Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2015, 7(8):36-45
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Thermodynamics and kinetics of adsorption of azo dye titan yellow from aqueous solutions on natural plant material *Saccharum spontaneum*

***A. Lakshmi Narayanan, **M. Dhamodaran and ***J. Samu Solomon**

[*] *Research & Development Center, Bharathiar University, Coimbatore, Tamil Nadu, India*
[**] *Department of Chemistry, Perunthalaivar Kamarajar Institute of Engineering and Technology, Karaikal, Pudhucherry – UT, India*
[***] *Department of Chemistry, TBML College, Porayar, Tamil Nadu, India*

ABSTRACT

Natural plant material Saccharum spontaneum is used for the removal of the industrial dye (Titan yellow)from aqueous solution. The effects of contact time ,temperatures , initial concentrations and pH values have been investigated . Langmuir and Freundlich isotherms are fitted on the experimental data of adsorption of the studied system. Depending on the results obtained from the effect of temperatures , the thermodynamic parameters (ΔG°, ΔH° and ΔS°) are estimated. The work also included kinetic study conducted by applying two kinetic models, the pseudo first and second order equations . The results proved that, the studied system follows the pseudo second order model indicated by the agreement between the experimental and calculated values of adsorption capacity (qe) at equilibrium .The concentration of the adsorbed dye is determined spectrophotometerically.

Key words: *Saccharum spontaneum,* Titan yellow , Langmuir and Freundlich isotherms, and adsorption,etc...

INTRODUCTION

Azo dyes are a class of coloured organic compounds that have largely used in industry for many applications such as textiles, papers, leathers, additives and analytical chemistry [1]. During dye production and textile manufacturing process, a large quantity of wastewater containing dye stuffs with intensive color and toxicity are introduced into the aquatic systems [2] .In such cases, it is important to remove color from wastes, because the presence of even small amounts of dye [below 1 ppm] is clearly visible and influences water environment considerably .The degradation of azo dyes has been reported in many papers[3-7].The colourants have been used for painting and dyeing of surrounding, skin and cloth by people since the beginning of humankind and they were from natural origin until 19th century. Recent statistics have shown that the production and consumption of dyes in the world have arrived about 700,000 tonnes [8]. Dyes containing chromophores and auxochromes groups can be classified as reactive, metal complex, acid, direct, basic, disperse, pigment, mordant, vat, sulphur, anionic, solvent, ingrain and others. The most of the reactive dyes including a reactive group such as vinyl sulphone are azo or metal complex azo compounds and interact with cotton, wool, etc., to form covalent bond. The release of these dyes, which have the lower degree of fixation due to hydrolysis of reactive groups in the water phase, into the environment is undesirable. Generally, physicochemical and biological methods such as precipitation, flotation, ion exchange, adsorption, oxidation and, bacterial and fungal biosorption and biodegradation [aerobic, anaerobic and anoxic] can be employed to remove colour from dye containing wastewaters [9,10]. The photocatalytic degradation, microemulsions and biological techniques were applied to reduce azo dye effects in the wastewater [11–13]. However, the many researchers have focused on the other alternatives [14–17] because the economically feasible of the process employed is very important. For this purpose, the cheap and efficient alternate materials including biosorbents. Large amounts of dye effluents are annually discharged by textile, cosmetics, paper, leather, pharmaceutical, food and other industries[18] . The dye-containing wastewater can adversely affect the aquatic environment by impeding light penetration.

Moreover, most of the dyes are toxic, carcinogenic and harmful to human health[19,20]. As a result, many governments have established environmental restrictions with regard to the quality of colored effluents and have required dye industries to decolorize their effluents before discharging [21]. Hence, various treatment processes such as physical separation, oxidation, biological degradation, coagulation and flocculation have been developed to remove dyes from waste waters[22,23] . Adsorption process is one of the most efficient and attractive methods for removing pollutants from wastewater, which has interesting characteristics, such as easy process control, low cost and energy requirements [24,25]. Biochar is produced by the combustion of biomass of *Saccharum spontaneum*(Fig. I) under limited oxygen conditions. Biochar is a fine-grained and porous substance and has been applied recently to remove dyes from aqueous solutions [26,27].

Titan yellow is a azo dye, suitable for the dyeing of wool and nylon . It usually exists as a disodium salt. Its molecular formula is $C_{28}H_{19}N_5Na_2O_6S_4$ [Na salt] , its molecular mass is 309.21 g mol $^{-1}$ and its λmax is 370 nm. It is a slightly brown powder soluble in cold water. It causes irritation in the eyes, skin, digestive tract, and respiratory tract.

Fig. I ***Saccharum spontaneum***

MATERIALS AND METHODS

Instrumentation

The pH was adjusted with a digital pH meter [Jenway Model 3320] using HCl [0.1 mol L −1] and NaOH [0.1 mol L −1]. Titan yellow was estimated with a UV/VIS spectrophotometer [Labomed UVD 3500] at λmax 370 nm.

