

A study on removal of Toluidine blue dye from aqueous solution by adsorption onto Neem leaf powder

Himanshu Patel and R. T. Vashi

Abstract— Adsorption of Toluidine blue dye from aqueous solutions onto Neem Leaf Powder (NLP) has been investigated. The surface characterization of this natural material was examined by Particle size analysis, Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR) spectroscopy and X-Ray Diffraction (XRD). The effects of process parameters such as initial concentration, pH, temperature and contact duration on the adsorption capacities have been evaluated, in which pH has been found to be most effective parameter among all. The data were analyzed using the Langmuir and Freundlich for explaining the equilibrium characteristics of adsorption. And kinetic models like pseudo first- order, second-order model and Elovich equation were utilized to describe the kinetic data. The experimental data were well fitted with Langmuir adsorption isotherm model and pseudo second order kinetic model. The thermodynamic parameters, such as Free energy of adsorption (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were also determined and evaluated.

Keywords— Adsorption, Isotherm models, Kinetic models, Temperature, Toluidine Blue dye, Surface chemistry

I. INTRODUCTION

THE textile industry is confronted with serious environmental problems associated with its immense wastewater discharge, substantial pollution load, extremely high salinity, and alkaline, heavily colored effluent [1]. Dyes have usually a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade. Degradation of dyes is typically a slow process [2]. The removal of color is needed to be considered in the disposal of textile wastewater due to aesthetic deterioration as well as the obstruction of penetration of dissolved oxygen into water bodies, which seriously affects aquatic life. Besides, the dye precursors and degradation products are proven carcinogenic and mutagenic in nature [3].

Most discharged textile wastewater is contributed mainly by scouring, bleaching, dyeing and finishing textiles [4]. These discharged textile wastewater contain very low

neutral suspended solids. Chemical and biological methods have been employed for color removal from textile effluents. The former has not been very successful due to the essential non-biodegradable nature of most of the dyes [5]. The adsorption process is one of the most efficient methods of removing pollutants from wastewater. Also, the adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available. Data available that various type of adsorbent material available such as activated carbons [6], sawdust [7], alunite [8], fly ash [9], zeolite [10], sepiolite [11] which can be utilized to removal dye from aqueous solution. Also, some variables like agitator speed, temperature, pretreatment, adsorption capacity, adsorption size, particle size, bed height, EBET, adsorption type, source of carbon materials, type of contact, decide regeneration/ disposal, cyclic adsorption process (pH swing cycle), conductive adsorbent and adsorbate and also, carbon refilling are helpful to make the sorption process affordable [12].

Toluidine Blue color (TBC), a phenothiazine type dye, has been widely used for different purposes in several fields such as medicine science, textile industry and biotechnology. It can be used as mediator for various chemical or biochemical reactions, colorant for cloths, photosensitizer for determining the actions of photoactivated microorganism and labelling agent for identifying organisms [13, 14]. Previously removal and adsorption kinetics of cationic dye, Toluidine Blue O, from aqueous solution using Turkish zeolite [15] and TBC using gypsum [16] was studied. Also, Neem (*Azadirachta indica*) leaf powder has been used to remove chromium (Cr) removal from aqueous solution [17] and color [18].

The present investigation deals with the preparation and characterization of natural material, Neem (*Azadirachta indica*) leaf powder and to study the adsorption capacity of NLP for Toluidine Blue dye from aqueous solution. The effect of initial concentration, pH, temperature and contact duration on the rate and the extent of adsorption were also examined. The Langmuir and Freundlich isotherm models were applied for their applicability. The pseudo and Elovich kinetic models were used to identify the possible mechanisms of such adsorption process. The thermodynamic analysis was also conducted to verify the nature of adsorption.

