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Adsorption Characteristics of Indian Neem Leaves (Azadirachta Indica) For Removal of Methyl Violet Dye From its Aqueous Solution : Isotherms & Kinetics

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ABSTRACT

Dyes and pigments are widely used in paper, plastic, leather, foodstuff , cosmetics, and specially in textile dyeing industries. The coloured wastes generated from these industries are highly toxic, resistant to aerobic digestion and photo oxidation . Thus removal of these undesirable complex materials from effluents is the most challenging problem for the environment. Searching for new, low-cost , eco-friendly technologies for removing these carcinogenic substances from industrial effluents has been withdrawing continuous attention of the researchers using bio-adsorption process.

In this paper, mature Neem leaves were used to develop a novel bio- adsorbent for removing Methyl Violet (MV) dye from synthetic solution. The developed adsorbent was analysed using SEM, FTIR, and XRD studies. The sorption efficiency of Neem Leave powder (NLP) has been studied using the batch adsorption process. It was found that NLP in the form of fine powder with a size range of 200- 400 µm are very effective for removing the MV from its dilute solution. Experiments were carried out using solutions with various dye concentrations of 10 to 100 mg/l. The removal percentage of MV was determined by UV visible spectro-photometer at wavelength of 585 nm. Results show that 96.93 – 97.77 % removal of MV may be achieved within 90-120 minutes using 1-3 gm /l NLP . The observation shows that the maximum adsorption capability of NLP depends on various operating parameters like dye concentration, size of adsorbents and it's activation process, pH of the solution and temperature. The applicability of the rearranged Langmuir and Freundlich model were studied. The maximum adsorption capacity of the activated NLP for removal of MV was obtained as 72.99 mg/g at 305 K and pH 7.45. The correlation coefficient value (R^2) of rearranged Langmuir and Freundlich isotherm was obtained as 0.995 and 0.999 respectively at 305 K . The thermodynamic studies show that the sorption process is endothermic process. Kinetic studies at various temperature show the suitability of Pseudo Second order reaction for this sorption process. The satisfactory values of regression coefficients (0.999) at a different temperature, higher adsorption capacity and good fittings of adsorption isotherms indicate that activated NLP has an excellent potential to use as an alternative low-cost adsorbent for the effective removal of Methyl Violet (MV) from industrial effluents.

Key Words : **Keywords:** Neem Leaves; Methyl Violet; Adsorption Isotherms; Kinetics; SEM; FTIR

1. INTRODUCTION

Dyes and pigments are very important group of industrial chemicals which are used in many industries like leather, cosmetics, plastics, paints, pharmaceuticals, paper, waxes and specially textile materials [1]. Those complex dyes are responsible to harm skin, liver, kidney and heart. These toxic dyes are highly poisonous and carcinogenic in nature, hence it is very much essential to eliminate these undesirable toxic materials from the effluents, before their discharge to the environment [2]. Dye bearing effluents are treated usually by several technical processes like chemical precipitation , coagulation, electrochemical degradation, biological stabilization, ion exchange process, photo-catalytic degradation , membrane filtration, reverse osmosis, solvent extraction, solar photo-Fenton , Sono-chemical degradation [3]. Many of these processes are expensive, specific and may need additional attention and infrastructure facilities. Adsorption is found to be highly cost effective among all these treatment processes. Due to its high porosity, large surface area and intrinsic adsorption properties, activated Carbon is widely used as a good adsorbent but it is expensive in contrast to naturally obtained leaves and agriculture wastes. Thus, effective utilization of various agriculture wastes like rice husk, sugarcane bagasse, coconut fiber, groundnut cell, and natural Neem Leaf Powder (NLP), dry grass powder etc as a low-cost bio-adsorbent for removal of hazardous carcinogenic dyes and heavy chemicals from dying industry effluents and to investigate its separation characteristics still remains challenging research area to the investigators. Saw dust , wood dust and charcoal powder were used as adsorbent for removal of color from textile effluent by various researchers [1,4,5]. Adsorption of Congo red dye from aqueous solutions by prepared activated carbon from Coffee waste was studied by Lafi et. al [6]. Removal of Congo red dye from industrial effluent using garlic peel as a bio-adsorbent was also studied by Ezaz et. al [7] . Furthermore, assessment of Adsorption Properties of Neem Leaves Wastes for the Removal of Congo Red and Methyl Orange were performed by Ibrahim et. al [8]. Phatai et al used activated carbon derived from coffee residues for removal of MV [4] and found the maximum adsorption of MV on coffee residue takes place at pH 9 . Das et.al studied on adsorption efficiency of fly ash for removal of Malachite Green and Methylene Blue dye [9,10]. Dahri et al [11] used *Casuarina equisetifolia* needle (CEN) to remove methyl violet 2B (MV) from aqueous solutions, and achieved the maximum capacity of 164.99mg/g. Kooh et al [12, 19] used Artocarpus odoratissimus stem axis as adsorbent for removal of MV. They achieved an excellent adsorption capacity q_m of 263.7 mg g-1. They also observed that the adsorption system is spontaneous and endothermic in nature .

