Adsorption Isotherm of dyes from Aqueous Solutions on Spent tea leaves

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Abstract:

Adsorption studies for Methylenen blue,Methyl red,Murixed,Birilliant green removal from aqueous solutions on T.L. were carried out. Batch kinetic and isotherm studies were carried out under varying experimental conditions at contact time ,initial ions concentration, adsorbent dose and pH .The adsorption data fitted the Langmuir and Freundlich isotherms equations in the whole range of concentrations studied .The adsorption capacity of compounds was higher (14.22-27.26 $mg.g^{-1}$)with the lower values of the temperature (30-60C°),higher values of the initial pH (2-14) and agitation rate(180rpm). The effect of temperature and thermodynamic parameters wear also studied , the adsorption amount was increased with decreased the temperature and the reaction was exothermic . The adsorption isotherms data was analyzed using the Freundlich and Langmuir .

Key Words :adsorption ,tea leaves ,dyes ,isotherms ,Freundlich, Langmuir

Introduction:

Since the end of the last century a large amount of products, such as medicines, disinfectants, contrast media, laundry detergents, surfactants, pesticides, dyes, paints, preservatives, food additives, and personal care products, have been released by chemical and pharmaceutical industries threatening the environment and human health. Currently there is a growing awareness of the impact of these contaminants on groundwater, rivers, and lakes. Therefore the removal of emerging contaminants of concern is now as ever important in the production of safe drinking water and the environmentally responsible release of wastewater [1, 2].

Although very little investment has been made in the past on water treatment facilities, typically water supply and treatment often received more priority than wastewater collection and treatment. However, due to the trends in urban development along with rapid population increase, wastewater treatment deserves greater emphasis. Several research studies showed that, treated wastewater, if appropriately managed, is viewed as a major component of the water resources supply to meet the needs of a growing economy. The greatest challenge in implementing this strategy is the adoption of low cost wastewater treatment technologies that will maximize the efficiency of utilizing limited water resources and ensuring compliance with all health and safety standards regarding reuse of treated wastewater effluents.

Treatment options which are typically considered for the removal of emerging contaminants from drinking water as well as wastewater include adsorption, Advanced Oxidation Processes (AOPs), Nanofiltration (NF), and Reverse Osmosis (RO) membranes, coagulation, floation, adsorption, oxidation and filtration etc [3-5]. However, the shortcomings of most of these methods are high investment and maintenance costs, secondary pollution (generation of toxic sludge, etc.) and complicated procedure involved in the treatment. On the other hand physicochemical treatments such as coagulation/ flocculation processes were generally found to be unable to remove Endocrine Disrupting Compounds (EDCs) and Pharmaceuticals and Personal Care Products (PPCPs). Although AOPs can be effective for the removal of emerging compounds, these processes can lead to the formation of oxidation intermediates that are mostly unknown at this point. Conversely adsorption processes do not add undesirable by-products and have been found to be superior to other techniques for

wastewater treatment in terms of simplicity of design and operation, and insensitivity of toxic substances [6].Among several materials used as adsorbents, Activated Carbons (ACs) have been used for the removal of different types of emerging compounds in general but their use is sometimes restricted due to high cost. Furthermore when AC has been exhausted, it can be regenerated for further use but regeneration process results in a loss of carbon and the regenerated product may have a slightly lower adsorption capacity in comparison with the virgin-activated carbon. This has resulted in attempts by various workers to prepare low cost alternative adsorbents which may replace activated carbons in pollution control through adsorption process and to overcome their economic disadvantages [7].

Tea is one of the most popular beverages and about 3.5 million tons of tea was consumed annually in the world. A big volume of spent tea leaf or tea leaf residue was disposed to environments through daily tea drinking and extractions of instant tea and ready-to-drink teas. Many investigations have been conducted to test tea waste, a fibrous by-product during tea processing, for many uses, such as adsorbent of heavy metals [8-10], fertilizer [11-12].