Preparation of adsorbent

Stems of *Saccharum spontaneum*, collected from the karaikal coastal area, was crushed with laboratory-scale crushers, powdered with a disk pulveriser, and sieved to 0-63 mesh [ASTM]. The powdered adsorbent was washed, dried at 105 ◦ C for 10 h in an oven, and stored in high-density polythene [HDPE] bags. The proximate analysis of the coal was carried out by using standard methods [ASTM D 5142-90]. Powdered adsorbent was soaked in HCl [0.1 mol L −1] for 24 h, followed by filtering and washings with distilled water. Afterwards, it was dried in an oven at 105 ◦ C for 10 h and stored in HDPE bags.

Chemicals

All c h e m i c a l s used d u r i n g experimental work were of analytical grade and were used as such without purification. Titan yellow[Fluka], HCl [E.Merck 11.6 M]. Double distilled water was used for the reparation of all types of solution and dilution when required.

Instrumentation

Balance ER-120A [AND], Electric grinder [Kenwood], pH meter HANNA pH 211 [with glass electrode], UV/VIS s p e c t r o p h o t o m e t e r [Labomed, Inc. Spectro UV-Vis double beam UVD =3500].

Standard Solutions

1.0 g of Titan yellowwas taken in 1000 mL measuring flask and dissolved in double distilled water, making volume up to the mark. This was 1000 ppm stock solution of dye. Standard solutions of dye were prepared by successive dilution of stock solution.

Adsorption Experiments

The adsorption studies were carried out at 30 ± 1 °C. pH of the solution was adjusted with 0.1 N HCl.A known amount of adsorbent was added to sample and allowed sufficient time for adsorption equilibrium. Then the mixture were filtered and the remaining dye concentration were determined in the filtrate using [Spectro UV-Vis Double

Beam UVD-3500, Labomed.Inco] at λmax = 370 nm.The effect of various parameters on the rate of adsorption process were observed by varying mesh size of adsorbent contact time, t , initial concentration of dye Co ,adsorbent amount , initial pH of solution and temperature. The solution volume [V] was kept constant 50 mL].The dye adsorption [%] at any instant of time was determined by the following equation:

Dye adsorption [%] = [Co –Ce] × 100/ Co
Where Co is the initial concentration and Ce is the concentration of the dye at equilibrium. To increase the accuracy of the data, each experiment was repeated three times and average values were used to draw the graphs.

Isotherm studies
A series of experiments Were carried out for isothermal and kinetic study of *Saccharum spontaneum* adsorption of Titan yellow dye. Langmuir [eq :1], Freundlich[eq :2], Redlich-peterson[eq :3] and ,Dubinin-Kaganer-Radushkevich[DKR] [eq :4] were plotted by using standard straight-line equations and corresponding parameters were calculated from their respective graphs.

$Ce/X = 1/K*K_L + Ce/ K$ ---------------------- [1]
$\log qe = \log K_F + 1/n \log Ce$ --------------------- [2]
$qe = K_R Ce / [1+bRCe\beta]$ ------------------------ [3]
$\log qe = \log Xm – \beta\varepsilon 2/2.303$ ---------------------- [4]

Ce is the equilibrium concentration of the adsorbate [mg/L] and X is the amount of adsorbate adsorbed [mg/g]. KL indicates monolayer adsorption capacity [mg/g],K is the Langmuir equation constant[L/mg],KF and 1/n are constants for a given adsorbate and adsorbent at a particular temperature and bT [KJ/mol] is adsorption potential of the adsorbent . K_R, b_R,,β are Redlich Peterson constants. Xm is maximum sorption capacity; β is mean sorption energy and ε sorption potential in DKR isotherms

RESULTS AND DISCUSSION

Adsorption of Titan yellow dye on *Saccharum spontaneum* was studied through batch mode, making use of different variables like adsorbent dosage, pH of the medium, contact time, initial concentration of Titan yellowR dye and temperature. The size of adsorbent particles were maintained constant at below 63µm. Experiments were carried out so that the effect of any one variable was studied, keeping all others constant. This was repeated with all the other variables.

Effect of particle Size
The effect of adsorbent's particle size was studied in the range of 0-200 microns mesh particle [0-63, 63-125, 125-200] for checking the maximum adsorption of Titan yellow and the smallest mesh particle [0-63] was shown to be best for adsorption, as particles with smallest size presents a larger surface area and the results are shown in Fig. II.

