Removal of Methylene Blue from Aqueous Solution Using Raw and Modified Pine Tree Leaves as Adsorbent

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Abstract:

Pine tree leaves, an agricultural waste, was chemically modified and used for the removal of Methylene blue from aqueous solution. The chemical modification was prepared using 0.1 M Hcl and 0.1 M NaOH. Overall, the extent of methylene blue dye adsorption is increased with the increase in initial dye concentration, contact time, solution pH, and system temperature but is decreased with the increase of salt concentration. Equilibrium data were described by both Langmuir isotherm and Freundlich adsorption isotherm. The isotherm study indicated that MB

adsorption on raw and treated pine leaves could be fitted well with the Langmuir model other than Freundlich model. The maximum adsorption capacity for MB at 30 ^{0}C determined from the Langmuir isotherm is 126.58 mg/g occurred at pH of 9.2 for an initial dye concentration of 10 ppm by raw pine leaves, whereas for acid-treated and bae-treated pine leaves the maximum adsorption of 140.44 and 132.56 mg/g respectively for the same experimental conditions. Freundlich constant 'n' also indicated favourable adsorption.

Keywords: *Adsorption characteristics, Dye removal, Low cost adsorbents*

1.0 Introduction:

The presence of colorant pollutant in wastewater streams has become a major problem on human and environment. The removal of dyes from wastewater is a matter of great interest in the field of water pollution. The effluents from many industries such as leather, plastics, cosmetic, printing, textiles, rubber, paper, food processing, and dye manufacturing contains one or more of toxic dyes (Ayyappan et al., 2005). Methylene blue (MB) is the most general water-soluble dye, generally used for dyeing leather, cotton, printing calico, tannin, printing calico, and for medicinal purposes (Gupta et al., 2004). Although this dye is not greatly toxic to people, it can cause eye/skin irritation, and systemic effects including cyanosis and blood changes (Tsai et al., 2009, Sen et al., 2011). It can make breathing difficult and may cause nausea, vomiting, profuse sweating, diarrhoea, gastritis and mental confusion (Sen et al., 2011). Therefore, an increased interest has been focused on removing such dyes from wastewaters. In general, several methods such as membrane filtration, reverse osmosis, ion exchange,

chemical precipitation, conventional coagulation and adsorption are the mainly common practiced for the removing dyes from wastewater(Mahmoode et al., 2011).

Between the treatment methods, adsorption is comparatively superior because of simplicity of design, low cost, availability and ability to treat dyes more concentrated than other methods (Mahmoode et al., 2011, Yagub et al., 2012). Activated carbons are generally used as adsorbents because they have high adsorption abilities for a large number of inorganic/organic metal ions. However, the cost of activated carbon is relatively high which limits their usage(Cui et al., 2008). Natural materials that are available in large quantities or certain waste products from industrial or agricultural materials may have the potential to be used as inexpensive adsorbents. Agricultural wastes are renewable and available abundantly at no or low cost.

Many types of agricultural by-product such as orange peel (Sivaraj et al., 2001), barley husk (Robinson et al., 2002), sawdust (Garg et al., 2004), walunt shell (Ghazi et al., 2015), rice husk (Vadivelan and Kumar, 2005), cereal chaff (Han et al., 2006), capsicum straw (Jianxis and Muqing, 2014), Vitex negundo stem (Kavitha and Senthamilselvi. 2014), fly ash (Visa et al., 2010), pine cone (Sen et al., 2011), and pine leaves(Yagub et al., 2012) have been used for the removal of methylene blue from its aqueous solution. However, no systematic work has been reported on the use of raw and modified pine leaves (PL) as an effective adsorbent for the removal of cationic dye MB from colour solution.

The modified pine leaves were treated with an aqueous 0.1 M sodium hydroxide (BPL) and also with an aqueous 0.1 M hydrochloric acid (APL). Moreover, great amount of salt have been utilised in the dyeing

process and there should be an effect at the dissolved salt concentration on the adsorption capacity of organics. Therefore, salt effect on MB adsorption which is a further new part of this study work has also been presented here. Basically the indirect mechanisms in adsorption vary quantitatively and qualitatively according to the type of agricultural biomass, it's processing and also its origin. Therefore, it is necessary to understand the kinetics and mechanism of adsorption, which will help the selection of designing of an adsorption column and adsorbent.

The main objective of this research was to find out the possibility of raw and modified pine tree leaves as inexpensive agricultural natural adsorbent for MB dye adsorption from its aqueous solution. The effect of initial dye concentration, initial solution pH, contact time, temperature and Nacl concentration on methylene blue adsorption ware studied.

