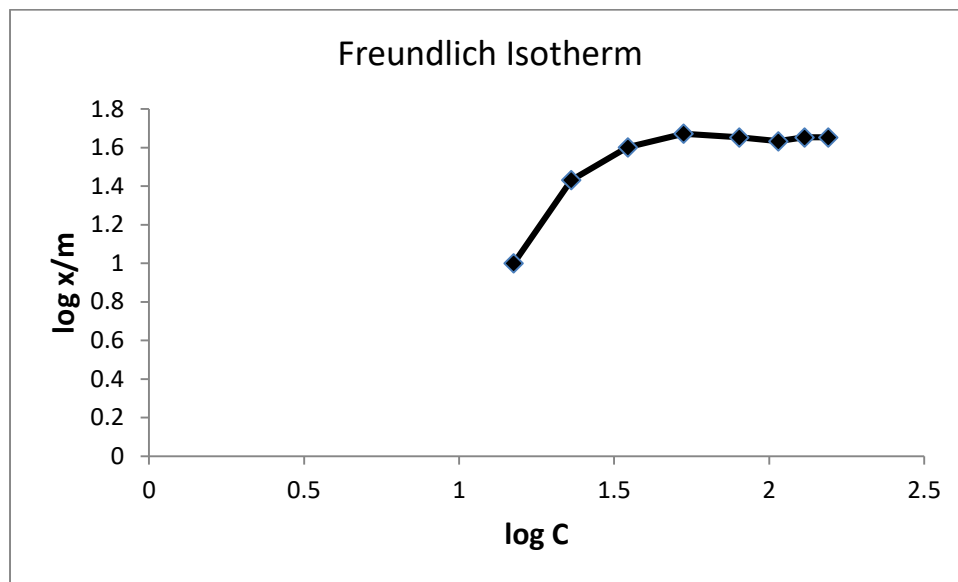


Fig. 8 Freundlich adsorption isotherm for MG adsorption on NITTS

Table 1: Langmuir and Freundlich isotherm constants for MG adsorption on to NITTS

Langmuir constants			Freundlich constants		
ϑ (mg g ⁻¹)	b (L mg ⁻¹)	R^2	K_f (mg g ⁻¹) (mg L ⁻¹) ^{1/n}	n	R^2
50.0	0.1884	0.9884	17.454	0.2024	0.5551

3.7. Adsorption Kinetics

The pseudo-second order kinetic models were utilised to derive the rate constants for the adsorption of MG on NITTS.

3.7.1. Pseudo-second order kinetic model

The pseudo-second order kinetic model (Rais Ahmad and Rajeev kumar 2010; McKay and Ho, 1999). Table 2 displays the values of k_2 and q_e , which were determined from the intercepts and slopes of the linear plots of t/q_t vs t , respectively. The investigations were carried out at concentrations of 25 mg L⁻¹, 50 mg L⁻¹, and 100 mg L⁻¹ at various temperature variations. As can be observed in Table 2, there is a good correlation for the 100 mg L⁻¹. The predicted q_e values are extremely similar to the experimentally measured q_e values, and the correlation coefficients (R^2) are nearer to one, suggesting that pseudo-second order dynamics govern the MG adsorption onto NITTS (Figure 9).