Effect of adsorbent dosage
The adsorbent dosage is an important parameter, which influences the extent of dye uptake from the solution and thus the effect as shown in Fig. III. It was evident that the amount of dye uptake increases from 55.89 % with 50mg adsorbent up to 93.10% with 200mg adsorbent. Prior to that, it is apparent that the percent removal of Titan yellow dye increases as the adsorbent dosage increases from 50mg up to 200mg due to the limited

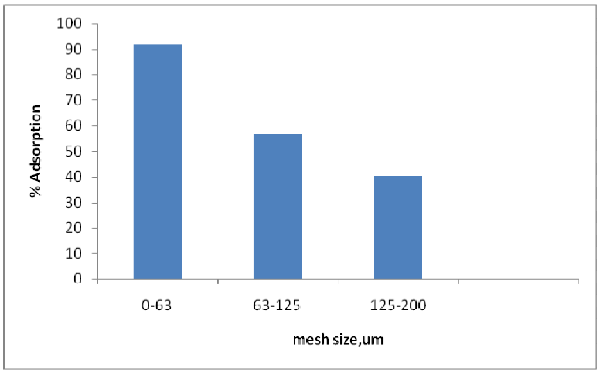

Fig II

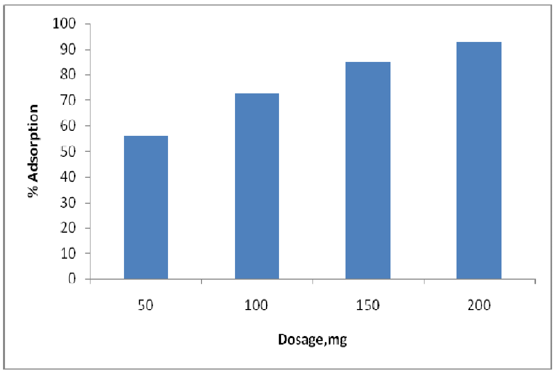

Fig III

availability of the number of adsorbing species for a relatively larger number of surface sites on the adsorbent at higher dosage of adsorbent. It is plausible that with higher dosage of adsorbent there would be greater availability of exchangeable sites from dye. Besides, Fourest and Roux suggested that the reduction in adsorbent dosage in the suspension at a given dye concentration enhances the dye/adsorbent ratio, and thus increases the dye uptake per unit adsorbent, as long as the latter is not saturated. However, in some cases, the adsorption capacity decreased sharply with the increasing of adsorbent dosage these results may due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles. Moreover, the high adsorbent dosage could impose a screening effect of the dense outer layer of the cells, thereby shielding the binding sites from dye. The effect of the mass of the adsorbent in the adsorption of Titan yellow dye was studied at the optimum pH 1.0 and at room temperature [30^0C]. 50 ml of a solution of Titan yellow dye with an initial concentration of 50 mg/L was mixed with 50.0 mg of the adsorbent and the mixture was shaken for 180 minutes. After centrifugation, the amount of Titan yellow dye in the supernatant was estimated quantitatively. From this the percentage of dye adsorbed on the adsorbent was deduced. This procedure was repeated with 100, 150, 200 and 250 mg of the adsorbent and the results are recorded in figure 2. With the adsorbent dosage of 200 mg or more, adsorption reached the maximum. Hence adsorbent dosage was fixed at an optimum amount of 150 mg.

Effect of pH

The acidity of solution pH is one of the most important parameters controlling the uptake of dyes from wastewater and aqueous solutions. The uptake and percentage removal of dye from the aqueous solution are strongly affected by the pH of the solution as illustrated in Fig. 3. The uptake of dye decreases from 92.01 % to 15.04% when the pH increases from pH 1 to pH 6 , sorption is noted to decrease significantly 99.66% adsorption capacity at pH 1. After that the capacity of adsorption decreases deeply in pH range of 7 to 9.The maximum adsorption observed at low pH [pH 1] may be due to the fact that the higher concentration and higher mobility of H^+ ions present favoured the preferential adsorption of Titan yellow dye compared to hydrogen ions. It would be plausible to suggest that at lower pH value, the surface of the adsorbent is surrounded by hydronium ions [H^+], thereby replacing by the dye from the binding sites of the sorbent . In contrast, as the pH decreases, more negatively charged surface becomes available thus facilitating greater dye removal. It is commonly agreed that the sorption of dye cations decreases with increasing pH [Fig IV] as the dye species become high stable in the solution. However, at higher pH values [pH 7, pH 8 and pH 9] there is a decrease in the adsorption capacity. This is due to the occurrence of dye precipitation.