Used black tea leaves (UBTL) is considered as a low cost adsorbents for removal process because of its high adsorption capacity [13]. The association of dyes, particularly acidic dyes with health related problems is not a new phenomenon. A lot of well established literature is already available on the role of dyes as a major cause in skin and respiratory diseases. The adsorbents which are of low cost, locally available and are relatively new for their acidic dyes removal capacity from aqueous solutions were investigated. The effects of various experimental parameters, initial pH, dye concentration, sorbent dosage, ion strength, contact time were examined and optimal experimental conditions were decided.

In this study we present the results of an experimental study aimed at a preliminary assessment of the adsorption characteristics of dyes on spent leaves of black. dyes adsorption was investigated in a batch system over a wide range of initial dyes concentrations. The performance of tea waste was compared to that attained with a similar biomass residue.

Experimental

Materials

Spent black and green tea leaves were used for the experiments. Soluble and coloured components were removed from the leaves by repeated washing with boiling water until the filtrate was virtually colorless. Then the solid was washed with distilled water and oven dried at 60 °C for 24 h. The dried leaves were ground and sieved to particles <600 μm which were stored in polyethylene bags until use.

Analysis of adsorbate

A stock solution of 50 ppm Methylen blue,Methyl red,Murixed,Birilliant green solutions was prepared by dissolving required amount of commercial grade dyes in distilled water. Quantitative analysis of Methylen blue,Methyl red,Murixed,Birilliant green in solutions was performed using UV-visible spectrophotometer (Model TR (UV – 754) , Italy). For construction of calibration curve, a series of different concentrated Methylen blue,Methyl red,Murixed,Birilliant green solutions were prepared by required dilution of stock solution and the pH of each solution was adjusted at a definite value of 2.0 using 0.1 mol/L HNO3 or 0.1 mol/L NaOH solution. The absorbance of different concentrated Methylen blue,Methyl red,Murixed,Birilliant green solutions at pH 7.0 was measured at the predetermined wavelength of absorption maxima (λmax) of 661, 493, 510 and 625nm respectively . Beer–Lambert law was verified by plotting the measure absorbance against the concentration of Methylen blue,Methyl red,Murixed,Birilliant green within the range of 2-20 ppm. The calibration curve at pH 7.0 was used to determine the concentration of Methylen blue,Methyl red,Murixed,Birilliant green in different solutions of before and after adsorption.

Methods

To determine the equilibrium time that is needed for the adsorption system to reach equilibrium at a given temperature , the following procedure was the concentration of 20ppm

for dyes put in 15ml of dyes glass bottles that was shaken with 0.2gm from the granite , that the concentration of adsorbate solution was determined spectrophotometry at different times 0.5-4 hours , until the equilibrium time of adsorption. The effect of pH is by the range (2-14) and the effect of initial concentration The quantities of dyes adsorbed were calculated according to the following equation [14] .

$$Qe = (Co - Ce)\ V/\ m \quad \ldots\ldots\ldots(1)$$

Qe : is the amount of dyes adsorbed (mg/g)
Co and Ce : are the initial and equilibrium concentrations (ppm) of the adsorbate in solution , respectively,
V : is the volume of solution (L) and (m) is the mass of adsorbent(g)

Result and Discussion

Effect of contact time

(Fig. 1) The nature of the adsorption of dyes on SPENT TEA LEAVES as a function of time at a fixed initial concentration 20ppm was studied, for each dyes at different times between 0.5,1,1.5,2,2.5,3,3.5,4 hour .From the experimental data, it was observed that the amount of adsorption increasing ,with optimum contact time up to 1.5,2.5 hour of methylene blue, methyl red respectively , Brilliant green of 4 hour and Murixed of 3 hour .

Effect of weight of charcoal derived

The effect of the weight of the charcoal derived on the adsorption process was studied using group of weights between (0.01-0.2gm) at optimum pH at room temperature .It was found that the amount of adsorption increasing of optimum weight from SPLT in the dyes 0.2gm and the adsorption capacity 1.125mg/g to 1.921 0mg/g. This means any increase in the weight of adsorbent had no effect because of the perfect saturation of centers of adsorbent by ions compounds Fig (2).