Bhattacharya et al [13] studied the adsorption performance of NLP for removal of Brilliant Green and Neem sawdust was used by Khattri et al [14] for elimination of malachite green dye from wastewater. Yao et al [15] investigated the adsorption behavior of methylene blue on carbon nanotubes. Activated carbon derived from Borassus aethiopum flower biomass was used for removal of Malachite Green dye by Nethajia et al [16]. Das et al studied the efficiencies of activated NLP for removal of malachite green [13, 17] and found NLP act as potential bio-adsorbent for treatment complex dyes.

The present study shows the adsorption characteristics of Neem Leaf Powder (NLP) for removal of methyl violet dye (MV) from its synthetic solution. Effect of solute concentration, pH, adsorbent amount, time and temperature on removal of MV has been studied . Applicability of Freundlich Isotherm and rearranged Langmuir model for this sorption process has been observed. Special emphasis has been provided to find out the first order and second order reaction kinetics for this adsorption process.

2. MATERIALS AND METHOD

2.1 Materials:

Matured Neem leaves were collected from from local areas of the college campus. Methyl violate (MV) , molecular formula $C_{24}H_{28}N_3Cl$ and molecular weight: 344.5 g/mole is taken as water-soluble dye, yielding a dark violet colloidal solution. Analytical grade MV was purchased from Merck Specialties Pvt. Ltd (Mumbai, 40018). Laboratory grade HCl and NaOH (Fisher Scientific, Kolkata) were used in this experiment. Chemical structure of MV dye is shown in Fig. 1.

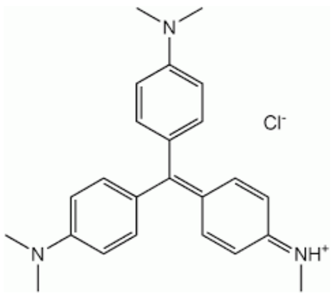

Fig. 1 Molecular Structure of Methyl violate dye

2.2 Experimental :

Impurities present in the collected Neem leaves were removed by washing them repeatedly using distilled water and then dried at room temperature followed by heating at 80-100 °C for 4-6 hrs. till it became crispy. Dried leaves were grounded and screening was done using 200-300 µm mesh. Then 30 gm NLP were boiled in a 250 ml beaker adding a few drops of 5 N HCl to activate the adsorbents , to remove soluble impurities and dark green colour from the powder. The detailed preparation method of NLP and their characterization is given in our earlier work [17]. Experiments were done using various amount of adsorbents 3 to 8 gm /L of NLP and MV solution having concentration of 10 to 100 mg/l at various pH and temperature. Experiments were done at a constant temperature shaker which was running at 250-300 r.p.m. for different contact time of 10-180 min. The percentage removal of dye was determined by Spectro-photometrically at wavelength of 585 nm. The MV adsorption per unit mass of adsorbent, NLP (Q) and the dye removal percentage (R) calculated following the Equation (1) :

$$R = 100\ (C_0 - C_t)/\ C_0 \qquad (1)$$

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3.0 RESULTS & DIACUSSION

3.1 Characterization

Characterization of the prepared NLP were carried out using Scanning Electron Microscopy (SEM), IR spectroscopy and Energy (electron) Dispersive X-ray analysis (EDX) technique to understand the surface topography, information of functional groups presents, elemental analysis or chemical characterization. The obtained results is as illustrated below

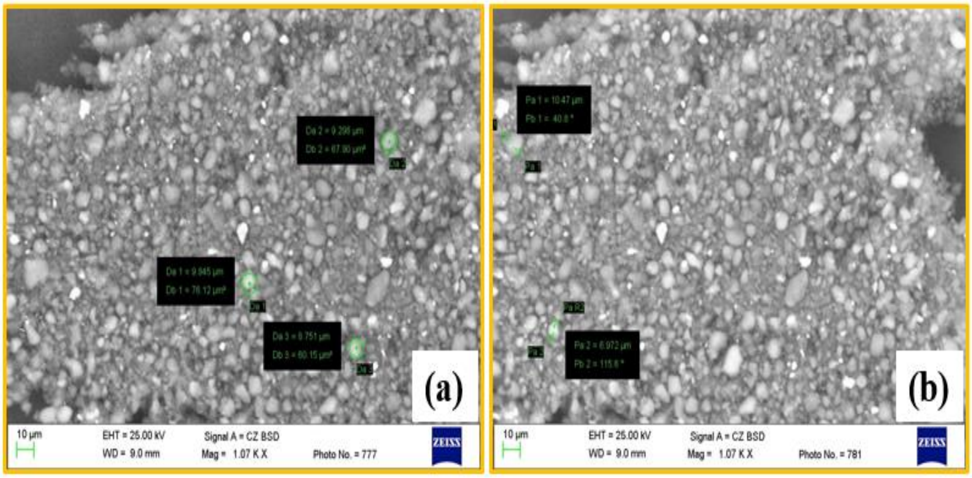

Fig. 2. SEM images of adsorbent: Neem leaf powder showing the low agglomerated with average spherical particles (Reproduced with permission from [17])