2.0 Materials and Methods:

2.1 Adsorbent:

Pine tree leaves were collected and washed several times with distilled water to remove dust and soluble impurity then dried in an oven at 65^{o}C for 1day. Dried pine leaves were cut into pieces then ground by using a crusher. The resultant powders were passed through British Standard Sieves and particles below 350µm collected in a plastic container and used as adsorbent for adsorption experiments.

Base and Acid modified pine leaves powder adsorbent was prepared by mixing 10g of raw pine leaves powder with 100 ml of 0.1M NaOH solution and with 100 ml of 0.1 M Hcl solution. The whole reaction mixture was stirred in a magnetic stirrer for a period of 24 hr and then the powders were filtered and repeatedly washed with distilled water. The

washed powders were then oven dried overnight at 50 ^{o}C and used for adsorption.

2.2 Adsorbate and Other Chemicals:

The basic cationic dye, Methylene Blue (MB), was tested as the adsorbate in this study. The formula of methylene blue is C16H18 N3SCl·3H_2O, and molecular weight as 319.85 g. It was used without further purification. The stock dye solution was prepared by dissolving 1g of methylene blue in 1000 ml distilled water. The experiment solutions were obtained by diluting the stock dye solution with deionised water to give the appropriate concentration of the experiment solutions. The pH of the experiment solutions was adjusted by addition of either dilute 0.1 M HCl or 0.1 M NaOH solutions. pH measurements were done using Orien pH meter. The SP-8001 UV/VIS spectrophotometer was used to determine the concentration of MB in solution. A calibration curve was also plotted between absorbance and concentration of dye solution to obtain absorbance-concentration profile. Unknown MB concentration was measured using calibration curve.

2.3 Adsorption Experiment:

Adsorption measurement was determined by batch experiments of known amount of the adsorbent with 50 ml of aqueous methylene blue solutions of known concentration in a series of 250 ml conical flasks. The mixture was shaken at a constant temperature using Thermoline Scientific Orbital Shaker Incubator at 120 rpm at 30°C temperature for 240 min. At predestined time, the bottles were withdrawn from the shaker, and the residual dye concentration in the reaction mixture was analysed by centrifuging the reaction mixture and then measuring the absorbance of the

supernatant at the wavelength that correspond to the maximum absorbance of the sample. Dye concentration in the reaction mixture was calculated from the calibration curve. Adsorption experiments were conducted by varying initial solution pH, contact time, adsorbent dose, initial methylene blue dye concentration, temperature and salt concentration under the aspect of adsorption kinetics, adsorption isotherm and thermodynamic study.

The amount of dye adsorbed onto pine leaves powder at time t is q_t (mg/g) which was calculated by the following mass balance equation:

$$q_t = \frac{(C_0 - C_t)}{m} V \qquad (1)$$

And the dye removal efficiency, i.e. % of Adsorption was calculated as:

$$\% \text{ Adsorption} = \frac{(C_0 - C_t)}{C_0} \times 100 \qquad (2)$$

where C_0 is the initial dye concentration (mg L^{-1}), C_t is the concentration of dye at any time t, V is the volume of solution (litres) and m is the mass of pine leaves powder in grams. All measurements are in general reproducible within ± 10%.

Equilibrium experiments were conducted following the above procedure with a wide range of initial dye concentration except that a solid-liquid contact time at 240 min was allowed which was more than equilibrium time.

3.0 Results and Discussion:

3.1 Effect of Initial Solution pH on MB Dye Adsorption Kinetics:

The effect of pH on MB is presented in Figure (1). Solution of pH is an important parameter in the adsorption process due to its influence on the surface properties of adsorbent(Quintelas et al., 2009). This is partially

due to the fact that hydrogen ions themselves are strong competing ions and partially that the solution pH influences the dye as well as the ionization of the functional groups onto the adsorbent surfaces (Quintelas et al., 2009, Saueprasearsit et al., 2010, Yu et al., 2009).

