Uptake Capacity of Methylene Blue by Adsorption onto Nitrated Biomass of Ailanthus excelsa.

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Abstract **- Adsorption capacity of Nitrated biomass of Ailanthus excelsa for removal of methylene blue (MB) from aqueous solutions was investigated. Batch experiments were carried out as functions of different process parameters such as pH, initial dye concentration, biosorbent dose and time and temperature. The optimum conditions for removal of MB were found to be pH (2.0), biosorbent dose (100 mg), and initial dye concentration (25 mg L^{-1}). The temperature (288K) had a strong influence on the biosorption process. The Langmuir, Freundlich and Temkin isotherms model, biosorption of MB onto Nitrated biomass were studied. The calculated values of ΔH°, ΔS° and ΔG° were found to be -6.0861 kJ/mol^{-1} +17.5887 KJ/mol^{-1} and -13.2167 KJ mol^{-1} respectively. The negative value of ΔH^0 (-6.0861 kJ/mol^{-1}) indicates that the Adsorption of MB onto of Nitrated biomass is an exothermic reaction. The calculated value of ΔG° -13.2167 KJ mol^{-1} indicates spontaneous nature of the adsorption process. Further the positive value of entropy change, ΔS^0 reflects the affinity of Nitrated biomass for MB dye. The rate of sorption was found to obey pseudo-second order kinetics and intraparticle diffusion model with correlation coefficient value R^2 is 0.9999. Thermodynamic studies showed that the biosorption process was spontaneous and exothermic. The Nitrated biomass is a promising biosorbent for MB removal from aqueous solutions.**

Index Terms **- Adsorption, Ailanthus excelsa, Methylene blue (MB), Langmuir, Freundlich Isotherms.**

1.INTRODUCTION

The effluents of wastewater in some industries such as dyestuff, textiles, leather, paper, plastics, etc., contain various kinds of synthetic dyestuffs [1]. The effluents of these industries are highly colored and the discharge of these wastes into receiving waters causes severe damages to the environment [2]. The introduction of waste products into the environment is an important problem that has been highlighted by various environmentalist groups [3]. The dyestuffs have a complex chemical structure and are stable to light, heat and oxidation agents [4]. A number of low cost adsorbents are reported in the literature. These include bagasse pith [3-4], maize cobs [4], sunflower [5], fly ash [6], and peat [7], saw dust [8], marine algae [9], fungal biomass [10], wasted activated sludge [11], digested sludge [12], red mud [13], coir pith [14], Neem leaf [15] waste organic peel [16] and tree fern [17]. However, sorption potential of most of these low-cost sorbents is generally low. Biosorption can be defined as sequestering of organic and inorganic species including metals, dyes and odors causing substances using live or dead biomass or their derivatives. Since the 1980s, biosorption has been continuously studied for the removal of heavy metals and other pollutants from wastewater, so it could be a promising alternative to replace or supplement present dye bearing wastewater treatment processes. Biosorption, if compared with other available technologies above, gives comparable performance at a very low cost. Apart from cost effectiveness and competitive performance, other advantages are possible regeneration at low cost, availability of known process equipment, sludge free operation and recovery of the sorbate [3]. The biosorption capacity of a biosorbent depends on several factors. It includes type of biosorbent (species, age), type of sorbate, and presence of other competing ions and method of biomass preparation, along with several physico-chemical factors (temperature, pH, and ionic concentration). The present work aims to study a convenient and economic method for methylene blue (MB) removal from water by adsorption on a low cost

and an abundantly available adsorbent, to gain an understanding of the adsorption kinetics, to describe the rate and mechanism of adsorption, to determine the factors controlling the rate of adsorption. The effects of initial MB concentration, solution pH, ionic strength, particle size and temperature on MB adsorption rate have been evaluated. In this study, MB was selected as sorption of this dye has been reported by other researchers using different sorbents *Ailanthus excelsa* biomass is used as adsorbents for adsorption of methylene blue dye from aqueous solutions [18], Biosorption of Hg2+ions by Sulphonated biomass of Stalks of *Prunus cerasus* [19] studied with the Langmuir, Freundlich and Temkin isotherm models.

2. MATERIALS AND METHODS

2.1. Adsorbate:

Methylene blue ($C_{16}H_{18}N_3SCl.{}_3H_2O$) was obtained from E.Merck, India and was used for sorption study. The required concentrations were prepared by dissolving MB dye in distilled water. The MB stock solution was prepared by dissolving accurately weighed dye in distilled water to a concentration of 500 mg/L. The experimental solution was obtained by diluting the dye stock solution in accurate proportions to different initial concentrations like 15 mg/L, 20mg/L, 25mg/L and 30mg/L.