Adsorption Isotherms

In this study the adsorption of dyes on spent tea leaves of their concentrations were studied at 303K, Fig (3), the Langmuir and Freundlich isotherm models were used to interpret the efficiency of dyes biosorption. Langmiur isotherm assumes that sorption occurs uniformly on the active sites of the sorbent , and once a sorbate occupies a sit , no more sorption can take place at this site [15] .The freundilsh isotherm was chosen to estimate the adsorption intensity of the adsorbent towards the adsorbent. The liearised form of freundlish adsorption isotherm was used to model [15]: Fig(4)

$$\text{Log } Qe = \log Kf + 1/n \log Ce \quad \ldots\ldots\ldots\ldots..(2)$$

Where

KF,n are calculated from the intercept and slops of the freundlich plots respectively are shown table(1)

The langmiur of albumine on surface. The following equation can be used to model the adsorption isotherm. Fig(5) [16]

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{a}{K_L} . C_e \quad \ldots\ldots\ldots\ldots\ldots(3)$$

Where:-
Ce = is the equilibrium concentration (mg/L)
Qe = is the amount of adsorption (mg/g)
a,K_L from intercept and slope respectively are shown on table (1)

pH Effect

The pH dependence of dyes adsorption onto spent tea leaves is shown in Fig(6). As it is shown in figure It is revealed that the adsorption capacity is high at optimum pH because of the dissolution of crystal structure and the competition between the protons and dyes for the exchange sites on the spent tea leaves particle [17-18]

Temperature Effect

The effect of temperature on the adsorption extent of dyes on spent tea leaves has been studied Fig (7) illustrate data and general shapes of BSA adsorption at (303 , 312 , 322 , 333 K). The results showed and an increase in the amount of dyes adsorbed on spent tea leaves with increasing temperature , hence the adsorption process appeared exothermic[19]

Thermodynamic parameter

The thermodynamic parameters for the adsorption of dyes on spent tea leaves such as :-
The change in free energy (ΔG) could be determined from the equation [20]

$$\Delta G = -RT \ln \frac{Ce}{Qe} \quad \text{.....(4)}$$

Where :- R is the gas constant (8.314 J. mol^{-1} . k^{-1})
T is the temperature (K)
The heat of adsorption (ΔH) may be obtained from the vant Hoff's equation [21] :

$$\text{Log } Xm = \frac{-\Delta H}{2.303RT} + \text{Constant} \quad \text{.....(5)}$$

Where :- Xm is the maximum value of adsorption . The plotting log Xm versus (l/T) should produced a straight line with a slope

$$\frac{-\Delta H}{2.303RT}$$

as shown in Fig. (8).
The change in entropy ΔS was calculated from Gibbs equation [22]

$$\Delta G = \Delta H - T\Delta S \quad \text{.....(6)}$$

The change of entropy (Δ S) and free energy (Δ G) of adsorption at different temperatures were calculated from Eq. (4) and (6), respectively and are presented in Table 2. Positive values of entropy change at different temperatures indicate that the increased randomness at the solid/liquid interface during the adsorption process and suggests good affinity of the dyes towards the spent tea leaves. Negative values of Δ G indicate that the adsorption process was spontaneous in nature and confirm the affinity of the adsorbent towards the dyes at all temperatures studied and Positive values of Δ G indicate that the adsorption process was unspontaneous . Similar thermodynamic findings have also been reported in the literature [23-26].

Conclusion

1. The adsorption of dyes from aqueous solutions on Spent tea leaves surface is a function of initial drug concentration, temperature and contact time.
2. The contact time for the maximum adsorption of the dyes on Spent tea leaves required is 1.5,2.5 hour of methylene blue, methyl red respectively , Brilliant green of 4 hour and Murixed of 3 hour .
3. Adsorption isotherm of the dyes under study on the Spent tea leaves obeyed Freundlich isotherm as the adsorption increases with increasing the concentration at equilibrium. This result indicated the surface heterogeneity leading to different adsorption force from site and different affinities toward dyes molecule.
4. The thermodynamic study of this work relieved that the adsorption of this dyes was found to exhibit an exothermic process on the Spent tea leaves.