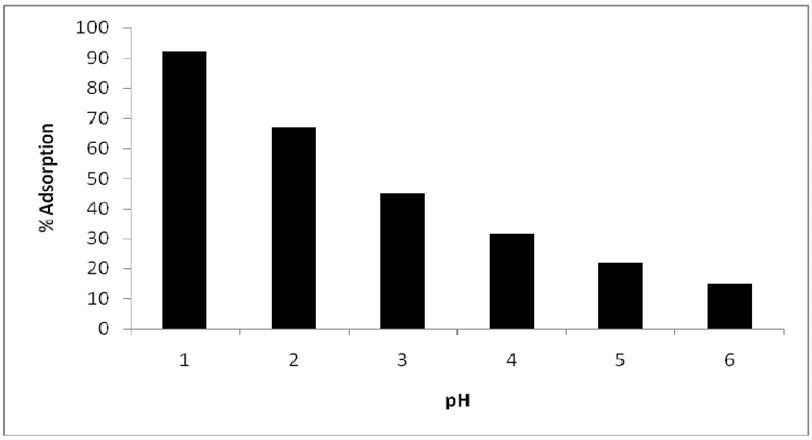

Fig IV

Effect of contact time

The effect of contact time on the adsorption of dye on *Saccharum spontaneum* is shown figure V. Adsorption increases as contact time increases and is maximum [98.45 %] at 3 hours. Figure 4 reveals that the curve is smooth and continuous, Titan yellow dye to saturation, suggesting possible monolayer coverage of the dye on *Saccharum spontaneum*. Nearly 68.04% adsorption has taken place within 30 minutes of contact time with the adsorbent which indicates the efficiency of *Saccharum spontaneum* as adsorbent. More time is required for attainment of equilibrium. In this study, all the batch experiments were carried out for a time interval of 180 minutes.

Effect of initial concentration

Figure VI show that adsorption capacity decreases from 94.21% to 58.84% as the dye concentration increases from 10 to 60 mg/l. The trend is that of the result of the progressive decrease in the electrostatic interaction between the Titan yellow dye and the absorbent active sites. Moreover, this can be explained by the fact that less adsorption sites were being covered as the dye concentration decreases. Besides, lower initial concentrations to an increase in the affinity of the Titan yellow dye towards the active sites. The decline in the adsorption capacity is due to the availability of smaller number of surface sites on the adsorbent for a relatively larger number of adsorbing species at lower concentrations. The experimental results of adsorption of Titan yellow dye on *Saccharum spontaneum* at various initial concentrations are shown in figure 5. It reveals that, the actual amount of dye s adsorbed per unit mass of *Saccharum spontaneum* decreased with increase in dye concentration. Adsorption is maximum when the initial concentration of Titan yellow dyes were 10 mg/L.As the concentration increases, all the adsorption sites are being filled up and there remains unadsorbed dye, hence the decrease in percentage adsorption. This result is in favour of only monolayer coverage and suggests the application of the Langmuir isotherm model. Since 94.21% adsorption occurs when the initial concentration was 10 mg/L, *Saccharum spontaneum* appears to be very effective adsorbent in removing even traces of dye

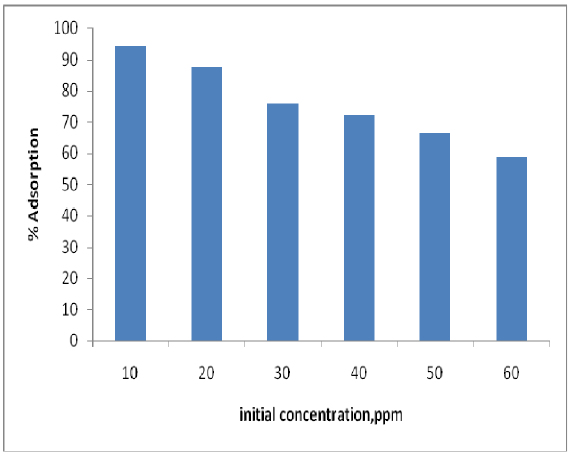

Fig VI

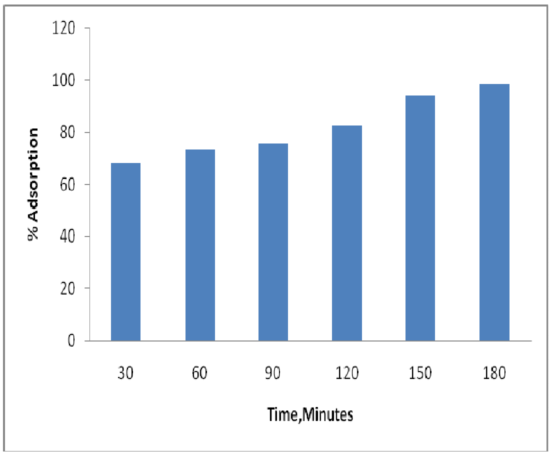

Fig V

Adsorption isotherms

Isotherm parameters, evaluated from the linear plots of equations 1-4 are illustrated in Table I, [Fig. VIIa and VII.b].The K_L [sorption equilibrium constant] value for the Langmuir isotherm, ie. 3.984 mg/g indicated the high adsorption capacity of biosorbent toward dye adsorption. This is in turn supported by the values of the dimensionless separation factor [R_L], which are less than 1.The R^2 [correlation coefficient] value 0.983 indicated that the Langmuir isotherm is good for explaining the dye adsorption. The R^2 value calculated for the Freundlich isotherm was found to be 0.989, indicating that the experimental data can be explained by the Freundlich isotherm. The K_F [ultimate adsorption capacity] value as calculated from the Freundlich isotherm was 3.9536. The values of Freundlich constant, n, are much greater than 1, implying that the adsorption process is governed by physisorption only The R^2 value calculated for the Redlich-peterson isotherm was found to be 0.992, indicating that the experimental data can be explained by the Redlich-peterson isotherm. The β value as calculated from this isotherm was 1.1653. The Dubinin–Kaganer–Radushkevich [DKR] model was adopted to describe the single-solute adsorption isotherms. The R^2 value calculated for the DKR isotherm was found to be 0.959, indicating that the experimental data can be explained by the DKR isotherm poorly. The β value as calculated from this isotherm was 0.301. The values of desorption constant, β, in the Redlich-Peterson and the Dubinin-Kaganer-Radushkevich isotherms is a measure of the desorption constant. Its values are less than 1, indicating favourable adsorption. The sorption energy ε in the DKR isotherm is a valuable parameter to distinguish between physisorption and chemisorptions. Lower values suggest physisorption is more.