2.2. Experimental:

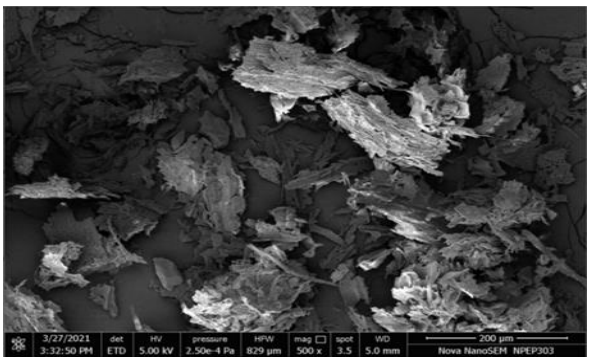
The batch adsorption experiments were conducted in a set of 250 ml of Erlenmeyer flask containing adsorbent and 100 ml of MB solution with various initial concentrations. The flasks were agitated in an isothermal water-bath shaker at 100 rpm and 27^0C until the equilibrium is reached. After decantation and filtration, the equilibrium concentrations of dye in the solution were measured at 665 nm using UV-visible spectrophotometer. The pH of solution was adjusted with 1N HCl and 1N NaOH solutions. The amount of dye adsorbed and percentage removal of MB were calculated using Equations. (1) and (2), respectively

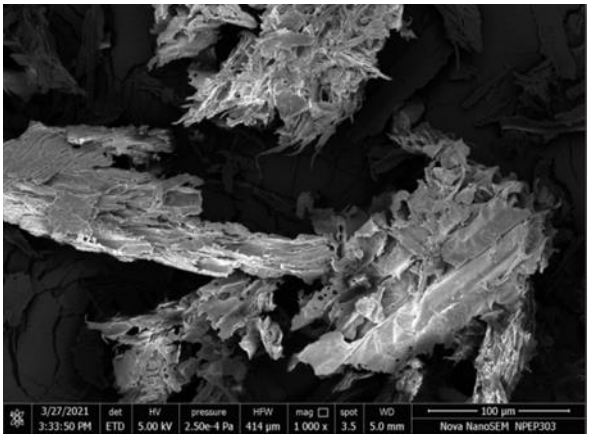
$$qe = (Co\text{-}Ce)\frac{v}{m} \quad (1)$$

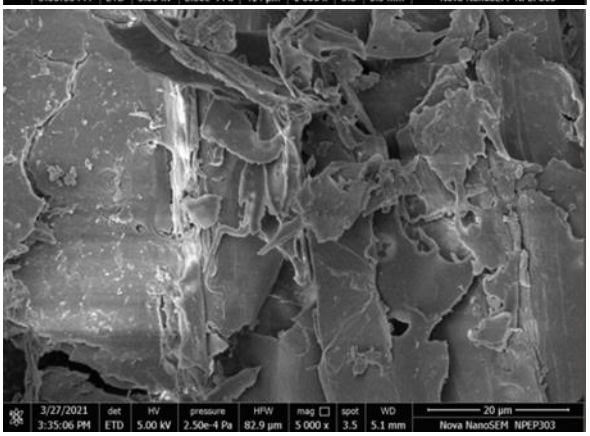
$$\% \text{ Removal} = \frac{Ci - Ce}{Ci} \quad (2)$$

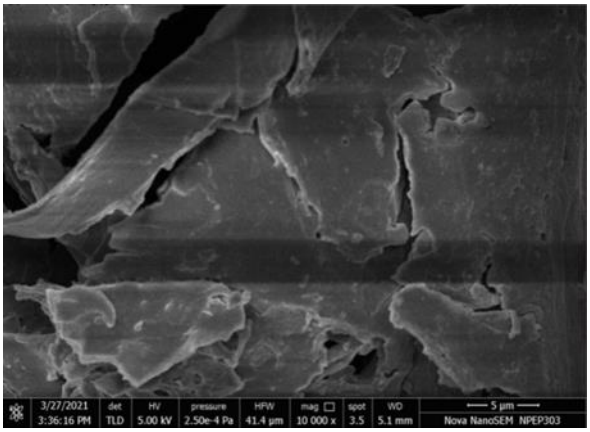
Biosorbent: *Ailanthus excelsa* plant commonly known as tree of heaven is a large deciduous tree found in Himachal Pradesh, Chhattisgarh and Western Ghats of Maharashtra state in India. The biomass *Ailanthus excelsa* was collected from farm of Pune district. The stalks of *Ailanthus excelsa* were dried washed with distilled water to remove adhered impurities from its surface. The dried biomass was crushed, milled and to 100µm particle size. The dried biomass was soaked with Conc. HNO_3 for period of 6 hr and the resulting reaction mixture was kept overnight in fume hood. The reaction mixture was repeatedly washed with cold water till to complete remove acid and filtered to obtain Nitrated carbon. This is then dried in oven a 100^0C time for 12 hr. The resulting Nitrated carbon of Ailanthus excelsa was preserved and used as an adsorbent for MB removal.MB concentration determined by the Beer-Lambert law. The MB Absorbance measured at 660 nm on double beam spectrophotometer. Methylene blue has a net positive charge which would be favorably adsorbed by electrostatic force onto a negatively charged adsorbent surface. The aromatic moiety of MB contains nitrogen and sulphur atoms. In the aromatic unit, dimethyl amino groups attach to it. The aromatic moiety is planar and the molecule is positively charged. XRD of Nitrated biomass of Ailanthus excelsa used to provide, non-destructively and quickly, most of the basic structural information that is essential for materials characterization. The ultra-structural features of the wood cell walls, the structures formed by micro fibrils, and the distribution of cell wall polymers, as revealed by TEM. Signals produced in an SEM/EDS system includes secondary and backscattered electrons that are used in image forming for morphological analysis as well as X-rays that are used for identification and quantification of chemicals present at detectable concentrations. The detection limit in EDS depends on sample surface conditions, smooth surface have lower the detection limit. EDS can detect major and minor elements with concentrations.