Table 1 Freundlich, Langmuir parameters for the adsorption of dyes on spent tea leaves at 303k

Dyes	K_f	n	R^2	-a	k	R^2
Brilliant green	0.681	0.521	0.815	o.162	0.051	0.294
Methylene Blue	0.514	0.812	0.902	0.114	0.431	0.103
Methyl Red	0.048	0.531	0.945	0.533	0.069	0.533
Murixide	0.161	0.278	0.976	0.342	0.404	0.717

Table 2. Thermodynamic parameters for the adsorption of dyes on spent tea leaves at different

temperatures

Dyes	$-\Delta H(Kj.mol^{-1}.k^{-1})$	$\Delta G(Kj.mol^{-1}.k^{-1})$	$\Delta S(j.mol^{-1}.k^{-1})$
Brilliant green	5.687	-0.122	18.366
Methylene Blue	6.721	0.756	24.676
Methyl Red	7.008	1.802	29.075
Murixide	2.547	4.662	23.792

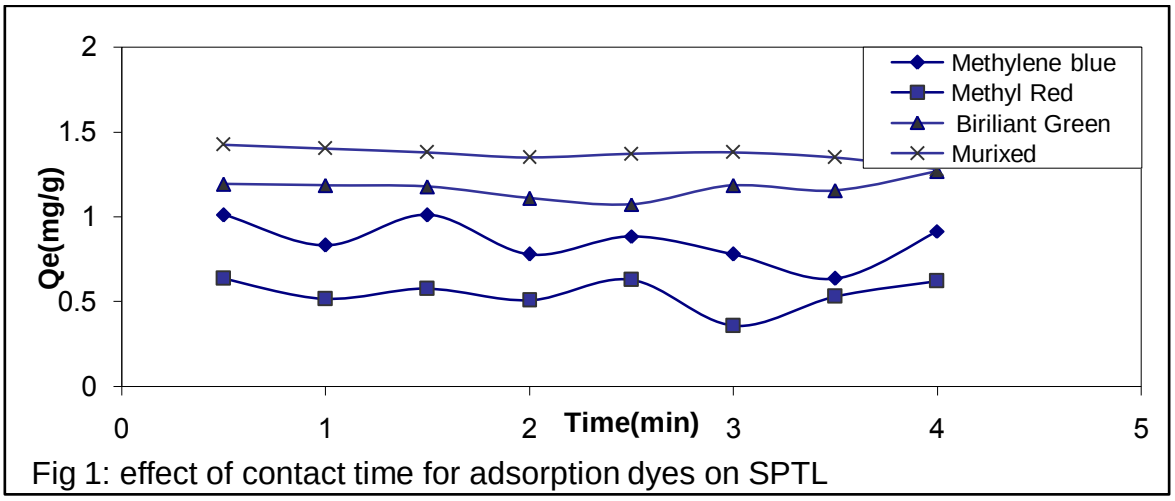

Fig 1: effect of contact time for adsorption dyes on SPTL