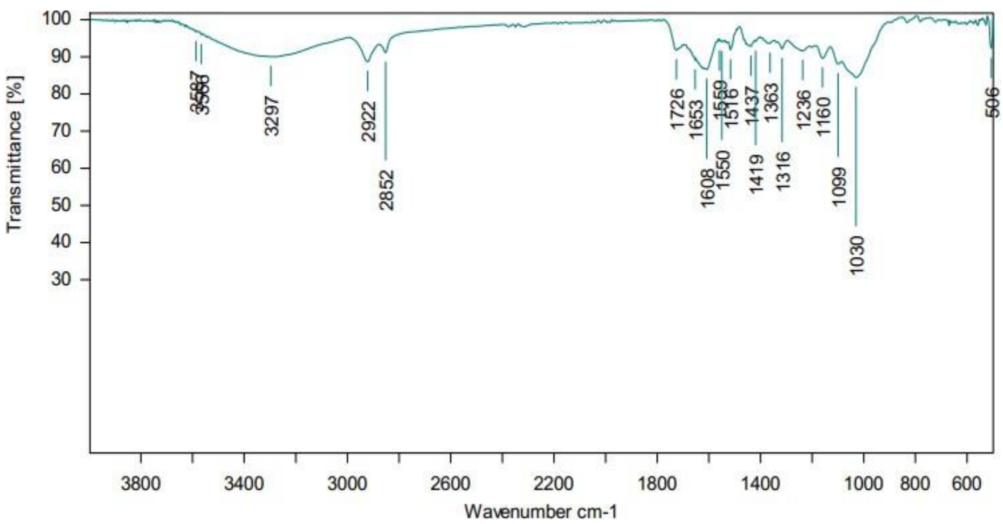

Fig. 3 FTIR- spectral analysis of Neem leaf powder having the amines vibration at the high frequency region of the absorption band which is suitable for the adsorption kinetics (Reproduced with permission from [17])

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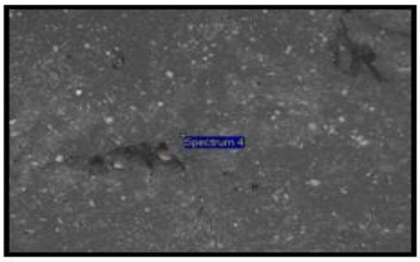

Element	Weight%	Atomic%
C K	67.70	91.95
O K	15.18	7.22
Mg K	2.23	0.12
Si K	8.60	0.27
Ca K	9.41	0.13
Fe K	1.23	0.05
Totals	100.00	

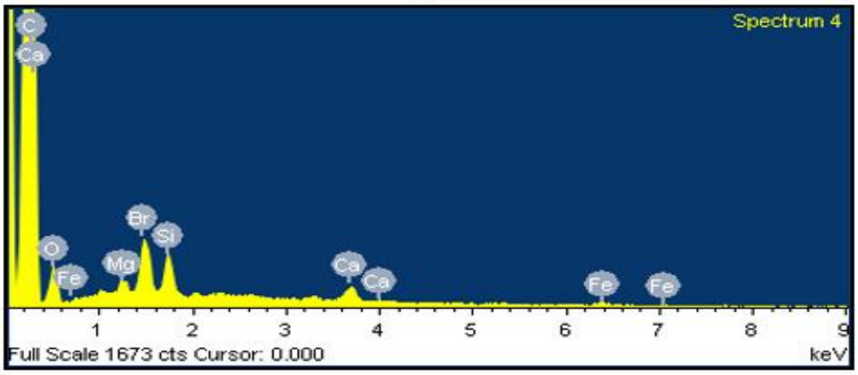

Fig. 4 EDS analysis of NLP sample showing the presence of carbon content in very high percentage compare to other elements which is suitable for adsorption (Reproduced with permission from [17])

3.2 Influence of Adsorbent amount

The influence of adsorbent (NLP) amount and time of contact on removal of MV from its solution with concentration of 100 mg/l has been shown in **Fig 5**. Results show that the removal of MV increases from 94.9 to 97.77 % for the change of adsorbent amount from 1 to 3 gm/L. Results also indicate the percentage of dye removal increases with time of contact and reached an equilibrium after about 120 mins depending on solute concentration and adsorbent amount