SEM of Nitrated Biomass of Ailanthus excelsa:

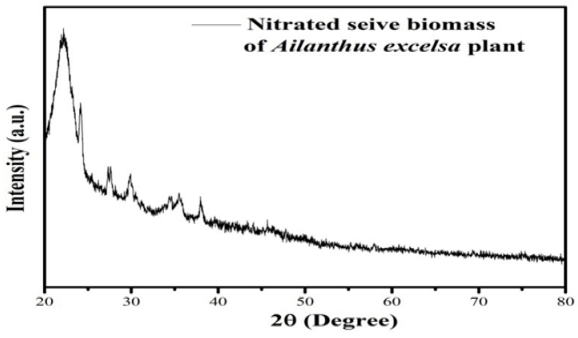




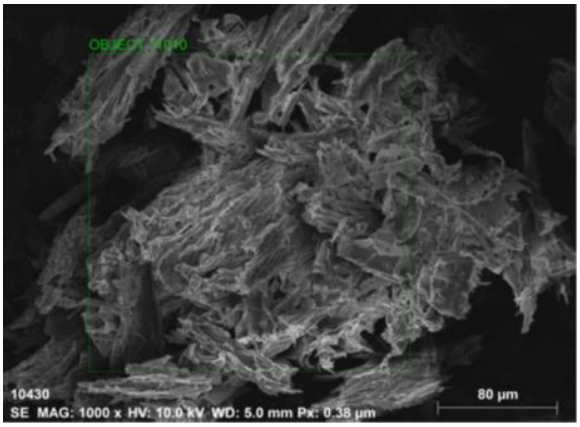


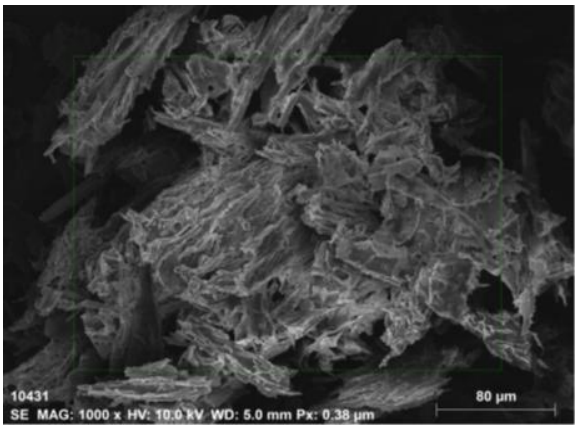


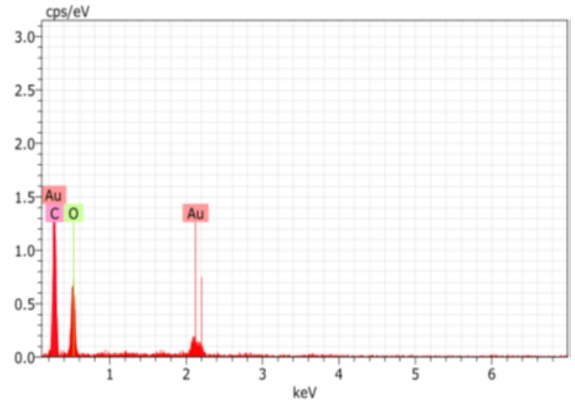
XRD of Nitrated Biomass of Ailanthus excelsa:

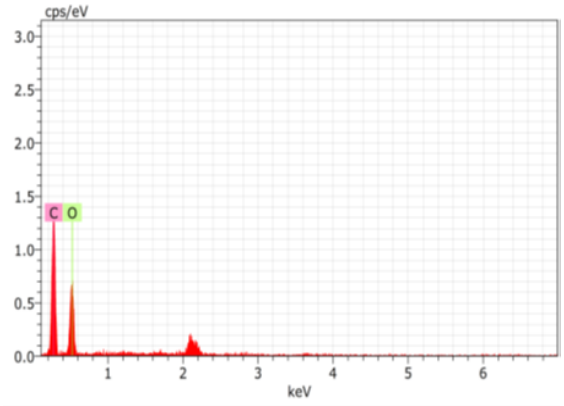


EDS of Nitrated Biomass of Ailanthus excelsa:







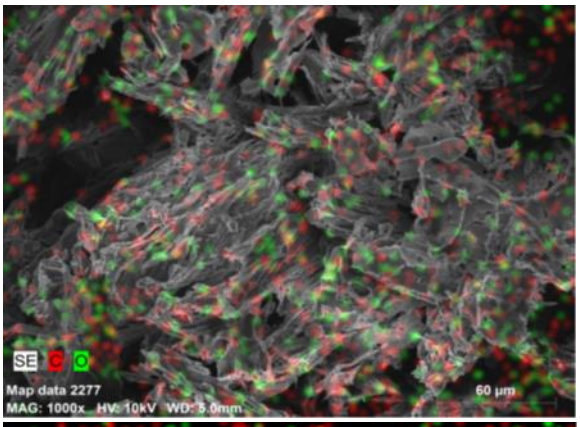


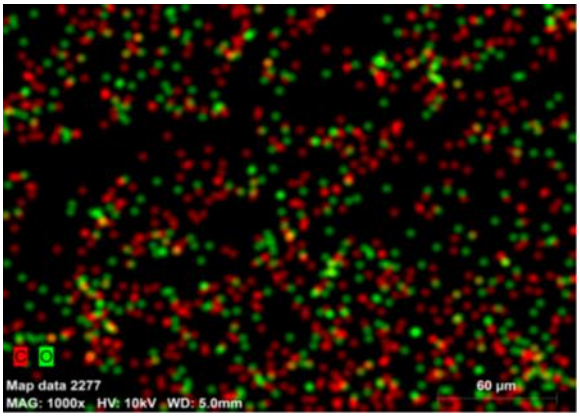
Spectrum: OBJECT 11010

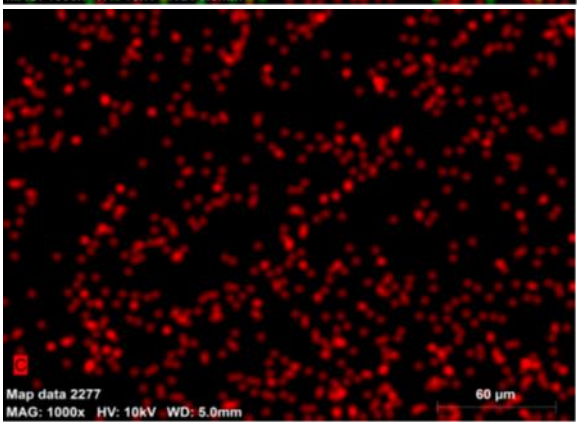
El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	51.11	51.11	58.20	9.75
O	8	K-series	48.89	48.89	41.80	10.32
Au	79	M-series	0.00	0.00	0.00	0.00
		Total:	100.00	100.00	100.00	

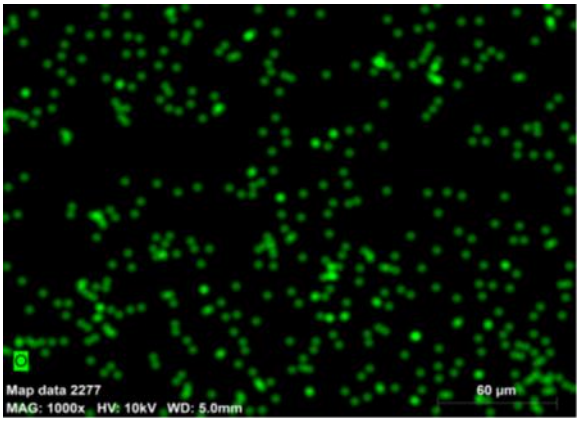
Spectrum: OBJECT 11010

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
C	6	K-series	53.60	53.60	60.61	9.15
O	8	K-series	46.40	46.40	39.39	8.95
		Total:	100.00	100.00	100.00	









2.3. Batch Biosorption:

Batch mode biosorption experiments were performed in 250 mL glass stoppered, conical flasks with 25 mL of dye solution of known initial concentration (25 mg L-1). A weighed amount (25mg) of biosorbent was added to the solution. The flasks were agitated at a stirred with magnetic stirrer. The influence of pH (2.0–10), initial dye concentration (15-30 mg L-1,), biosorbent dose (25mg-100mg) and temperature (288-318K) were evaluated during the present study. Samples were collected from the flasks at regular time intervals and the residual dye concentration in the solution was analyzed by monitoring the change in absorbance values at maximum wavelength of 660 nm using UV-Visible spectrophotometer.

3. RESULTS AND DISCUSSION

To design effective and user-friendly adsorption model it was considered necessary to carry out adsorption with a kinetic viewpoint, and effects of contact time initial MB concentration, initial solution pH, particle size and temperature on the uptake rate of the dye were monitored very carefully.

3.1 Effect of Material Dose and Contact Time:

Effect of biosorbent dose on biosorption of MB by Nitrated biomass was investigated. The amount of biosorbent was varied from 25, 50, 75 and 100 mg in 25 mL dye solution, while all the other variables such as pH, contact time, and temperature were kept constant. Data obtained from the experiments are presented in Fig.1. With increase in biosorbent dose from 25mg to100 mg, the dye removal efficiency increases from 90 to 95.9 %, which is probably due to an increase in the number of binding sites available for

biosorption. Further increase in biosorbent dose reduces the percentage removal. The effect of contact time on the removal of MB is shown in Figure 2 and about 92.29% dye removal takes place in 2 min by Nitrated biomass. The equilibrium was reached after 5 minutes (Fig.2). The changes in the rate of adsorption might be due to fact that initially all the adsorbent sites are vacant and solute concentration gradient is very high. Later, the lower adsorption rate is due to a decrease in number of vacant sites of adsorbent and dye concentrations.

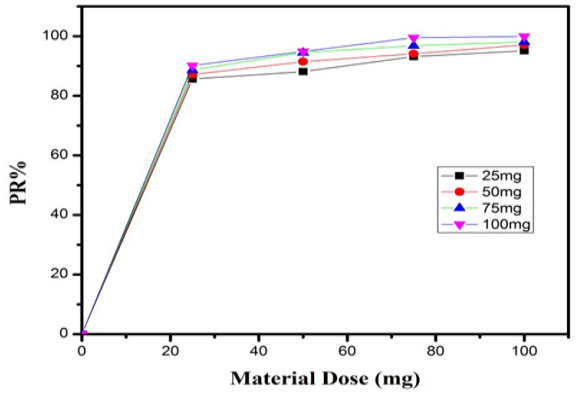


Figure-1 Effect of Biomass Dose.