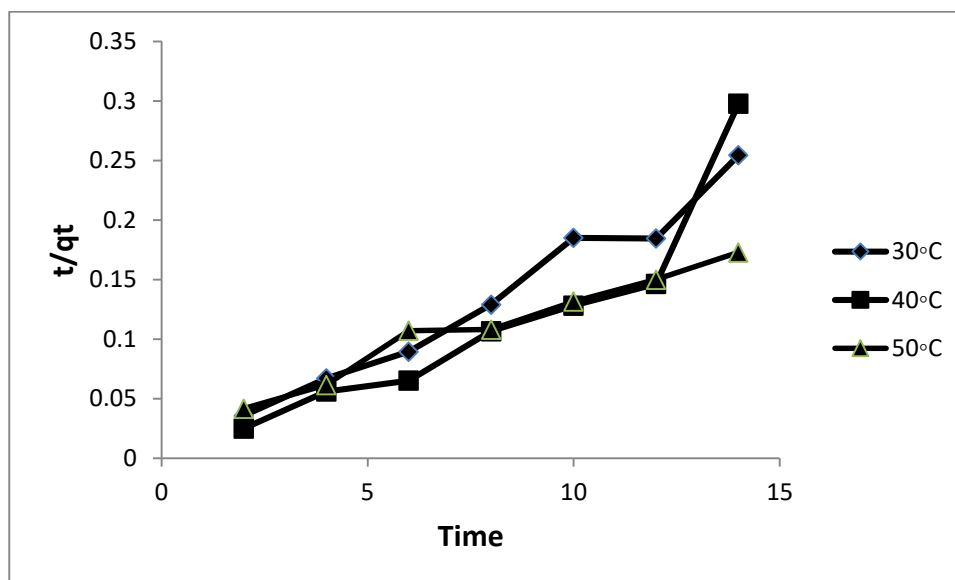


Fig. 9 Pseudo-second order kinetic model of NITTS on MG at 100 mg L⁻¹

Table 2: Pseudo second order kinetic constants for MG adsorption on to NITTS

Concentration (mg L ⁻¹)	Temp (°C)	q_e (exp) (mg g ⁻¹)	k_2 (g/mg min)	q_e (cal) (mg g ⁻¹)	R^2
100	30	50.0	-78.125	54.940	0.96059
	40		33.34	54.945	0.9525
	50		-177.825	47.619	0.8043

3.8. Thermodynamic Parameters

Utilising the least squares approach and the Arrhenius equations, the activation energy (E_a) for the reaction is calculated (Low P.S. et al., 1973; G.Feller and C. Gerday 1997; ChayaG. and Bibi ahmadi khatoun, 2017). The linear plot of $\ln K_c$ vs. $1/T$ can be used to calculate ΔH° , ΔG° , and ΔS° (Figures 10 and 11) by examining its slope and intercept (Rais Ahmad and Rajeev kumar 2010).