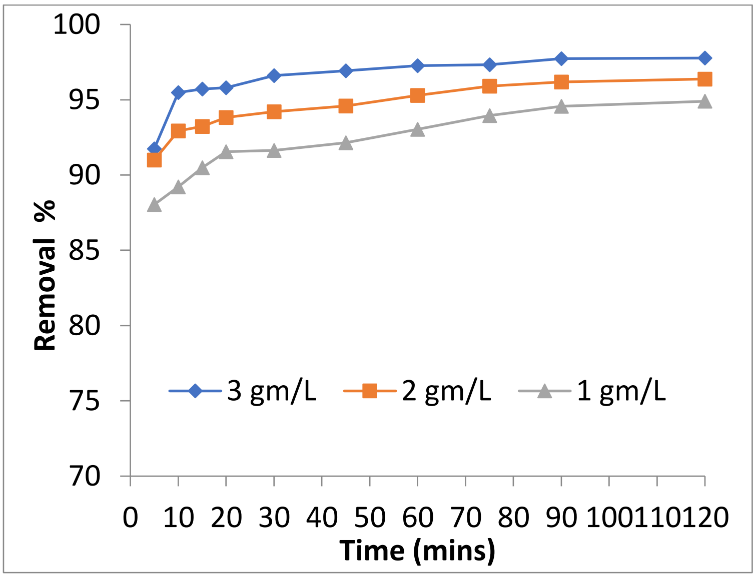

Fig 5. Effect absorbent (NLP) amount on removal of Methyl Violate dye (MV Concentration 100 mg/L, pH :7.03, Temp : 303 K)

3.3 Effect of Solution Concentration on MV removal

The influence of dye concentration on removal of MV has been shown in **Fig. 6**. Results show that the removal percentage of dye increases from 88.06 to 94.9 % if the solution concentration increases 20 to 100 mg/L . This behaviour is explained with Fick's diffusion law where the concentration gradient as the driving force for the mass transfer rate, hence higher initial concentration resulted in higher q_e [12]

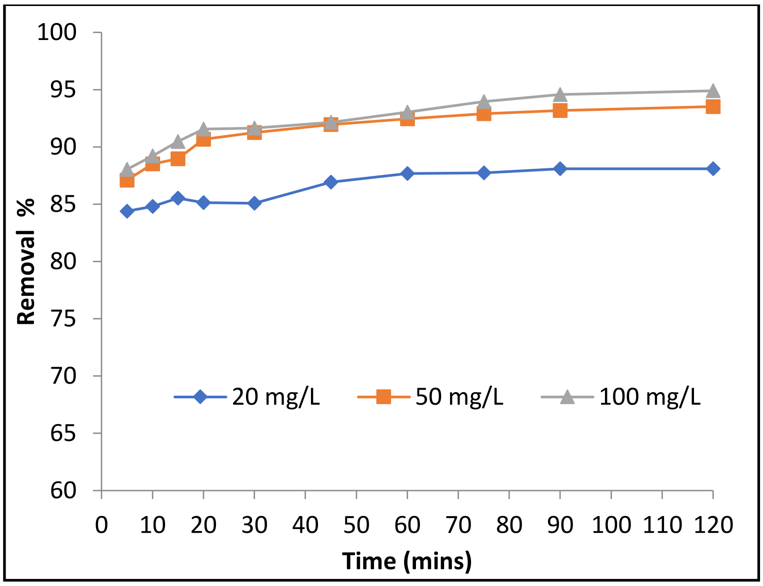

Fig.6. Effect of solution concentration on removal of MV
(NLP: 1 gm/l, pH : 6.45 , Temperature : 309 K)

3.4 Influence of temperature on removal of MV

The influence of temperature on removal of MV has been described in **Fig. 7.** From experimental results it was found that with the rise of temperature from 303 to 333 K removal percentage of MV increases from 97.41 to 98.28 %, which indicates that the reaction is endothermic in nature. Findings of other researchers also agree with our results [12].

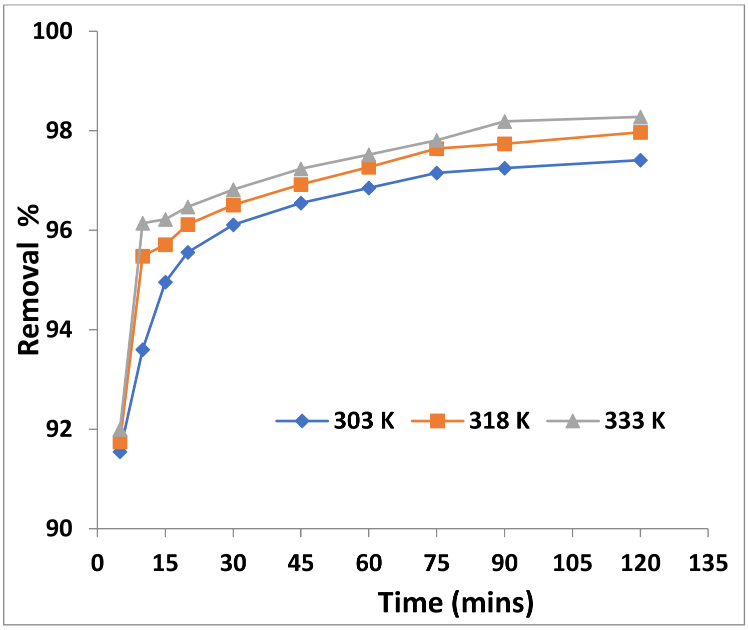

Fig. 7. Effect of temperature on removal of MV dye
(MV : 50 mg/L , NLP : 3 gm/L , T : 303 K, pH : 6.45)