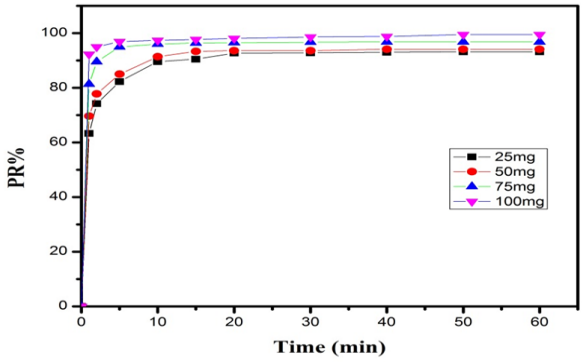


Figure-2 Effect of Contact Time on MB Removal

3.2 Effect of pH:

The effect of pH on biosorption of MB onto Nitrated biomass was studied over a pH range of 2–10. Results are shown in Fig.3. The amount of dye removal at equilibrium decreases with decreasing pH, appreciably up to pH 2.0. With further increase in pH, there is no significant increase in the amount of dye removed. Maximum removal is observed at pH 2.0. The pH of the aqueous solution affects both the surface charge of the biosorbent material as well as the degree of ionization of the dye molecule. It mainly contain N–H, C=O and C–H functional groups on their surface. Protonation of these functional groups at low pH values renders a net negative charge to the biosorbent surface while deprotonation of the functional groups at high pH values render it positively charged. At low pH values, there exists a strong electronegative repulsion between the positively charged dye ions and the negatively charged biomass surface resulting in high dye uptake capacity.

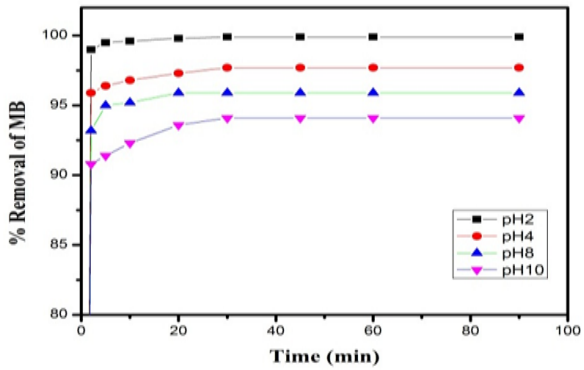


Figure-3 Effect of pH on MB Removal.

3.3 Effect of Initial Dye Concentration:

Most suitable 25ppm Biosorption of MB onto Nitrated biomass was also carried out at different initial dye concentrations (15, 20, 25, and 30 mg L-1) and the results are shown in Fig.4. It is clearly evident from the figure that the biosorption capacity increases with increasing initial dye concentration. Initial dye concentration provides an important driving force to overcome all mass transfer resistances of all molecules between the aqueous and solid phases. Hence, a higher initial dye concentration of dye will enhance the biosorption process.

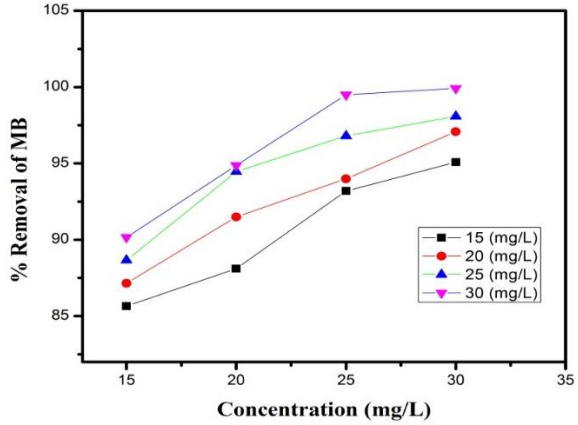


Figure-4 Effect of Concentration on MB Removal

3.4 Effect of Temperature:

The effect of temperature on the biosorption process of MB was studied in the range of 288 to318 K and the results are depicted in Fig. 5. The figure shows that the dye uptake capacity decreases with increasing temperature. This finding suggests that MB uptake process was exothermic in nature. The negative correlation between temperature and dye biosorption capacity may be due to the weakening of bonds between the dye molecules and the active site of the biosorbent. Also with increasing temperature, the solubility of MB increases. Consequently, the interaction forces between the solute and the solvent are stronger than those between the solute and the biosorbent.