The effect of pH on adsorption was studied in the range of 2.05 to 9.2 in case of raw pine leaves powder and treated pine leaves which are presented in Figure (1). From Figure (1), it was found that the amount of dye adsorbed increased with the increase in pH or alkalinity. The percentage removal of MB dye was also found to increase when the solution pH was increased from pH 2.05 to pH 9.2 for which the plot is not presented here. From Figure (1), It was found that the amount of dye adsorption increased from 6.74 mg/g (20.24 % removal efficiency) to 26.81 mg/g (80.45 % removal efficiency) due to change in pH from 2.05 to 9.2 for a fixed initial dye concentration of 10 ppm at equilibrium for raw pine leaves, whereas for modified pine leaves, it was found that the amount of dye adsorbed increased from 7.82 mg/g (23.46% removal efficiency) to 27.51 mg/g (82.53% removal efficiency) and from 11.38 mg/g (34.41% removal efficiency) to 31.72 mg/g (95.16% removal efficiency) for base and acid treatment respectively with the change in solution pH from 2.05 to 9.2 for a fixed initial dye concentration of 10 ppm at equilibrium as will. Basically, the acid treated pine leaves had higher dye sorption capacities Figure (1) than the base treated and the untreated pine leaves. This is because of increase of the internal surface of treated sample than the raw and base treated pine leaves powder which will lead to increased adsorption of MB for the treated samples over the raw sample. Maximum adsorption of dye occurs at acidic pH Figure (1).

This can be explained by the electrostatic interaction of cationic dye methylene blue with negatively charged surface of the pine leaves. The negative charge on leaves biomass increased with increasing pH, which was reported by (Postai et al 2016). In addition, lower adsorption of methylene blue at acidic pH might be due to the presence of excess H^+ ions competing with dye cations for the available adsorption sites (Bendaho et al., 2015), (Vadivelan and Kumar, 2005). Another possibility can be the development of positive charge on the adsorbent in highly acidic solution, which inhibits the adsorption of dye, resulting in low adsorption. Similar results are also reported for other system(Mahmoode et al., 2011, Dawood and Sen, 2012).

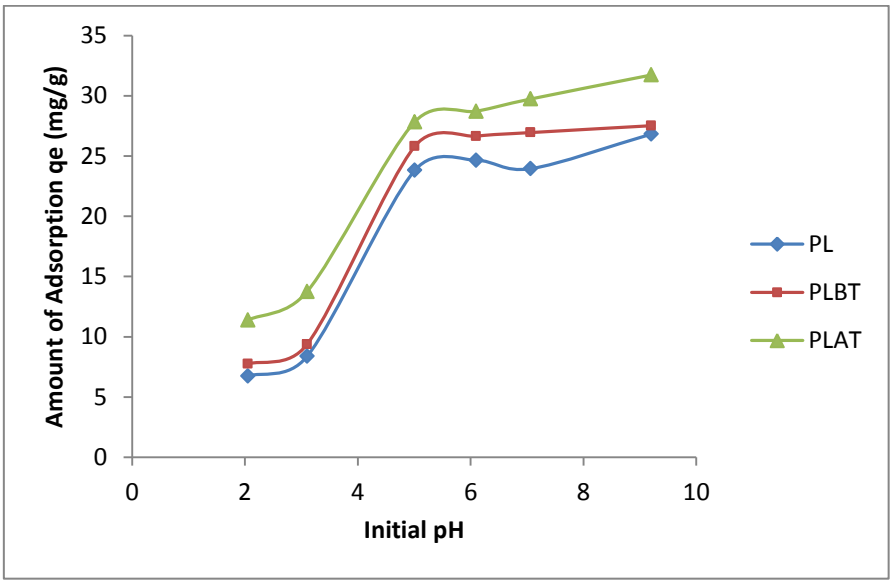

Figure (1) Effect of initial solution pH on the adsorption of MB onto raw and treated pine leaves, sorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm

3.2 Effect of Contact time on MB Dye Adsorption Kinetics:

Effect of contact time is one of the physical parameters for economical wastewater treatment plant design application (Saueprasearsit et al., 2010). Figure (2) shows the removal of MB dye solutions on raw and modified pine leaves. It was found that fast adsorption at the initial period and decrease slightly until the equilibrium is reached for both raw and treated pine leaves. A rapid adsorption of the dye at the initial stages of the adsorption and equilibrium was attained within 90 min. This kinetic experiment clearly indicated that adsorption of methylene blue dye on raw and modified pine leaves is a less or more two-step process: a very raped adsorption of dye to the external surface followed by possible slow intrapartical diffusion in the interior of the adsorbent.