Table I

K_L	q0	b_L	R^2
3.9840	13.15789	0.3027	0.983
K_F	N		R^2
3.9536	2.8328		0.989
β	B	q0	R^2
1.1653	0.549	3.2062	0.992
β	b_R	K_R	R^2
0.301	3.3222	0.8704	0.959

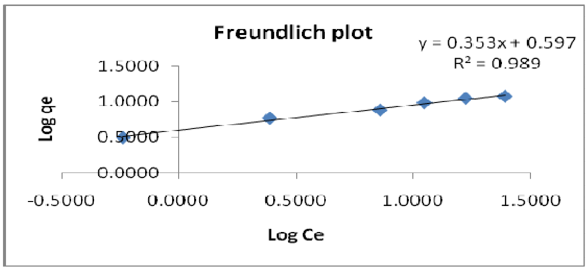

Fig. VIIa

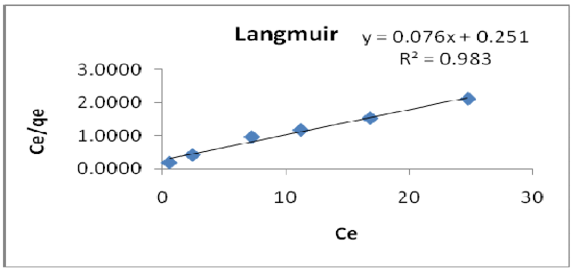

Fig. VIIb

Kinetics

Kinetics of adsorption is a characteristic responsible for the efficiency of adsorption. Since the initial sorption rate plays a crucial role, adsorption was measured at time intervals 10, 20,30,40,50 and 60 minutes. The kinetics of adsorption of Titan yellow dye on *Saccharum spontaneum* was followed by the use of four models:

Lagergren's pseudo-first order kinetics
Pseudo-second order kinetics.
The Elovich kinetics
The intra-particle diffusion model.

The kinetics parameters are given in table II [Fig. VIII]. Analysis of the kinetics parameters shows that there is no correlation between theoretical and experimental qe values for the Lagergren's first order kinetics and hence the adsorption process is not likely to be of the first order. The R^2 values for the second order[eq 5] kinetics shows high precision suggesting that second order kinetics is a best fit.

Log [qe-qt] = log qe - [K1t / 2.303] ----------------- 5

Table II

I Order	K1	0.00921	Qe	1.3073	R^2=0.834
II Order	qe	3.6764	K2	0.0948	R^2=0.972
Int part diff	Kp	0.130	C	1.443	R^2=0.914
Elovich model	β	0.320	α	1.152	R^2=0.898

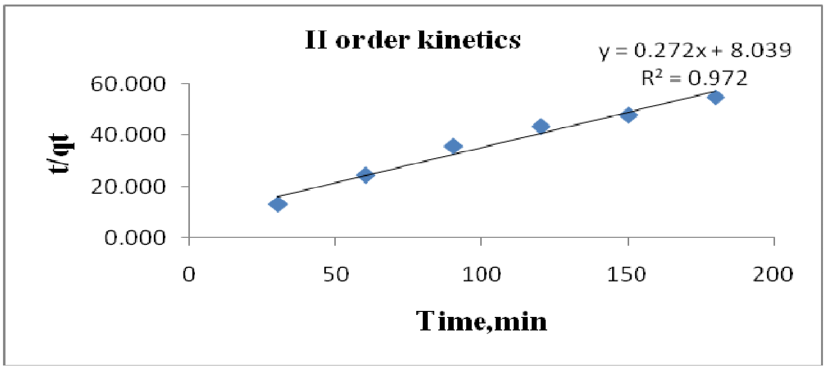

Fig VIII

Thermodynamic parameters

Thermodynamic parameters such as standard Gibbs free energy [ΔG0],Enthalpy [ΔH0] and entropy [ΔS0] were also calculated using equations 6 and 7 and the results obtained are illustrated in table-III [Fig IX].