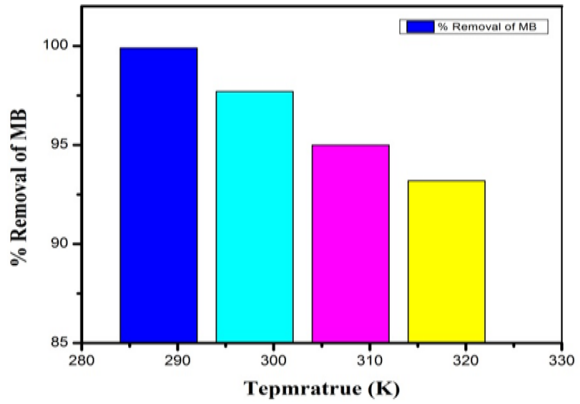


Figure-5 Effect of Temperature on MB Removal

3.5 Adsorption Kinetics:

A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process. The applicability of the pseudo-first-order and pseudo-second-order model was tested for the adsorption of MB onto Nitrated biomass. The best-fit model was selected based on the linear regression correlation coefficient, R2 values. If the second-order kinetics is applicable, then the plot of t/qt vs. t (Fig.6) and Fig.7 log (qe-qt) vs.T should show linear relationship

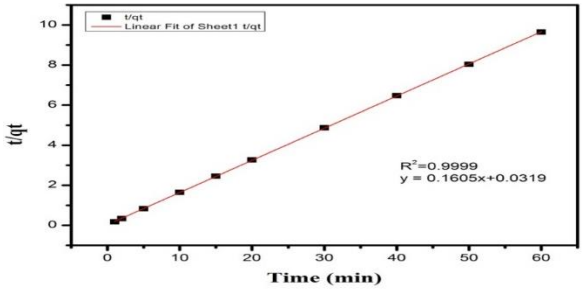


Fig.6 Plot t/qt vs. T (Pseudo-Second-Order Kinetics.)

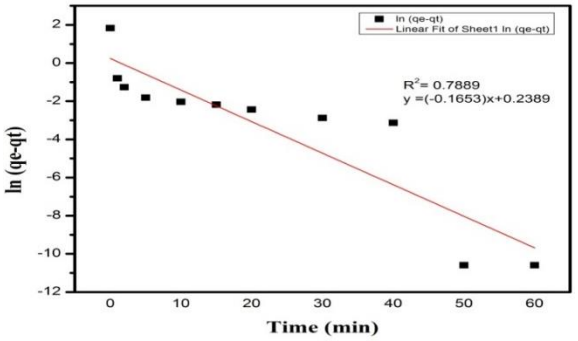


Fig.7 log (qe-qt) vs. T (Pseudo-First-Order Kinetics.)

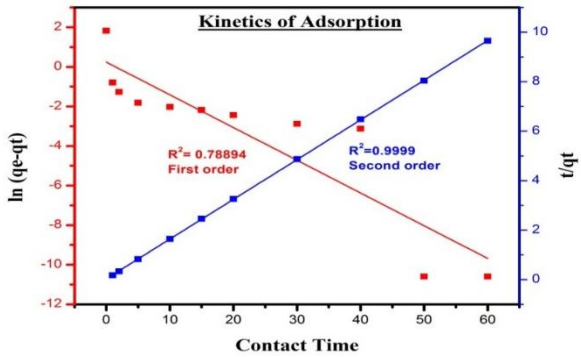


Figure-8 Kinetics of Adsorption

Table- 1 Kinetic and thermodynamic parameters for the sorption of MB onto Nitrated biomass of Ailanthus excelsa, Pseudo first order and Pseudo second order model

Pseudo first order model k1 (min^{-1}) 0.1653	qe (mg/g) 0.6253	R^2 0.7889
Pseudo second order model k2 (g/(mg min) 1.2383	qe 6.2305	R^2 0.9999
Intraparticle diffusion model kd (mg/g min) 2.7772	C (mg/g) 0.731	R^2 0.9926
Thermodynamic parameter ΔH^0(kJ/mol) -6.0861	ΔS^0 (KJ/mol K) +17.5887	$\Delta G°$ (kJ/mol) -13.2167

Kinetics and thermodynamics of methylene blue sorption on Nitrated biomass of *Ailanthus excelsa*). The intraparticle diffusion equation is expressed as follows,

$qt = Kd\ t^{1/2}+C$ (3)

Where, kd is the intraparticle diffusion rate constant (mg/g min1/2). The data for intraparticle diffusion are given in Table-1. The linear portion of the plot does not pass through origin. This deviation from the origin may be due to the variation of mass transfer in the initial and final stages of the adsorption process. This confirms that the adsorption of MB on of *Ailanthus*

excelsa plant was a multi-step process involving adsorption on the external surface and diffusion into the interior.

3.6 Adsorption Thermodynamics

Thermodynamic parameters evaluated for MB adsorption onto Nitrated biomass are the free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0). These parameters were calculated using the following equation.

$$\Delta G^o = -2.303\ RT \log Kd \quad (4)$$

Where qe is MB concentration at equilibrium onto Nitrated biomass (mg/L), R is universal gas constant (8.314 J/mol K), and Ce is MB concentration at equilibrium in solution (mg/L).The values of ΔH^0 and ΔS^0 were determined from the slope and intercept of the plot of ln KD versus 1/T (Fig.9). Gibbs free energy. Change of sorption (ΔG^0) was calculated using Eq. (4).The adsorption of dye increases rapidly with an increase in temperature. The increase in adsorption capacity of Nitrated biomass was attributed to the enlargement of pore size and activation of the sorbent surface with temperature. The results also indicated that the adsorption of MB is an exothermic process. Thermodynamic parameters (ΔH^0, ΔS^0 and ΔG^0) for MB. Adsorption was evaluated using Eqs. (3and 4). The values of ΔH^0 and ΔS^0 were determined from the slope and intercept of the plot of ln KD versus 1/T. Table -1 show the thermodynamic parameters for MB adsorption of Nitrated biomass. The calculated values of ΔH°, ΔS° and ΔG° were found to be -6.0861 kJ/mol^{-1} +1758.87 KJ/mol^{-1} and -13.2167 KJ mol^{-1} respectively. The negative value of ΔH^0 (-6.0861 kJ/mol^{-1}) indicates that the Adsorption of MB onto of Nitrated biomass is an exothermic reaction. The calculated value of ΔG° -13.2167 KJ mol^{-1} indicates spontaneous nature of the adsorption process. Further the positive value of entropy change, ΔS^0 reflects the affinity of Nitrated biomass for MB dye.