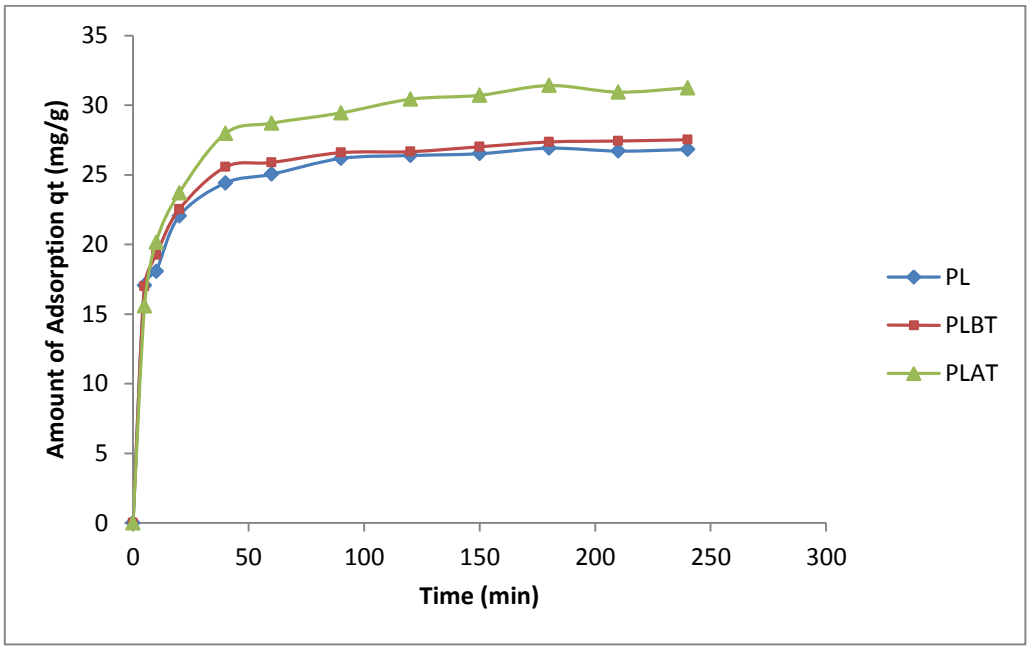

Figure (2) Effect of contact time on the adsorption of MB onto raw and treated pine leaves, sorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm

3.3 Effect of Initial MB Dye Concentration on Adsorption Kinetics:

The initial dye concentration has an obvious effect on its removal from aqueous solutions. The effect of initial dye concentration on the adsorption of methylen blue dye was investigation at different initial dye concentration onto raw and treated pine leaves, and the results are presented in figures 3 and 4. Figures (3 and 4), show that the amount of adsorption increases with the increased initial dye concentration for raw and modified pine leaves, as the initial dye concentration increased from 10 to 90 mg/L, the adsorption capacity of dye onto raw and treated pine leaves increased from 26.81to 146.38 mg/g. Moreover, the adsorption capacity also increased with acid modified pine leaves. This indicates that the initial dye concentration plays a significant role in the adsorption ability of dye. However, the percentage removal of dye decreased from 95.5 to 39.9%, on increasing the initial dye concentration from 10 to 90 mg/L after 240 minutes for which plot is not shown here. Further, it was observed that the amount of methylene blue dye uptake, qt mg/g, is increased with increase in initial dye concentration. Basically, from both the figures, the adsorption percentage decreases and the extent of adsorption increases with increasing initial dye concentration for both raw and modified pine leaves. This is so because the initial dye concentration provides the driving force to overcome the resistance to the mass transfer of dye between the aqueous and the solid phase. For constant dosage of adsorbent, at higher initial dye concentration, the available adsorption sites of adsorbent become less, and hence, the removal of MB dye depends upon the initial concentration (Shahryari et al., 2010). The increase in initial concentration also enhances the interaction between adsorbent and dye. Therefore, an increase in initial dye concentration leads to increase in the amount of adsorption of dye.

Similar types of results are reported by various researchers for methylene blue adsorption on activated carbon (Sharma, 2009), on carbon nanotube (Shahryari et al., 2010), on oak sawdust (Abd EI-Latif et al., 2010), on rice husk and rice husk ash (Sharma et al., 2010), on water weeds biomass (Peng et al., 2016) and on cashew nut shell (Kumar et al., 2010).