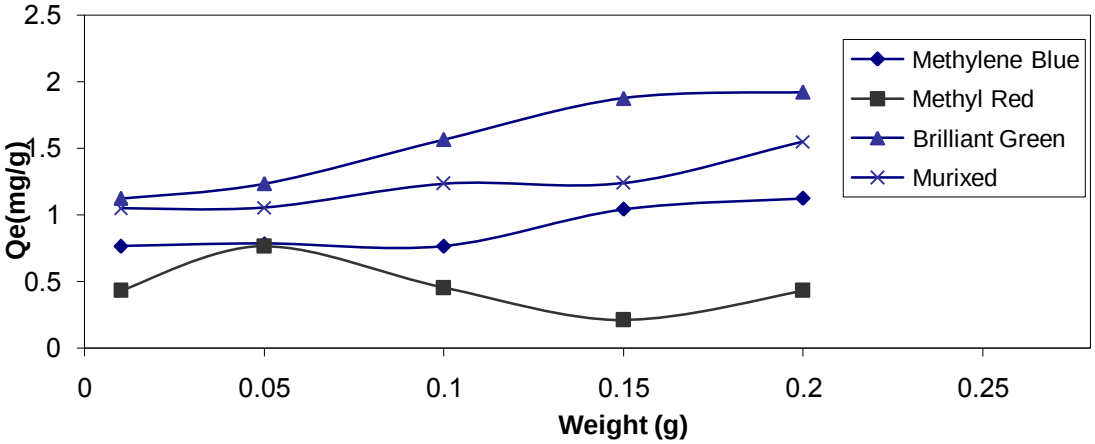

Fig 2: effect of surface weight for dyes on SPLT

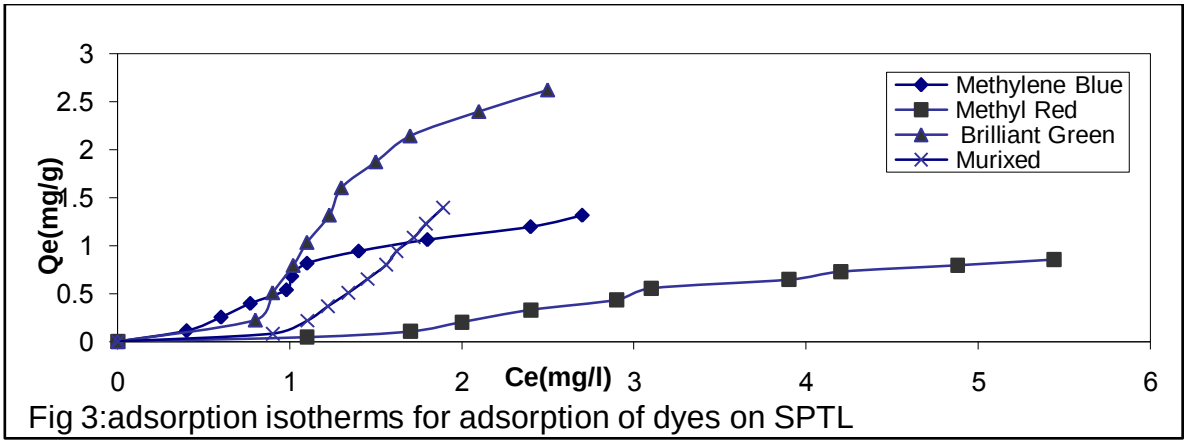

Fig 3:adsorption isotherms for adsorption of dyes on SPTL

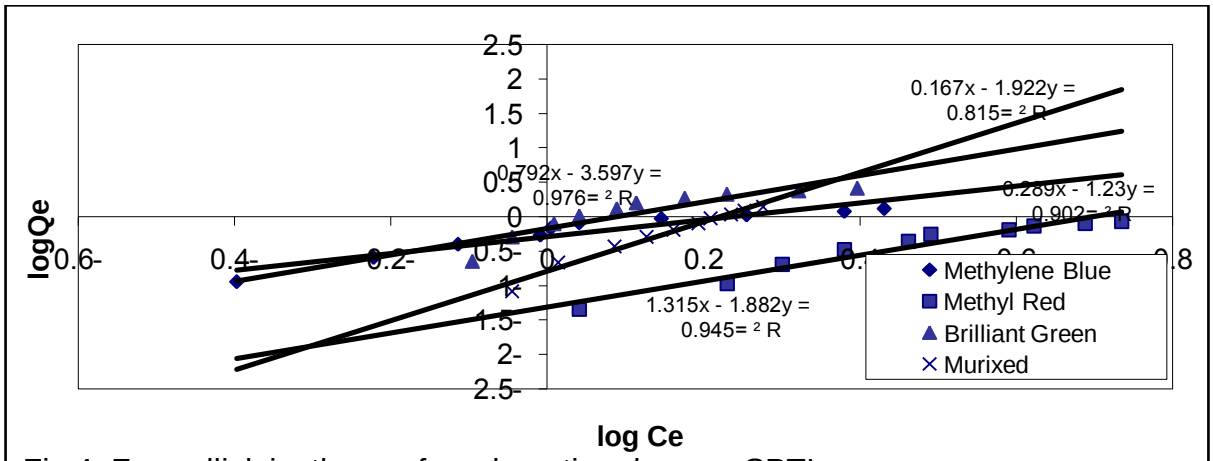

Fig 4: Freundlich isotherms for adsorption dyes on SPTL

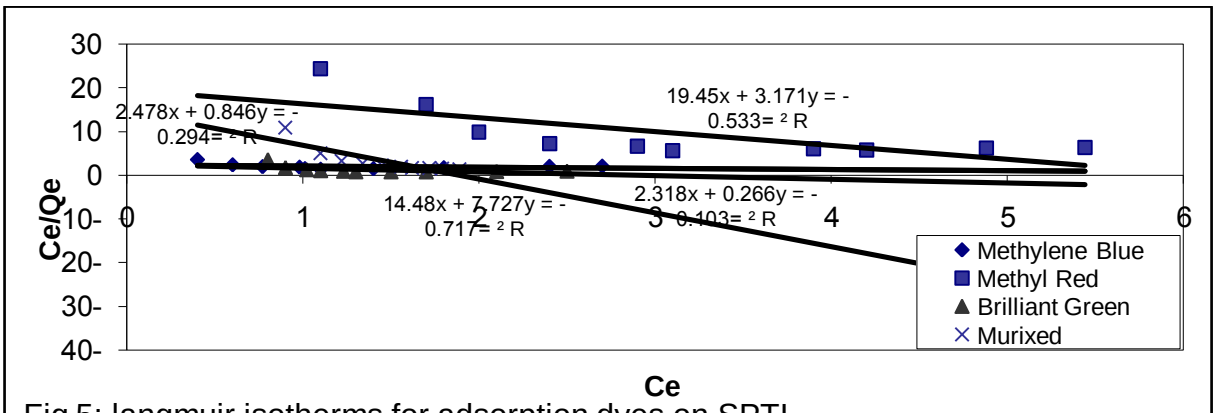

Fig 5: langmuir isotherms for adsorption dyes on SPTL