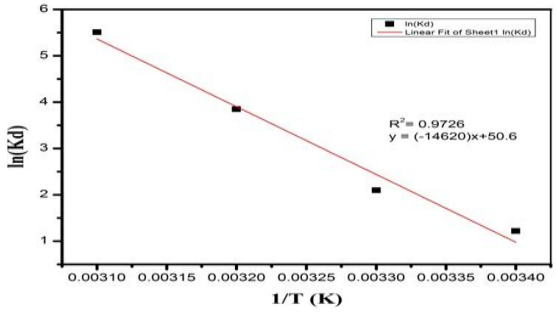


Fig.9 Plot of Ln KD vs. 1/T

3.7 Adsorption Isotherm

3.7.1 Langmuir Isotherm

The Langmuir equation is written as

$$\frac{1}{qe} = \frac{1}{qm} + \frac{1}{KLqmCe} \quad (5)$$

The shape of this isotherm can also be expressed in terms of separation factor (RL), which is given as follows: Where KL is Langmuir constant (L/mg) related to the affinity of binding sites and the free energy of sorption. qe is dye concentration at equilibrium onto bio sorbent (mg/g). Ce is dye concentration at equilibrium in solution (mg/l). qm is dye concentration when monolayer formation biosorbent (mg/g) on.

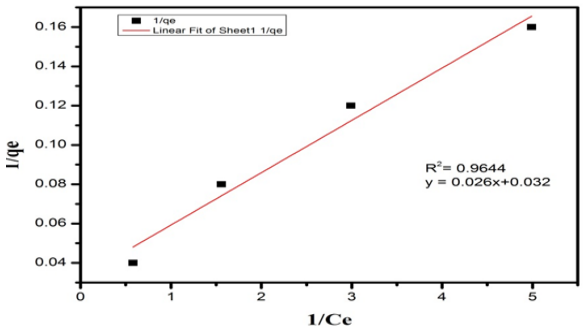


Fig.10 Plot of1/qe vs. 1/Ce

3.7.2 Freundlich Isotherm

The Freundlich equation for heterogeneous surface energy systems shown by is given by-

$$\ln qe = \ln KF + \frac{1}{n} \ln Ce \quad (6)$$

The KF and n are Freundlich constants, determined from the Plot of ln qe versus ln Ce. The parameters KF and 1/n are related to sorption capacity and the sorption intensity of the system. The magnitude of the term (1/n) gives an indication of the favorability of the sorbent/adsorbate systems.

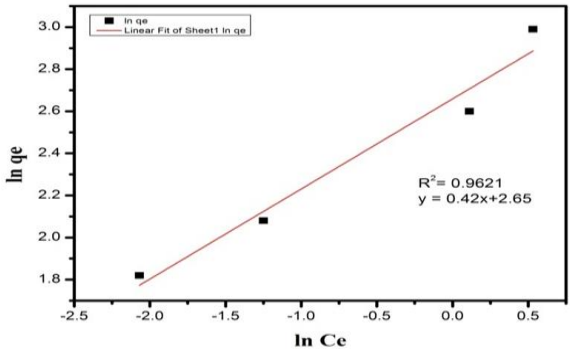


Fig.11 Plot of ln qe vs. ln Ce

3.7.3. Tempkin Isotherm.

The linearized Tempkin equation is given by the following equation

$qe = \beta \ln\alpha + \beta \ln Ce$ (7)

Where, $\beta = RT/b$

T is the absolute temperature in Kelvin, R is the universal gas constant (8.314 J/mol K), and b is the Tempkin constant related to heat of sorption (J/mg). The Tempkin constants a and b are calculated from the slope and intercept of qe versus lnCe.

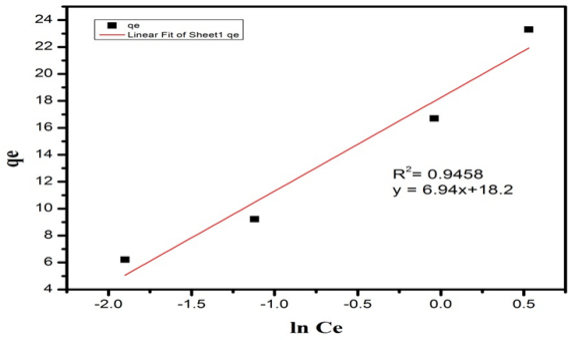


Fig.12 Plot of qe vs. ln Ce

Table -2 Results of various isotherm plots for the adsorption of MB onto Nitrated biomass of Ailanthus excelsa.