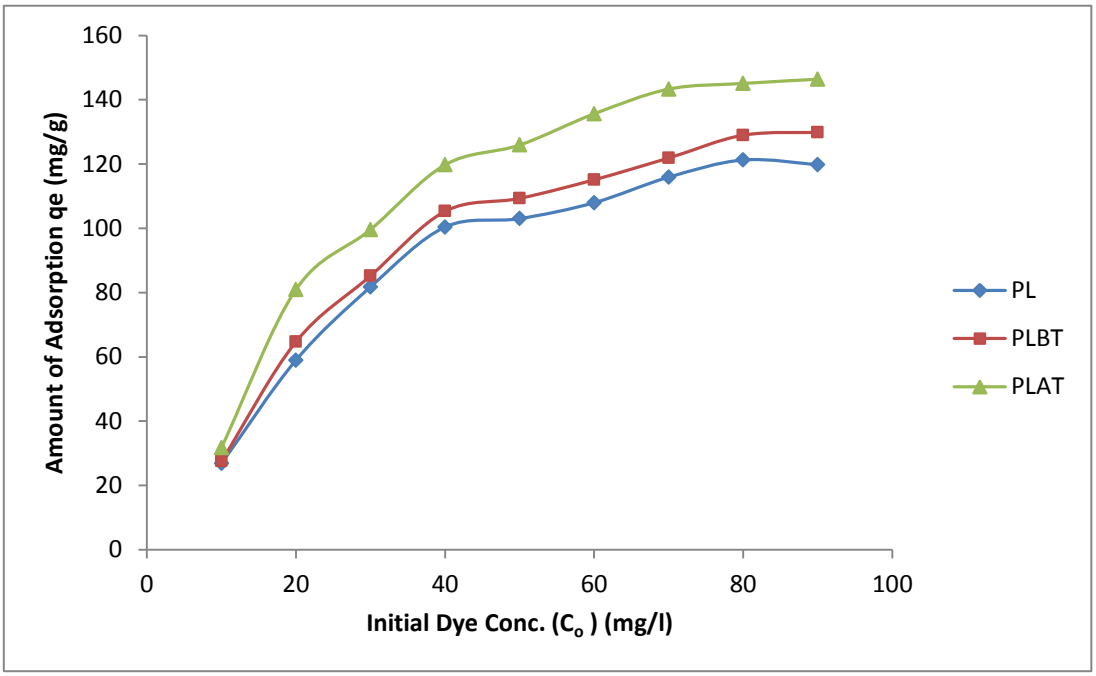

Figure (3) Effect of initial dye concentration on the adsorption of MB onto raw and treated pine leaves, sorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm

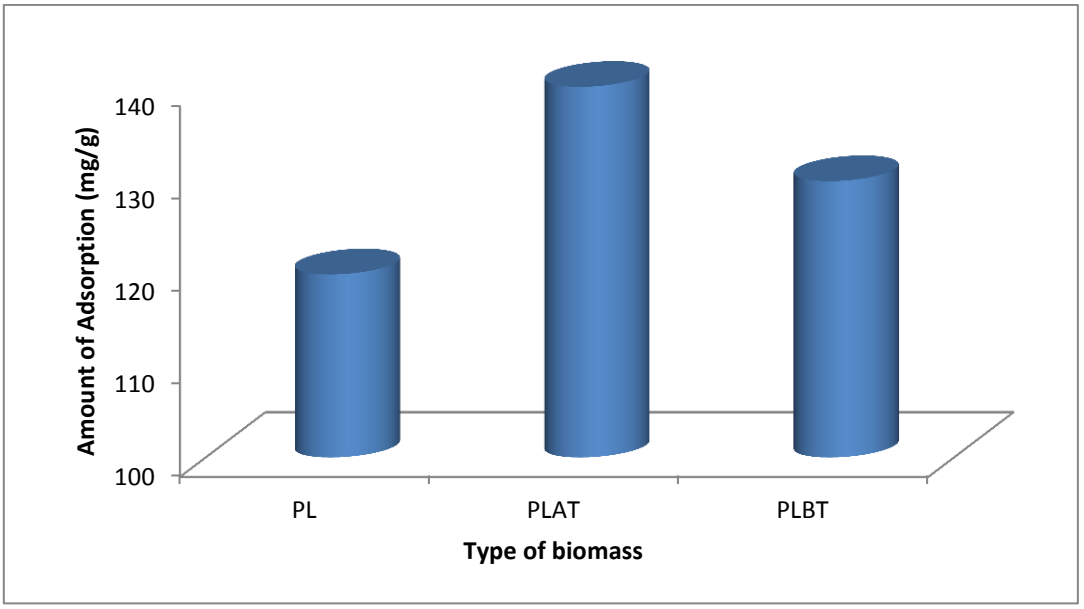

Figure (4) Effect of initial dye concentration on the adsorption of MB onto raw and treated pine leaves, sorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= 30°C; shaker speed=150 rpm

3.4 Effect of inorganic Monovalent Salt Concentration on MB Dye Adsorption Kinetic

The effect of salt concentration (NaCl) on removal of methylene blue MB was studied at different at concentrations of Nacl 50, 100, 150, and 200 mg L^{-1}. Figure (5) shows that the dye adsorption by raw and modified pine leaves decreased with increase of inorganic salt this is because of the increasing of salt concentration produces decrease in amount of dye adsorption. The results may be due to competition for adsorption sites between Na^{+} ions and MB. Mahmoode et al (2011) reported similar mention for different system.