3.5 Effect of pH

The **Fig. 8** show the influence of pH on removal of MV from its solution. It was noted that the adsorption of MV on NLP highly depends on the pH of the solution. The percentage removal of MV enhances from 94.04 to 99.6 % with the variation of pH from 2.4 to 11.2 from 50 mg/l solution at 303 K . Thus results explained that the MV adsorption on NLP favors at alkaline medium.

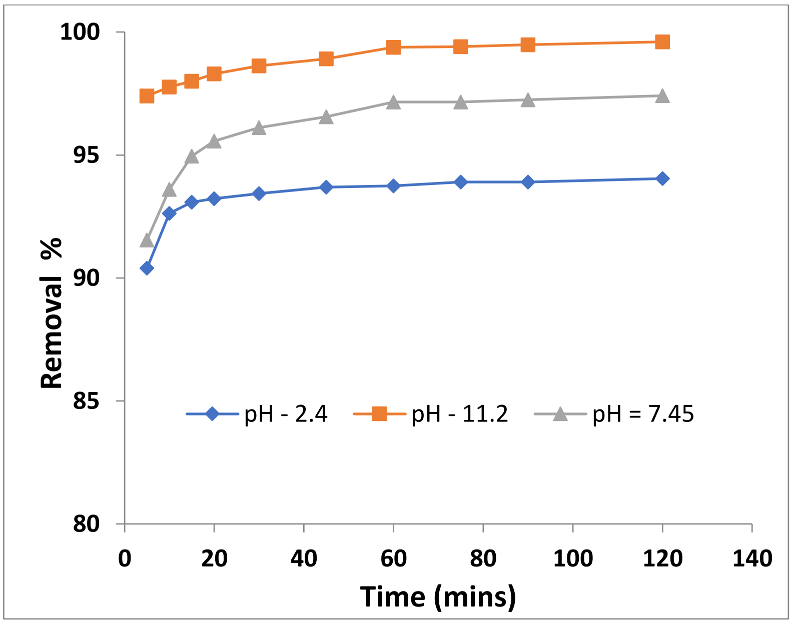

Fig.8. Influence of pH on removal of MV (Solute : 50 mg/L,
NLP: 3 gm/L, Temperature: 303 K)

3.6 Studies on regeneration of adsorbent :

Regeneration is a process to restore, renew or revitalize a substance to their own sources of energy and materials, enabling the recycling of those materials for a repeated number of times. In this observation, a regenerative study was conducted using used up NLP collected from various batches of adsorption experiment which was boiled with 5N HCl (1ml in 250 ml water) for 10 mins, two to three times. Then the adsorbent was washed using distilled water for another 3- 4 times till a clear filtrate was obtained. This absorbent was dried for 2-3 hours in an oven at 70-80 °C. The adsorption performance of regenerated NLP is shown in **Fig. 9**. It was observed that adsorption percentage decreases only 2% after 2rd time regeneration of NLP , which is very insignificant.

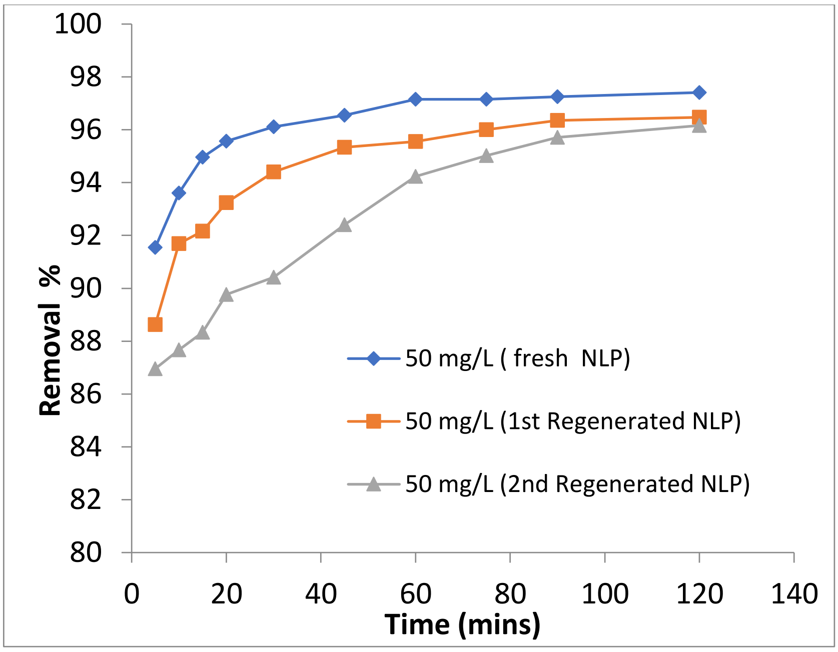

Fig. 9 Performance of regenerated NLP for removal of dye (NLP: 3 gm/L, T: 303 K, pH :7.02)