ΔG0 =-RTlnK ----------------------------6
lnKc = [ΔS0/R]-[ΔH0/RT]--------------------------7

Here, K denotes the distribution coefficient for the adsorption. R is the universal constant and T is the absolute temperature in Kelvin. The negative value of the Δ G 0 at the studied temperature range indicated that the sorption of Titan yellow on sorbent was thermodynamically feasible and spontaneous. The increase in the value of Δ G 0 with temperature further showed the increase in feasibility of sorption at the elevated temperature for *Saccharum spontaneum*. In other words, sorption is endothermic in nature .The positive value of ΔH0 for *Saccharum spontaneum* showed that the sorption was endothermic. The positive value of ΔS0 showed an increased randomness at the solid Titan yellow solution interface during the adsorption of alizarin yellow, reflecting the affinity of *Saccharum spontaneum* for alizarin yellow.

Table III

ΔG0	ΔH0	ΔS0	Log 10 Ka	1/T
-3844.96	16.0836	67.78088	0.662534	0.003299
-5069.51			0.845644	0.003193
-6048.34			0.977701	0.003095
-7341.05			1.151045	0.003002

Arrhenius equation

Activation energies for adsorption of Titan yellowon adsorbent was calculated using the Arrhenius equation [eq 8],plotted in Fig IX and tabulated in table IV.The activation energy obtained[Table IV] in this case ,indicate that physical forces are involved in the sorption mechanism and sorption feasibility.

Arrhenius equation

Log K = Log A – [EA / 2.303 RT] ------------- 8

Table IV

Ea	Log A	R2
30.88434	5.986	0.996

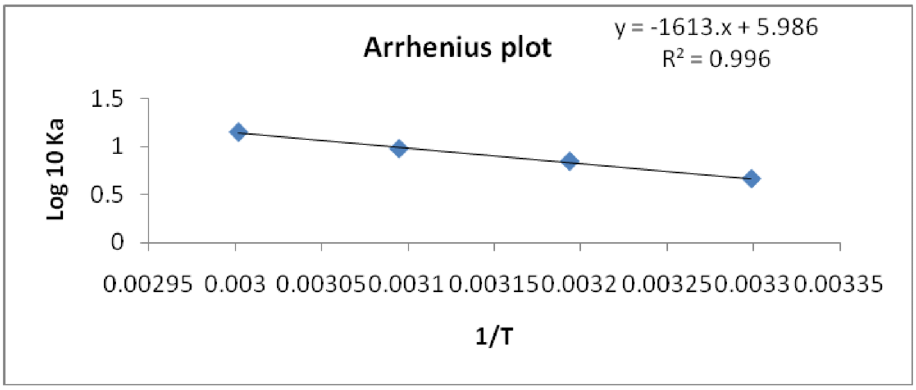

Fig IX

The thermodynamic parameters for the adsorption of Titan yellow dye on *Saccharum spontaneum* are given in table IV. For the adsorption of dye on *Saccharum spontaneum*, the free energy values are all negative confirming that the process is spontaneous even at room temperature. The entropy change is positive and explains the increase in randomness of the process. The endothermic nature of the adsorption process is evident from the positive values of enthalpy change. Presumably, the randomness factor [TΔS] overcomes the energy factor [ΔH] and makes the overall process spontaneous [ΔG negative]. Activation energies for adsorption of Titan yellowR dye on adsorbent was calculated using the Arrhenius equation [eq 6-8], plotted in Fig 8 and tabulated in table 8b.The activation energy obtained in this case, indicate that physical forces are involved in the sorption mechanism and sorption feasibility.

Effect of temperature

Temperature has an important effect on the rate of adsorption. The percentage of dye adsorption was studied as a function of temperature in the range of 30-60 °C. It was observed that adsorption yield increase with increase in temperature. The minimum adsorption w a s 93.24 % a t 30 ° C a n d maximum adsorption was 97.70 % at 60 °C for 50 ppm initial concentration of dye solution. The effect of temperature on the percentage adsorption of dye on *Saccharum spontaneum* is shown in figure X and table IX. This is only natural because increase in temperature provides the necessary energy for the endothermic process of adsorption, to an increase in the rate of the process. The point to be appreciated is that even at room temperature sufficient [more than 90%] adsorption has taken place. This in turn confirms the efficiency of the adsorbent in the removal of toxic dye.