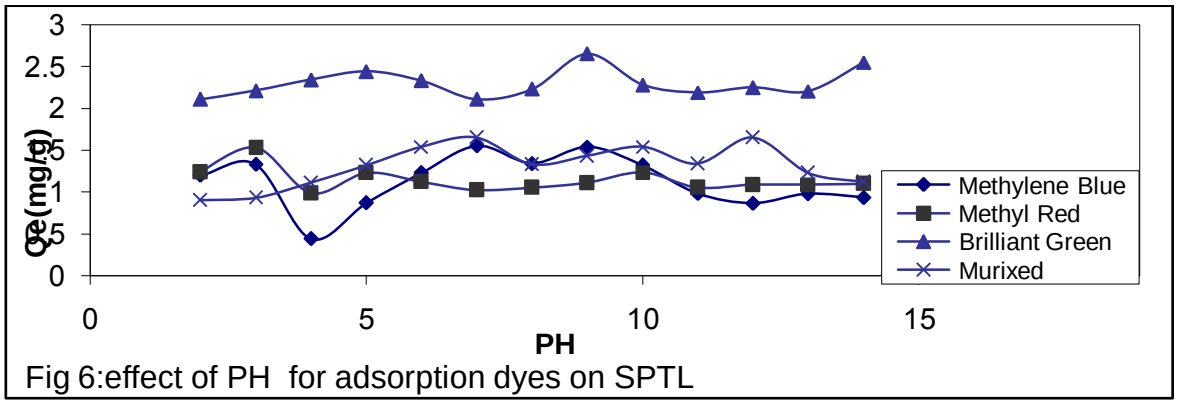

Fig 6:effect of PH for adsorption dyes on SPTL

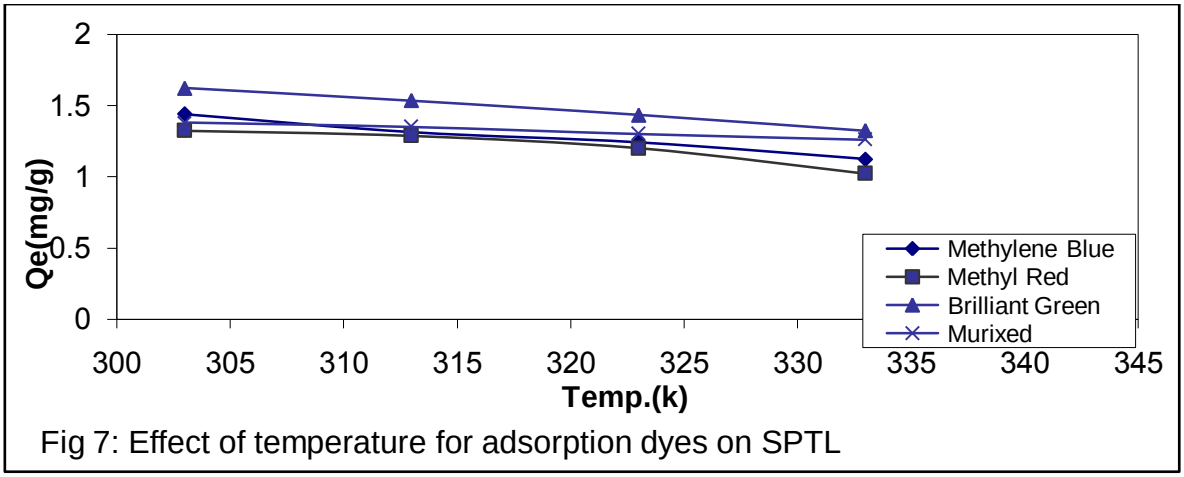

Fig 7: Effect of temperature for adsorption dyes on SPTL

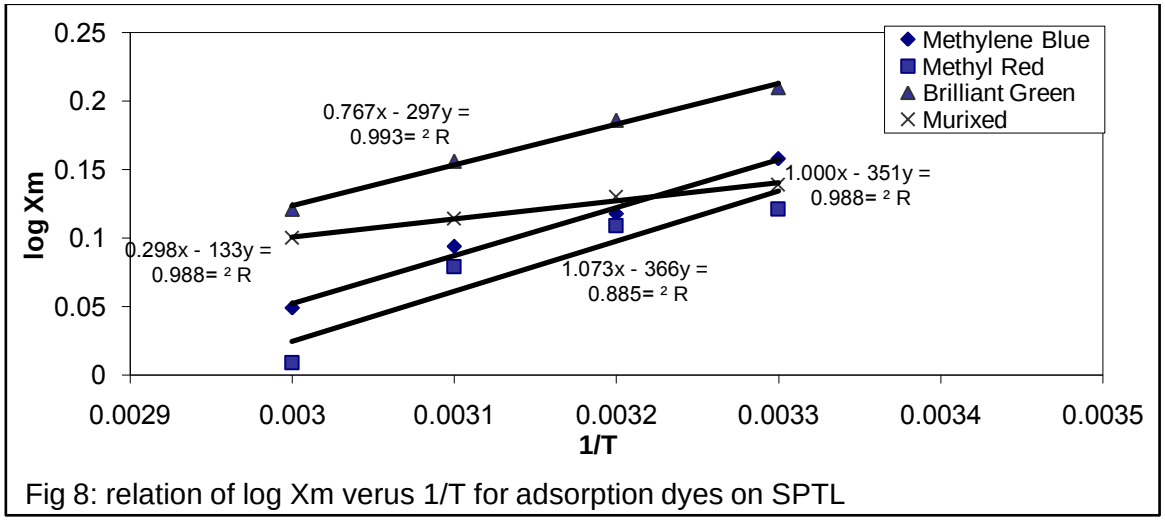

Fig 8: relation of log Xm verus 1/T for adsorption dyes on SPTL

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