4.0 ADSORPTION KINETICS

Kinetic model for this adsorption process is very important for removal of dye from industrial effluents or from synthetic solutions. Considering MV dye "A" is absorbing from solution on adsorbent "B" NLP, in a reversible reaction

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$$

If C_{A0} be the initial dye concentration of MV dye in the solution, in moles /litre , C_A as concentration of MV in the solution at any time " t", in moles /litre, and C_B is the concentration of dye adsorbed on the adsorbent, NLP at time " t", in moles /litre. If C_{Aeq} and $C_{B\ eq}$ are the equilibrium concentration of MV in the solution and on adsorbent, then the rate equation may be written as

$$- dC_A/ dt = K_1C_A - K_2 C_B \quad (2)$$

$$K_C = K_1 / K_2 = C_{Beq} / C_{Aeq} \quad (3)$$

$$C_B = C_{A0} - C_A \quad (4)$$

The detailed kinetics was explained elsewhere [10] , Considering U (t) as the fractional attainment of equilibrium and is given by $(C_{A0} - C_A) / (C_{A0} - C_{Aeq})$ after rearranging the equations 2-4, and integrating one can get the final equation

$$\ln [1 – U(t)] = - K_T.t \quad (5)$$

Hellfrich first order kinetics at different dye concentration, and Lagergren pseudo second order and pseudo second order reaction kinetics has been presented in the **Fig. 10** and **Fig**. 12. Results show that regression coefficients obtained for first order reactions are very satisfactory, values are about 0.993. But regression coefficients obtained for second order reactions are 0.9999 - 1.0 , which indicates that second order reaction kinetics fit well for this sorption process. It was also noted that reaction rate constants K increases with increase of solution concentration in each case, which also agrees with the experimental observation.

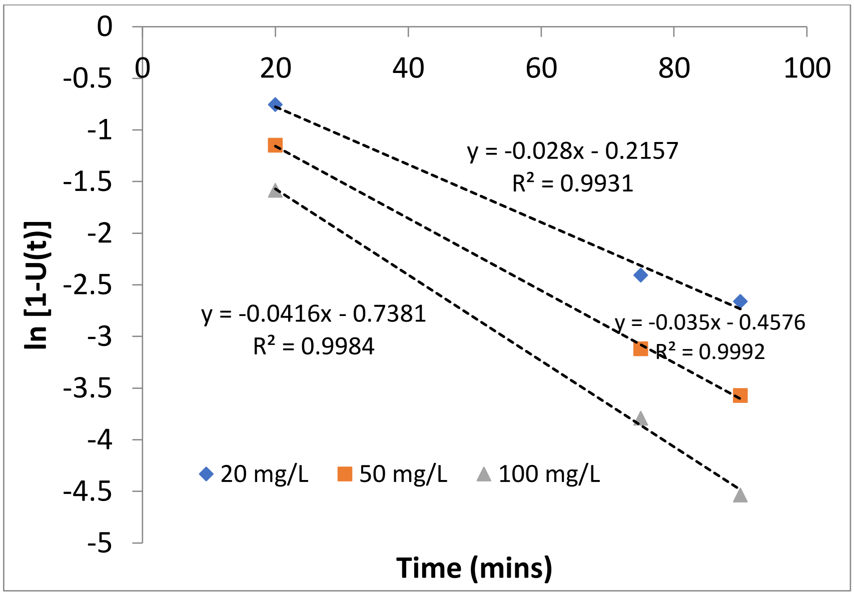

Fig 10 . Helfferich first order kinetics for MV sorption
(NLP: 3 gm/L, Solute : 50 mg/l, T : 303 K, pH : 7.45)