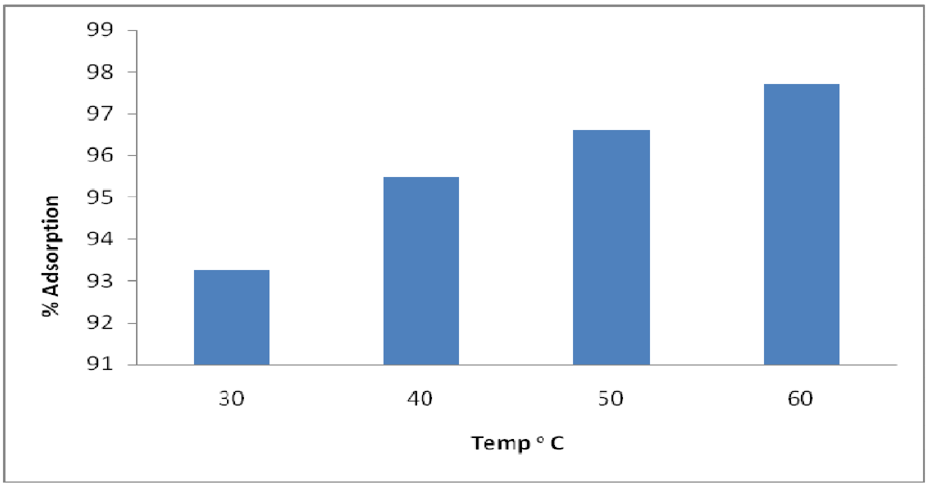

Fig X

FT-IR Study

The action of oxidizing Oxygen on the surface of the carbonaceous precursor causes formation of surface oxides Their structure have not been investigated completely because of the greater number of possible surface groups .The most common Oxygen groups on the surface are carboxylic, lactonic and phenolic .These groups have acidic character, which can be relatively easily determined by titration methods that are based on titrations using bases of different strengths. The method of Boehm has been followed to find the density of functional groups present on the carbon surface.FT-IR [SHIMADZU]spectra of the activated carbon samples before and after adsorptions are shown in the figures[XIIa &XIIb] respectively. The spectra provide the evidences for the presence of surface groups on the adsorbent's surface as established by Boehm. Notable differences among them are the peak intensities .The carbons have marked differences in the intensities of nearly all the absorption bands , reflecting that the density of corresponding functional groups differ a lot. After adsorption some peaks is vanished due to desorption in to adsorbate and few peaks are slightly shifted to higher or lower wave numbers due to electrostatic forces. There are no new peaks after adsorption confirmed the absence of formation of new compounds shown.

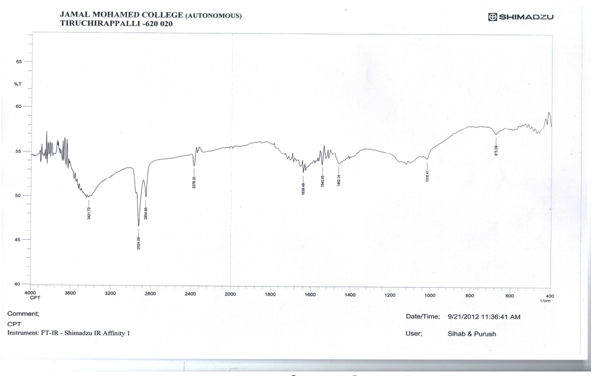

Figure XIIa, Before Adsorption

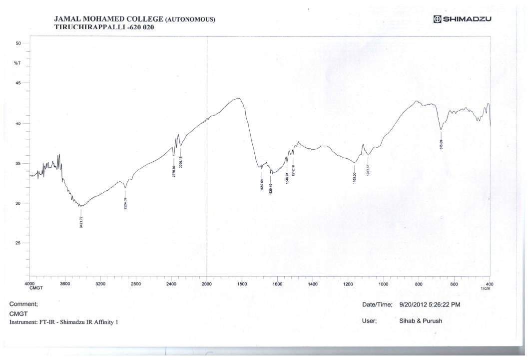

Figure XIIb, After Adsorption

SEM analysis

The surface morphology of *Saccharum spontaneum* was examined using Scanning Electron Microscopy [SEM], before and after adsorption and the corresponding SEM micrographs were obtained at an accelerating voltage of 15 kV [Hitachi SE 900] at 5000× magnification and are presented in figures XIII a and XIII b. At such magnification, the *Saccharum spontaneum* particles showed rough areas of surface within which micropores were clearly identifiable.