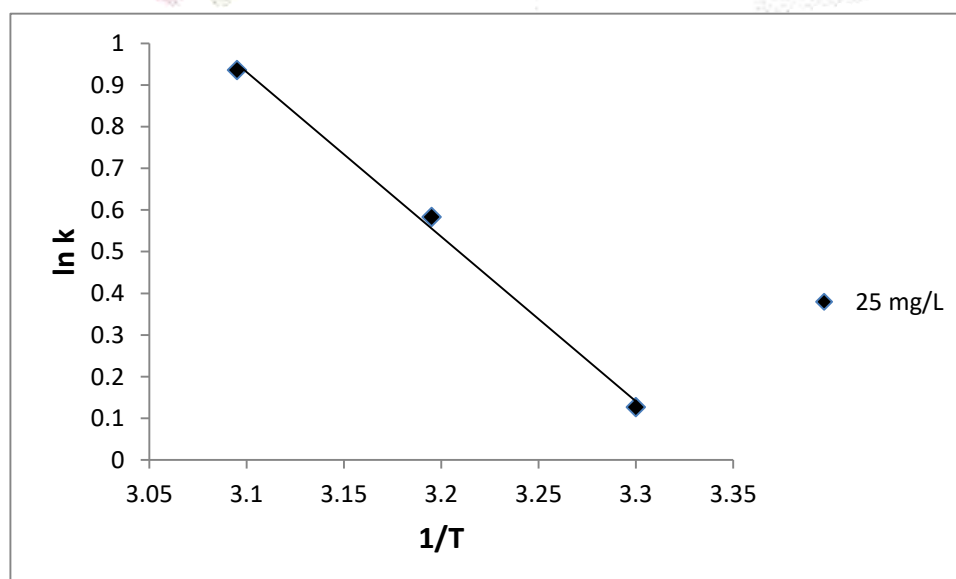


Fig. 10 Plot of Van't Hoff equation for adsorption Malachite green on NITTS

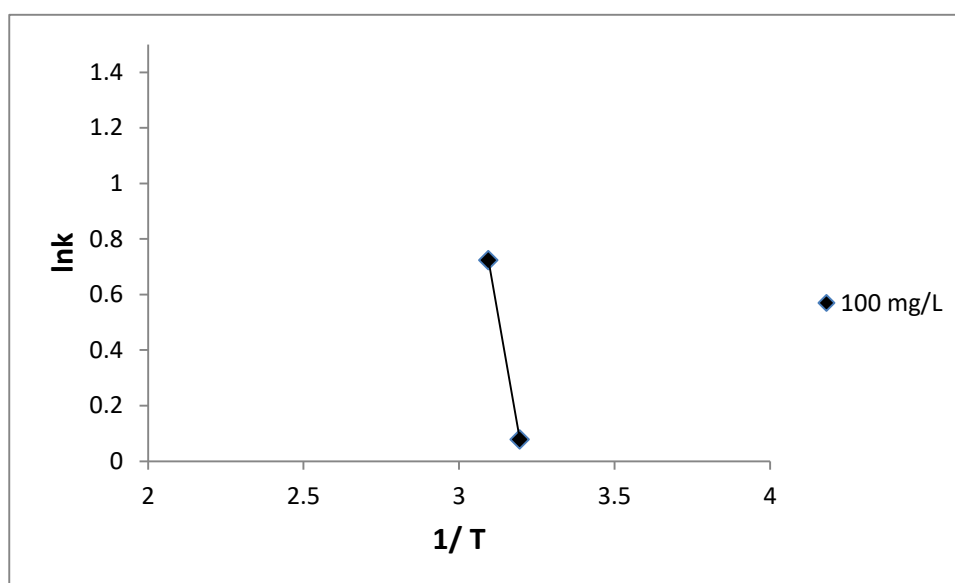


Fig. 11 Plot of Van't Hoff equation for adsorption Malachite green on NITTS

Table 3: Thermodynamic parameters for MG adsorption onto NITTS Spent

Concentration (mg L ⁻¹)	Temperature (K)	ΔH^0 (KJ mol ⁻¹)	ΔS^0 (KJ mol ⁻¹ K)	ΔG^0 (KJ mol ⁻¹)
25	303 K	-167.10	-239.51	302.93
	313 K	-175.41	-88.70	-116.89
	323 K	-183.72	-208.93	281.58
100	303 K	-98.42	-229.53	290.57
	313 K	-106.74	-224.08	293.00
	323 K	-115.01	-241.59	52.95

The Gibbs-Helmholtz and Van't Hoff equations were used to compute the enthalpy, entropy, and Gibbs free energy changes of adsorption. Table 3 illustrates how the exothermic character of adsorption is suggested by the negative ΔH^0 value. At certain temperatures under investigation, the ΔG^0 shows a positive value, suggesting that the adsorption of MG onto NITTS is non-spontaneous at higher temperatures. A negative value for ΔS^0 indicates that MG has a strong affinity for the adsorbent and that there is more randomisation at the surface of the solid solution.

4. Conclusion

For the remediation of the dye malachite green, NITTS has been developed as an effective, economical, and environmentally friendly biosorbent. The adsorption effectiveness of NITTS was impacted by operational factors such as pH, temperature, adsorbent dosage, and starting dye concentration. Thermodynamic analysis revealed that the biosorption process is exothermic and non-spontaneous. It also demonstrated that the adsorption is purely physical. The idea presented here will aid in combating resource depletion by making use of agricultural waste that is useless as fertiliser or feed. The NITTS matrix is suitable and ready for usage in the field of adsorption research.

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