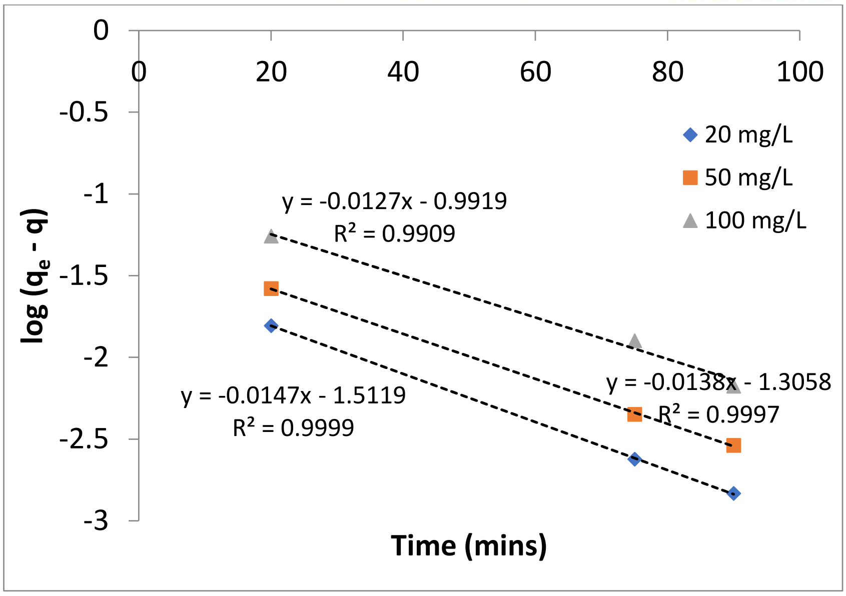

Fig. 11 Lagergren Pseudo Second order reaction kinetics for various MV concentration (NLP: 3 gm/L, T: 303 K, pH: 7.45)

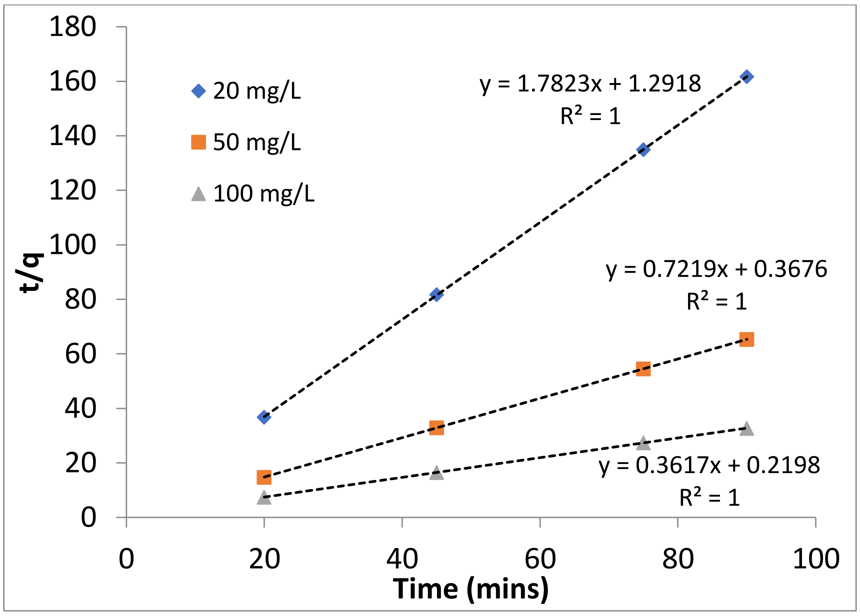

Fig. 12. Pseudo Second order reaction kinetics for various MV concentration (NLP: 3 gm/L, T: 303 K, pH: 7.45)

4.1 Adsorption Isotherms:

4.1.1 Langmuir isotherm model

The results obtained from adsorption of CR with various concentration using NLP and fitted with the rearranged Langmuir model of adsorption.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L\, q_m} \qquad (6)$$

Here, q_e is the amount of dye adsorbed per gram of adsorbent at equilibrium (mg/gm), C_e is the equilibrium concentrations (mg/lit.) of MV, K_L and q_m are Langmuir constant (L/mg) and maximum adsorption capability in mg/gm respectively. The **Fig. 13** indicates the maximum adsorption capacity q_m of the prepared NLP and K_L was obtained as 72.99 mg/gm and 0.118 L/mg respectively .

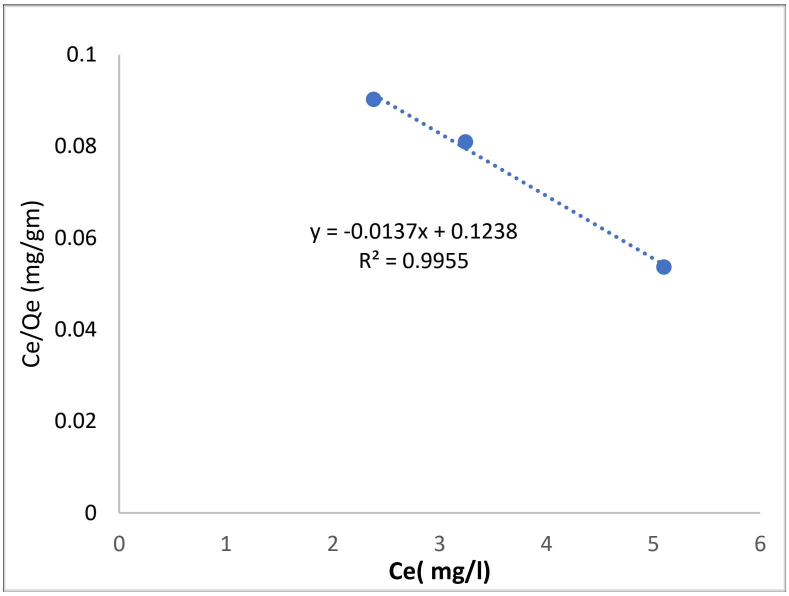

Fig. 13 Langmuir Isotherm plots for MV removal

(NLP: 2 gm/l , Temp : 305 K, Ph:7.45)