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II. METHODS AND MATERIALS

A. Adsorbent

The neem belongs to the meliaceae family and is native to Indian sub-continent. Its seeds and leaves have been in use since ancient times to treat a number of human ailments and also as a household pesticide. The trees are also known as an air purifier and easily available in Indian region. The medicinal and germicidal properties of the neem tree have been put to use in a variety of applications. The mature neem leaves used in the present investigation were collected from the trees in Navyug Science College, Surat, Gujarat. They were washed thrice with water to remove dust and water soluble impurities and were dried until the leaves become crisp. The dried leaves were crushed and powdered and further washed with distilled water till the washings were free of color and turbidity. Then the neem leaf powder was dried in an oven at $60 \pm 2^\circ\text{C}$ and placed in desiccator for the adsorption studies. The particle size of NLP was examined by Sympatic, Germany (Model: Helos-BF). The FTIR spectrophotometer (SHIMADZU, Japan: Model: 8400S) was used to analyze the functional group of adsorbent at wavelength $400\text{--}4000\text{ cm}^{-1}$. The XRD patterns of adsorbent were determined with an automated Philips, Heollant (Model: Xpert MPD) instrument using Cu Ka radiation at 40 kV and 40 mA over the range (2θ) of $5\text{--}70^\circ$. SEM image were taken using instrument, JEOL, Japan (Model: XL-30 JSM-5610LV).

B. Adsorbate

The TBC (C.I. number 52040) used in this study was procured from Merck Inc., Thailand. The empirical formula $\text{C}_{15}\text{H}_{16}\text{N}_3\text{SCl}$ and formula weight 305.84 g/mol. The structure formula mentioned in figure 1.

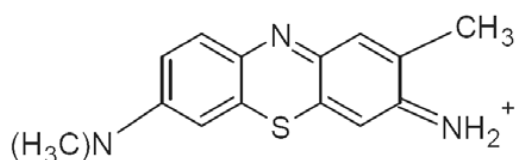


Fig. 1 Structure of TBC

C. Experimental Procedure

The experiments were carried out as shown table maintaining adsorption dose of 3.0 g/l and temperatures of 313 to 363 K.

TABLE I
EXPERIMENTAL DETAILS FOR COMPARISON OF GLP AND MLP FOR
ADSORPTION OF MBD

Effect of System	pH	Initial TBC conc. (mg/l)	Contact Duration (min)
pH	1, 3, 5, 7, 9 and 11	0.0005	240
Initial TBC conc.	7	0.0001, 0.0003, 0.0005, 0.0007 and 0.0009	240
Contact duration	7	0.0005	30, 60, 120, 240, 360 and 480

Briefly, 20 ml of the aqueous solution containing required amount of dye is treated with adsorbent in a 250 ml conical flask by shaking at 160 rpm on orbital shaker at requisite temperature, time duration and pH. The sample was allowed to settle down and then it was filtered through a Whatman filter paper No 1.

The concentration of the dye was measured by a spectrophotometer (ELICO SL 164 Double Beam UV-VIS Spectrophotometer) at $\lambda_{\text{max}} = 622\text{ nm}$ and quantity of dye adsorbed, q_e (g/g) by the NLP was calculated using the following formula:

$$q_e = (C_o - C_e) V / W \quad (1)$$

Where, C_o and C_e are the initial and equilibrium time solution concentrations of the dye (mg/l), respectively, V the volume of the solution (l) and W the weight of the NLP used (g).

The all solutions of TBC and others purposes were prepared by distilled water. 0.1 N NaOH and 0.1 N HCl used for adjustment of pH were analytical grade and purchased from Qualigens. All other chemicals used were of analytical reagent grade.