Models	Isotherm constants		
Langmuir	qm(mg/g) 38.4616	KL(L/mg) 0.8125	R^2 0.9644
Freundlich	n= 2.3809	KF(mg/g) 363.07	R^2 0.9621
Tempkin	(l/g) 345.01	KT(mg/l) 0.1440	R^2 0.9458

CONCLUSIONS

Nitrated biomass shows excellent adsorption capacity for methylene blue removal. The maximum sorption of MB with concentration (25mg/25ml), sorbent dosage (100mg/25 ml), contact time (2 to 4 min) and temperature (288 K) were observed. The maximum removal of methylene blue dye was attained at pH 2.0. The equilibrium data were fitted well in the Langmuir, Freundlich and Tempkin isotherm models which confirmed that the sorption is heterogeneous occurred through physico–chemical interactions. The KF and n are Freundlich constants, determined from the Plot of ln qe versus ln Ce. The parameters KF and 1/n are related to sorption capacity and the sorption intensity of the system (Figure.11). The Kinetics of Adsorption (Figure-8) rate of sorption was found to obey pseudo-second order kinetics and intraparticle diffusion model with correlation coefficient value R^2 is 0.9999 (Table-1). The negative $\Delta G°$ values indicated that the sorption of dye onto biosorbent was feasible and spontaneous. The negative ΔH^0 value depicted exothermic nature of the sorption. The parameters KF and n (Table-2) indicated the sorption capacity and the sorption intensity of the system.

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REFERENCES.

[1] Chiou M.S., Li, H.Y. Adsorption behavior of reactive dye in aqueous solution on Chemical cross-linked chitosan beads, Chemosphere, 2003, 50, 1095–1105.

[2] Aksum Z., Tezer, S. Equilibrium and kinetic modeling of biosorption of remazol black B by Rhizopus arrhizus in a batch system: effect of temperature, Process Biochem. 2001, 36 431–439.

[3] Lorenc-Grabowska E., Gryglewicz G., Adsorption characteristics of Congo Red on coal-based mesoporous activated carbon, Dyes Pigments.2007,74 34–40.

[4] Kapdan I.K., Kargi F., Simultaneous biodegradation and adsorption of textile Dyestuff in an activated sludge unit, Process Biochem. 2002, 37 973 981.

[5] McKay G., El-Geundi M., Nassar, M.M. External mass transport processes during the adsorption of dyes onto bagasse pith, Water Res. 1988 ,22 (12) 1527–1533.

[6] Sun G., Xu X., Sunflower stalks as adsorbents for colour removal from textile Wastewater, Ind. Eng. Chem. Res. 1997,36 (3) 808–812.

[7] Gupta V.K., Mohan D., Sharma S., Sharma M. Removal of basic dye (Rhodamine)B and Methylene blue) from aqueous solutions using bagasse fly ash, Sep. Sci. Technol. 2000, 35 2097–2113.

[8] Ramakrishna K.R., Viraraghavan, T. Dye removal using peat, Am. Dyestuff Rep. 1996, 85 (10) 28–34.
[9] El-Nabarwy T.H., Khedr S.A., Removal of pollutants from water using untreated In addition, treated sawdust and water hyacinth, Adsorb. Sci. Technol. 2000, 18 (4) 385–398.
[10] Basibuyuk M., Forster C.F., an examination of the adsorption characteristics of a basic dye (Maxilon Red BL-N) on to live activated sludge system, Process Biochem. 2003, 38 1311–1316.
[11] Annadurai G., Juang R.S., Yen P.S., Lee, D.J. Use of thermally treated waste biological sludge as dye absorbent, Adv. Environ. Res. 2003, 7 739–744.
[12] Weng C.H., Chang E.E., Chiang P.C., Characteristics of new cocaine dye adsorption onto digested sludge particulates, Water Sci. Technol. 2001, 44 279–284.
[13] Namasivayam C., Arasi D.J.S.E., Removal of Congo red from wastewater by Adsorption onto red mud, Chemosphere,1997,34 401–471.
[14] Namasivayam C., Dinesh K.M., Selvi K., Begum A.R., Vanathi T., Yamuna R.T, Waste coir pith—a potential biomass for the treatment of dyeing wastewaters, Biomass Bioenergy. 2001, 21 477–483.
[15] Bhattacharyya, K.G. Sarma A., Adsorption characteristics of the dye, Brilliant Green, on Neem leaf powder, Dyes Pigments. 2003, 57, 211–222.
[16] Namasivayam, C. Muniasamy N., Gayathri K., Rani M., Ranganathan K., Removal Of dyes from aqueous solutions by cellulosic waste orange peel, Bioresour. Technol. 1996 57 37–43.
[17] Ho Y.S., Chiang T.H., Hsueh Y.M., Removal of basic dye from aqueous solutions using tree fern as a biosorbent, Process Biochem,2005, 40 119–124.
[18] Kale Anandrao, Pawar Reshma, Naikodi Bhagyashri, Biosorption Potential for Methylene Blue by Biomass of Ailanthus excelsa. International Journal of Research and Analytical Reviews (IJRAR) 2021, 8, 2 www.ijrar.org. E-ISSN 2348-1269, P- ISSN 2349-5138.
[19] Kale A. A., Biosorption of Hg2+ions by Sulphonated biomass of Stalks of Prunus cerasus, International Journal of Scientific & Engineering Research, 2020. 11, 5. ISSN 2229-5518, pp 1319- 1331