4.1.2 Freundlich isotherm

Applicability of the Freundlich isotherm for the present system has also been estimated by correlating the results empirically using the well-known Freundlich Eq. (9) and Eq. (10) as:

$$\frac{X}{M} = Q_e = K_F.(C_e)^{1/n} \tag{7}$$

$$\log\left(\frac{X}{M}\right) = \log K_F + \frac{1}{n}\log C_e \tag{8}$$

where X/M or Q_e is surface load in (mg/gm). The linear plot of log(Q_e) vs log C_e in Fig. 14

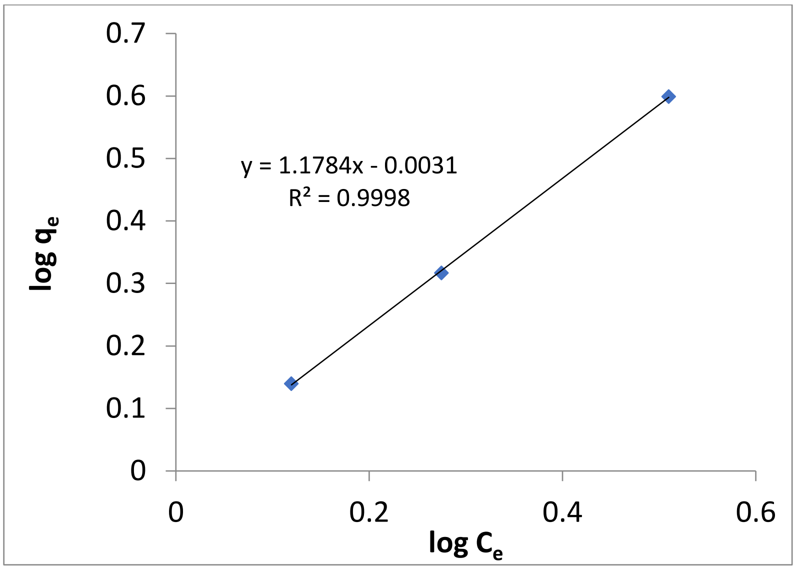

Fig. 14 Freundlich Isotherm model for MV dye adsorption (50 mg/L, NLP : 2gm/l, at 305 K, pH: 7.45)

The **Fig. 14** also suggests that the system follows Freundlich isotherm. The values of n is 0.848, K_F is 0.992 l/mg, R^2 is 0.9998. The values of regression co-efficient of Langmuir and Freundlich isotherm are 0.995 and 0.999 for MV. Results indicate that Langmuir's model and Freundlich's model both are applicable for this adsorption process .

The separation factor (R_l) related to Langmuir isotherm was used to evaluate the feasibility of adsorption on adsorbent. It can be calculated by Eq. (9) [18]

$$R_l = \frac{1}{(1+K_l C_o)} \qquad (9)$$

where C_o (mg/l) was initial dye concentration and K_L (l/mg) is Langmuir constant. The value of R_l indicates the type of the isotherm: irreversible ($R_l = 0$), favorable ($0 < R_l < 1$), linear ($R_l = 1$), unfavorable ($R_l > 1$). The R_l of MV adsorption onto NLP is 0..078 or solution having concentration of 100 mg/l. It can demonstrate the MV adsorption onto NLP is favorable.

5.0 CONCLUSIONS:

The activated NLP adsorbent was developed using Neem leaves and characterized by Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and Energy Dispersive X-ray (EDX) techniques. Maximum removal of CR MV was achieved as 95.6 % from 100 mg/l solution using only 3gm/l of NLP , but it depends on others parameter like surface area , particle size of NLP and also pH and temperature of solution. The maximum adsorption capacity of MV on activated NLP was obtained as 72. 99 mg/gm . The kinetic studies indicate that this sorption process followed second-order rate expression very satisfactorily . The linear plot and the values of correlation coefficients (R^2) , 0.996 and 0.999 suggests the applicability of both Langmuir's as well as Freundlich model for this process. It was noted that the process was endothermic in nature and adsorption favored at higher temperature. Thus, the present studies confirmed that the activated NLP has an excellent potential for waste management by removing various hazardous and carcinogenic dyes from industrial effluents.

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