D. Adsorption isotherm

The equilibrium of sorption is one of important physico-chemical aspects for the evaluation of the sorption process as a unit operation. Sorption isotherm is the relationship between the sorbate in the liquid phase and the sorbate sorbed on the surface of the sorbent at equilibrium at constant temperature. The distribution of dye molecules between the liquid phase and the sorbent is a measure of the position of equilibrium in the sorption process and can be generally expressed by the two well known models viz., Freundlich, and Langmuir isotherm. The Freundlich isotherm can be efficient on multilayer and also, heterogeneous surface and is expressed by the following equation.

$$q_e = K_F C_e^{1/n} \text{ or } \log q_e = \log K_F + 1/n \log C_e \quad (2)$$

Where, q_e and C_e is the amount of adsorbed adsorbate per unit weight of adsorbent and unadsorbed adsorbate concentration in solution at equilibrium, respectively and K_F and $1/n$ are Freundlich constant characteristics of the system, which are determined from the $\log q_e$ vs. $\log C_e$.

Also, Langmuir adsorption is useful for predicting adsorption capacities and also interpreting into mass transfer relationship. The isotherm can be written as follows:

$$(C_e/q_e) = (1/Q_{\text{max}}) + (b/Q_{\text{max}}) C_e \text{ or } (1/q_e) = (1/Q_{\text{max}}) (1/C_e) + (b/Q_{\text{max}}) \quad (3)$$

Where, Q_{max} and b were the Langmuir constants, which measures of monolayer (maximum) adsorption capacity (in mg/g) and energy of adsorption (in g/l) respectively. The Langmuir parameters were obtained from the linear correlations between the values of $1/q_e$ and $1/C_e$ [19].

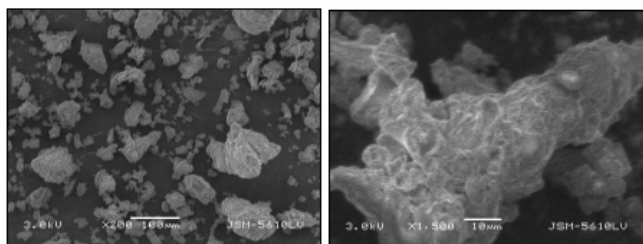


Fig. 4 SEM images of NLP

B. Effect of pH

The effect of pH (1 to 11) on adsorption of TBC by partially amorphous NLP at various temperatures at contact duration 4 hrs and initial dye concentration of 0.005 mg/l mentioned in Figure 3 (A). It was found that the color is stable or minor increase in the initial pH range 1 to 5, but color reduction increases in aqueous solution as pH increases from 7 to 11.

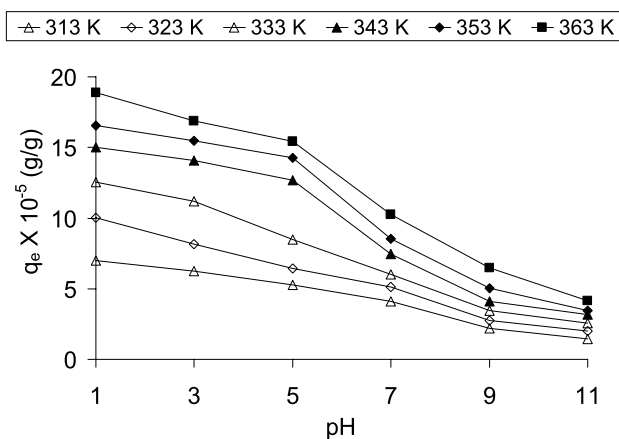


Fig. 5 Influence of pH on adsorption of TBC by NLP at different temperature

It is a commonly known fact that the anions are favorably adsorbed by the adsorbent at lower pH values due to presence of H^+ ions. At high pH values, cations are adsorbed due to the negatively charged surface sites of NLP [17].

C. Effect of initial concentration

Figure 6 depicted effect of initial concentration of TBC onto NLP having particle size 70-90 microns, in which the amount of the TBC adsorbed onto adsorbent increases with an increase in the initial concentration of dye solution varying from 0.0001 to 0.0009 mg/l for 0.1 to 0.9 mg/l dosage of adsorbent. This is due to the increase in the driving force of the concentration gradient with the higher initial dye concentration [24].