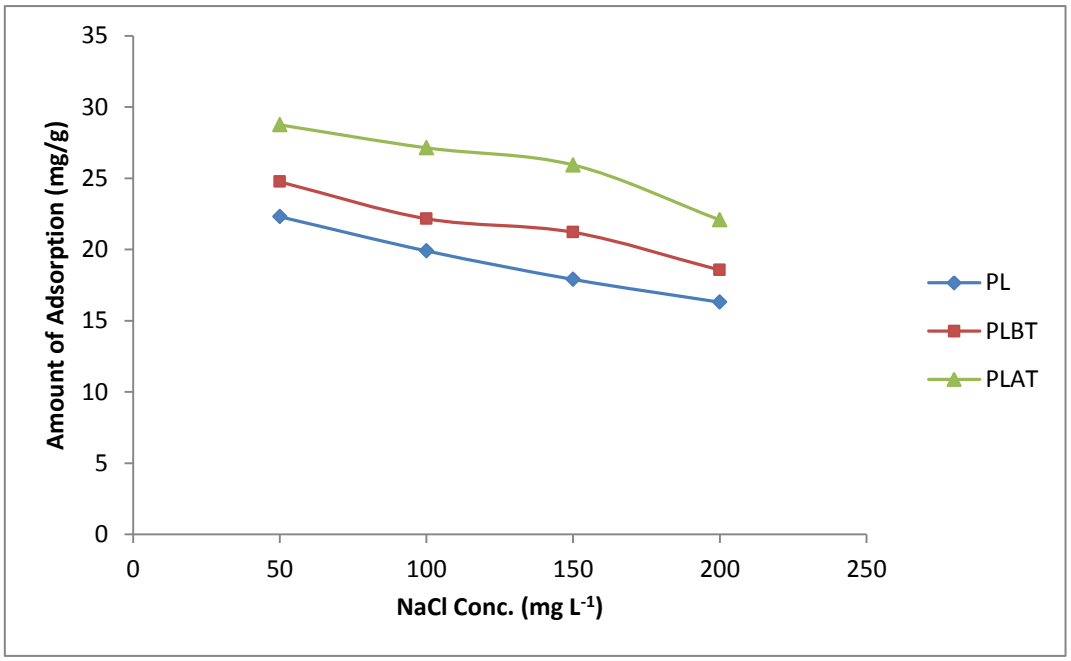

Fig (5) Effect of salt concentration on the adsorption of MB onto raw and treated pine leaves; volume of dye solution=50 ml; temperature= 30°C; pine cone dosage 15mg; pH=9.2; agitation speed 150 rpm.; and initial dye concentration 10 mgL-1

3.5 Effect of Temperature on MB Dye Adsorption Kinetics:

Effect of temperature is another important physical parameter because temperature will change the adsorption capacity of the adsorbent (Argun et al., 2008).To study the effect of temperature on the adsorption of MB dye adsorption by pine leaves, the experiments were carried out at temperatures of 30, 40, 50, and 60^{o}C. Figure (6), shows the influence of temperature on the adsorption of MB dye onto pine leaves. As it was observed, the equilibrium adsorption capacities of adsorption of MB onto raw and treated pine leaves were found to increase with increasing temperature. This fact indicates that the higher temperature is increased

surface activity signifying that adsorption between methylene blue and these biomasses were an endothermic process. This mean the higher temperature is in favour of biosorption,

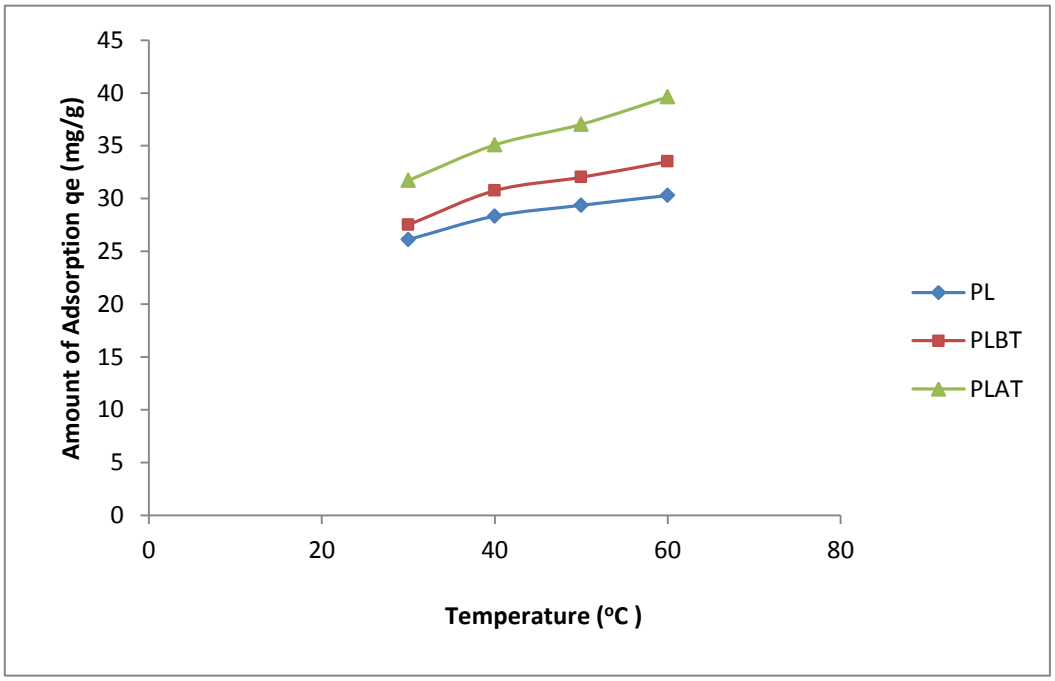

Figure (6) Effect of temperature on the adsorption of MB onto raw and treated pine leaves, sorbent=15mg; volume of dye solution=50 ml; initial dye concentration=10 ppm; temperature= (30, 40, 50, 60) °C; shaker speed=150 rpm; pH=9.18

3.6 Adsorption Equilibrium Isotherm:

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of equilibrium adsorption data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes(Sen et

al., 2011). The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2.

Figure (7) shows Langmuir isotherm fittings for pine leaves biomass adsorbent. The maximum monolayer adsorption capacity of raw and treated pine leaves, q_m, and constant related to the binding energy of the sorption system, K_a, is calculated from the slop and intercept from this plot which are 126.58 mg/g and 0.3435, respectively, for methylene blue–raw pine leaves system. Whereas the maximum monolayer adsorption capacity q_m of treated pine leaves PLAT and PLBT which plots are not presented here were 140.44, and 132.56 mg/g and the constant related to the binding energy of the sorption system, K_a were 0.2812, and 0.3122 respectively.

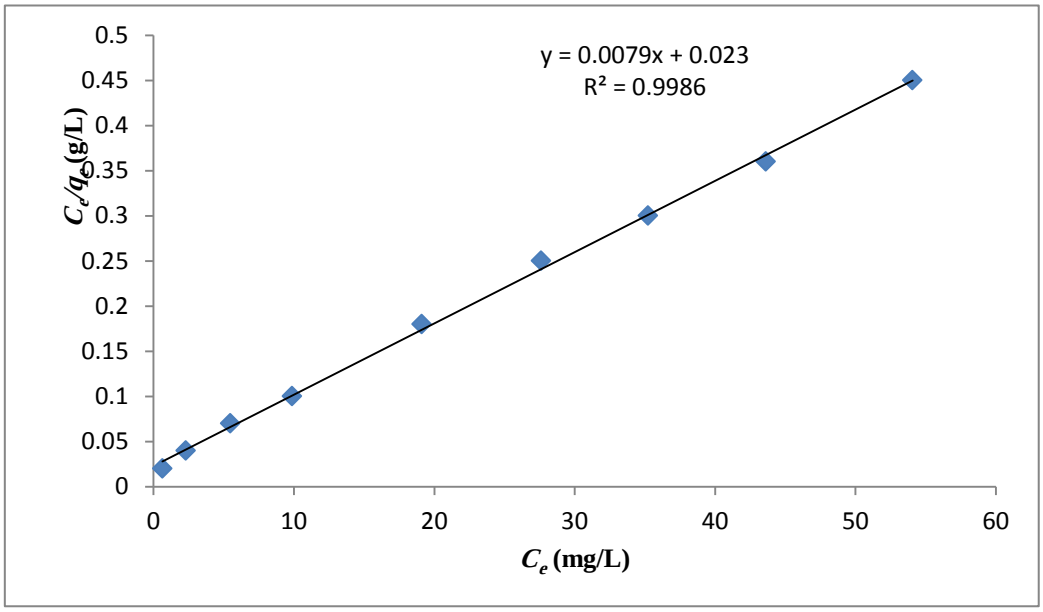

Figure (7) Langmuir plot: amount of adsorbent pine leaves added=15mg; initial dye (MB) concentration=20, 30, 40, 50, 60,70,80,90 ppm; pH=9.2; temperature=30°C; shaker speed=150 rpm

Figure (8) shows Freundlich isotherm fittings for pine leaves biomass adsorbent. The linear correlation coefficient R^2 is 0.926. Freundlich constants, i.e. adsorption capacity, K_f, and rate of adsorption, n, are calculated from this plot, which is 43.18 mg/g and 3.5, respectively. The value of 'n' is large than 1 which indicates the favourable native of adsorption and a physical process.