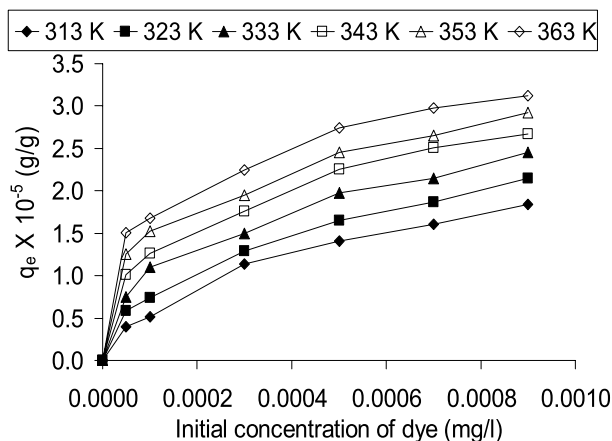


Fig. 6 Effect of initial concentration on adsorption of TBC by NLP at different temperature

D. Effect of contact duration

The influence of contact duration on adsorption of TBC was presented in figure 7, in which amount of adsorption of dye are continuously increasing with increasing contact durations (from 30 to 480 min). That is probably due to the larger surface area of adsorbent at the beginning for the adsorption of TBC. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [25].

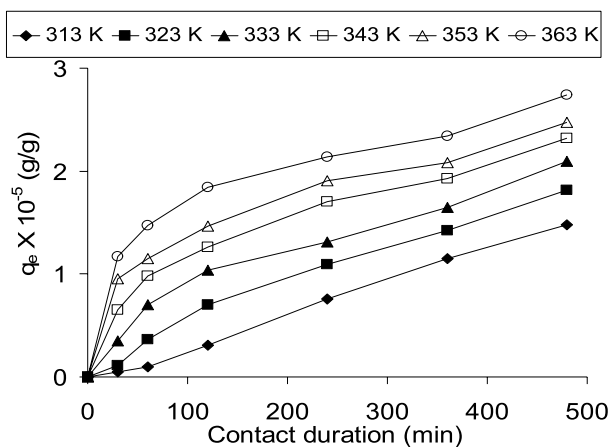


Fig. 7 Effect of contact duration with NLP at variable temperature

E. Adsorption isotherm

The non-linear graph of Freundlich and Langmuir isotherm models using NLP at different temperatures (310, 320 and 330 K) was depicted in above figure 8. It represented that the data were fitted to both isotherm. The parameters like Freundlich constants (K_F and n), Langmuir constants (Q_{max} and K_L) and their linear correlation coefficient (r^2) were mentioned in table II. Entire temperatures range studied with a good

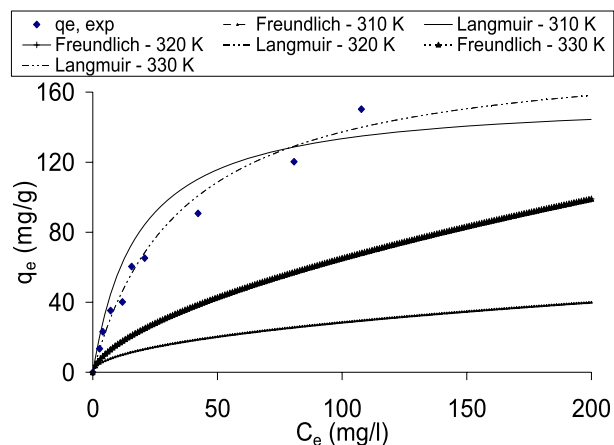


Fig. 8 Non-linear plots of Freundlich and Langmuir isotherm

linear correlation coefficient, showing that data correctly fit than Langmuir isotherm than correlation coefficient, showing that data correctly fit the Langmuir isotherm than Freundlich isotherm, proving monolayer and homogenous surface of adsorbent. The same pattern was observed for absorption of