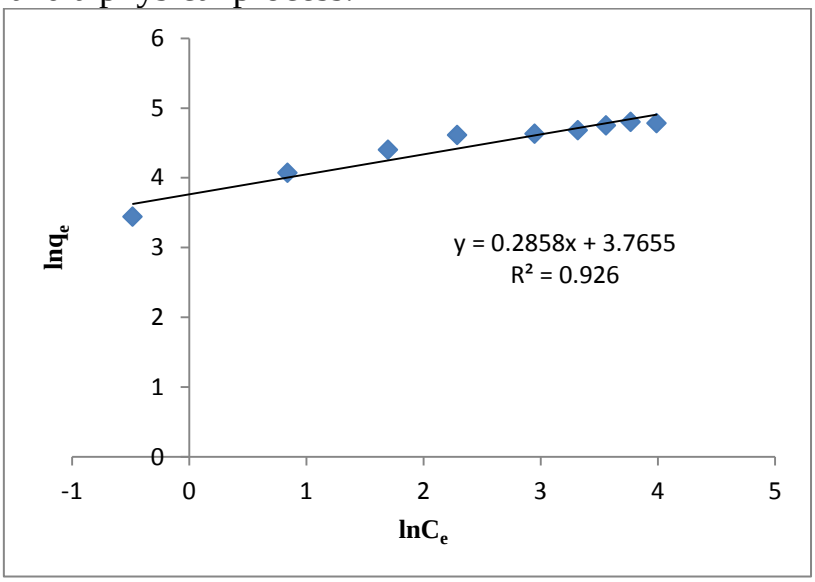

Figure (8) Freundlich plot: amount of adsorbent pine leaves added=15mg; initial dye (MB) concentration=20, 30, 40, 50, 60,70,80,90 ppm; pH=9.2; temperature=30°C; shaker speed=150 rpm

The separation factor, R_L has been determined from Langmuir plot as per the following relation

$$R_L = \frac{1}{1+K_a C_0} \qquad (3)$$

Where R_L values indicate the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), liner ($R_L = 1$) or unfavourable ($R_L > 1$) (Mohmoode et al 2011), K_a is the Langmuir constant and C_0 is the initial MB dye concentration (ppm). The separation factor, R_L, has been calculated from Langmuir plot. It has been found that the calculated R_L values are 0.1271, 0.0884, 0.0678, 0.0550, 0.0462, 0.0399, 0.0351, and

0.0313 at initial dye concentration of 20, 30, 40, 50, 60, 70, 80 and 90 ppm, respectively. These R_L values indicate favourable adsorption as it lies in $0< R_L<1$. From Figures 7 and 8, R^2 values indicate the suitability of both isotherm models for their experiment data. It is also found that the adsorption equilibrium data fit both Langmuir and Freundlich equations with a correlation coefficient value of 0.9986 and 0.925, respectively. The best fit of equilibrium data in the Langmuir isotherm expression confirms the monolayer coverage of MB onto pine leaves particles. The adsorption capacity of other agricultural natural adsorbents to remove of cationic dye reported as 67.6 mg/g of canola hull (Mahmoode et al., 2011), 114.9 mg/g of soy meal hull, 37.4 mg/g of pine cone (Mahmoode et al., 2011). Therefore, present results on the capacity of pine leaves for the removal of MB is very much comparable and also better adsorbent.

Conclusion:

The current study shows that both raw pine leaves and treated pine leaves as an agricultural by- product waste can be used as an effective alternative low-cost adsorbent for the removal of Methylene blue dye from aqueous solutions. The amount of MB dye uptake on raw and treated pine leaves biomass was found to increases with an increase in initial dye concentration, solution pH, contact time, temperature but was found to decrease with increase in salt concentration. It was observed that the adsorption was pH dependent and the maximum adsorption of 126.58 mg/g occurred at pH of 9.2 for an initial dye concentration of 10 ppm by raw pine leaves, whereas for treated pine leaves the maximum adsorption of 140.44 and 132.56 mg/g for PLAT and PLBT respectively at the same experimental conditions. Kinetic experiments clearly indicated that adsorption of MB on both pine leaves biomass is three step processes: a rapid adsorption of dye onto the external surface followed by intra-particle diffusion into the interior of adsorbent which has also been confirmed by intra-particle diffusion model. Langmuir and Freundlich models are gave good fitting with experimental data.

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