TABLE II
FREUNDLICH AND LANGMUIR PARAMETERS FOR ADSORPTION OF TBC USING NLP

Temp. (K)	Freundlich isotherm			Langmuir isotherm		
	n	K_F (L/g)	r^2	Q_{max} (mg/g)	K_L (L/g)	r^2
310	2.06	3.06	0.9246	157.4	0.055	0.9875
320	1.81	3.56	0.9277	165.3	0.040	0.9466
330	1.65	4.02	0.9683	186.6	0.028	0.9783

various types of dye onto adsorbents (26, 27). Maximum adsorption capacities related to Langmuir isotherm were found to be 157.4, 165.3 and 186.6 mg/g at 310, 320 and 330 K respectively. Previously, adsorption of TBC onto Turkish Zeolite was conducted by Alpat and maximum adsorption capacity was found to be 55 mg/g [15].

F. Adsorption kinetic

Table 3 described kinetic parameters for the adsorption of TBC onto NLP, in which the correlation coefficients (r^2) for the linear plots of pseudo-second order plots are better than the pseudo-first order reaction plots and Elovich equation. This shows that the pseudo-second order kinetic

TABLE III
CORRELATION COEFFICIENT VALUES OF KINETIC MODELS FOR ADSORPTION ON MBD

Sr. No.	Temperature (K)	r^2 Value		
		pseudo first-order	Pseudo second-order	Elovich equation
1	310	0.9438	0.991	0.984
2	320	0.9485	0.992	0.988
3	330	0.9744	0.993	0.981
4	340	0.9729	0.998	0.959
5	350	0.9791	0.995	0.952

model explains the sorption in better way. The pseudo-second order model is based on the assumption that the rate determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate [25].

G. Thermodynamic study:

The thermodynamic parameters such as Free energy of adsorption (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were tabulated in table no. 2. The negative values of ΔG° were -1.96, -2.64, -2.97, -3.62, -3.99 and -4.65 at 300, 310, 320, 330, 340 and 350 K respectively, which indicates that adsorption process is spontaneous. The value of ΔH° was -52.867 kJ/mol, which was in the range of chemisorption. The negative value of ΔH° also indicated that the adsorption process is exothermic. Further, negative values of ΔS° suggested that the TBC molecules are more regularly arranged (decrease in randomness) on the adsorbent surface. The same results indicated in reference literature [20].

TABLE IV
THERMODYNAMIC PARAMETERS FOR ADSORPTION OF TBC USING NLP

Sr. No.	Temperature (K)	Thermodynamic Parameters		
		ΔG° (kg/mol)	ΔS° (kg/mol)	ΔH° (kg/mol)
1	300	-1.9757	-13.801	-52.867
2	310	-2.6383		
3	320	-2.9651		
4	330	-3.6166		
5	340	-3.9985		
6	350	-4.6519		

IV. CONCLUSION

The NLP has shown to use for adsorption capacities compared to many other available non-conventional adsorbents. The various process parameters like pH, initial concentration, adsorbent dosage and contact duration were investigated in this study, in which pH is to found effective for adsorption of TBC onto NLP. Equilibrium and kinetic studies were conducted for the adsorption of TBC from aqueous solutions onto NLP. The equilibrium data have been analyzed using Langmuir and Freundlich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Freundlich isotherm was demonstrated to provide the best correlation for the adsorption of TBC onto NLP. At the same way, correlation coefficients were obtained for kinetic models like, pseudo first-order, second-order model and Elovich equation. The pseudo second-order model is more fitted than others. The thermodynamic results shows that adsorption process of TBC onto NLP was exothermic, chemisorption and spontaneous.

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Mr. Himanshu Patel, a corresponding author of this research article, is a Ph. D. student of Navyug Science College, Gujarat under the guidance of R. T. Vashi. My research area is to characterize of textile wastewater and its treatment using various adsorbents and coagulants prepared from natural plant materials like leaf, root, seed, etc. Also, adsorption of various types of dye from its aqueous solution onto natural plant materials.

Dr. R. T. Vashi is lecturer and research guide at Navyug Science College, Gujarat. He has deep acknowledged of all aspect of environmental and applied chemistry.