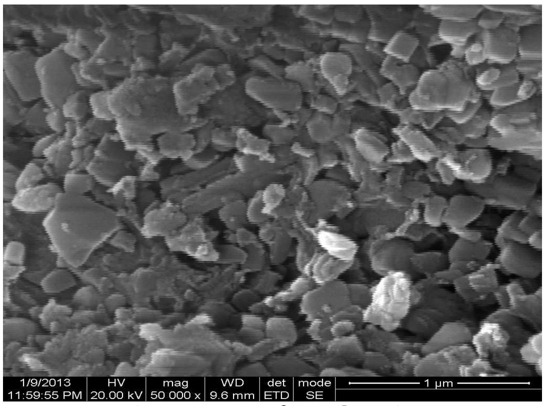

Figure XIII a ,Before Adsorption

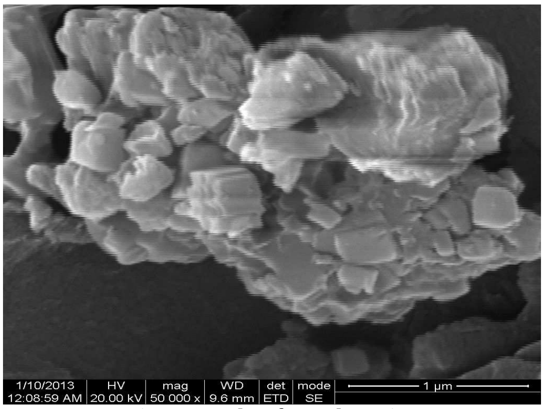

Figure XIII b, After Adsorption

XRD Study

The X-ray Diffraction Studies of the adsorbent *Saccharum spontaneum*, before and after adsorption of dye, were carried out using Rigaku Corporation, Japan X-ray Diffractometer 40KV / 30mA, Model D/Max ULTIMA III. The diffraction patterns are shows in figure XIV a and XIV b. It is evident from the figures that there is no appreciable change in the spectra of adsorbent before and after adsorption. This may be due to the fact that adsorption does not alter the chemical nature of the surface of the adsorbent. The adsorption is governed by weak Van der Waals forces and is physical in nature.

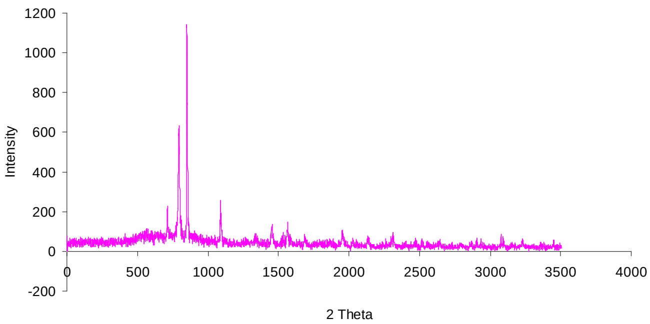

Figure XIV a, Before Adsorption

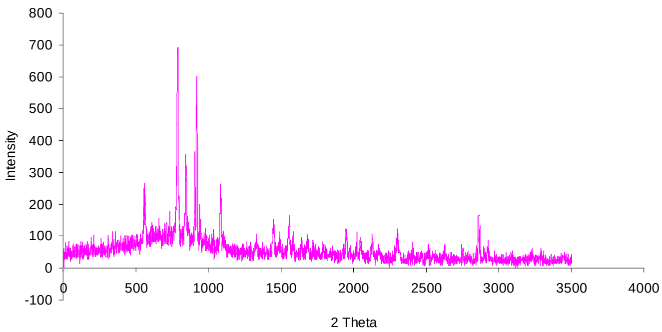

Figure XIV b, After Adsorption

REFERENCES

[1] M. Dakiky and I. Nemcova, *J.Dyes Pigments*, **2000**, 44, 181.
[2] M.A. Brown and S.C. De Vito, *J.Environ. Technol.* , **1993**, 23 249.
[3]A.O. Ibhadon, G.M. Greenway and Y. Yue,J. *Catal Commun*., **2008**, 9, 153.
[4] N. Sobana, M. Muruganadham and M. Swaminathan, *J. Mol. Catal. A: Chem*., **2006**, 258, 124.
[5]E. Bizani,K.Fytianos, I. Poulios and V. Tsiridis, *J. Hazard. Mater*., **2006**, 136, 85.
[6]C. Sahoo and A.K. Gupta, *J. Desalination*, **2005**, 181, 91.
[7]S. Songa, L. Xua, Z. He, H.Ying, J. Chen, X. Xiao and B. Yan, *J. Hazard. Mater*., **2008**, 152, 1301.
[8] H. Qllgaard, L. Frost, J. Galster, O.C. Hansen, Survey of Azo-colorants in Denmark: Consumption, Use Health and Environmental Aspects, Ministry of Environment and Energy, Denmark, **1998**.
[9] T. Robinson, G. McMullan, R. Marchant, P. Nigam, *Bioresour. Technol*. 77 [**2001**] 247–255.
[10] O. Tunay, I. Kabdasli, G. Eremektar, D. Orhon, *Water Sci. Technol*. 34 [**1996**] 9–16.
[11] N.M. Mahmoodi, M. Arami, N.Y. Limaee, *J. Hazard. Mater*. B 133 [**2006**] 113–118.
[12] T.N.C. Dantas, L.T.C. Beltrame, A.A.D. Neto, M.C.P.A. Moura, *J. Chem. Technol. Biotechnol*. 79 [**2004**] 645–650.
[13] M.S. Khehra, H.S. Saini, D.K. Sharma, B.S. Chadha, S.S. Chimni, *Dyes Pigments* 67 [**2005**] 55–61.
[14] S. Netpradit, P. Thiravetyan, S. Towprayoon, *J. Colloid Interface Sci*. 270 [**2004**] 255–261.
[15] S.D. Lambert, N.J.D. Graham, C.J. Sollars, G.D. Fowler, *Water Sci. Technol*. 36 [**1997**] 173–180.
[16] F.C. Wu, R.L. Tseng, r.S. Juang, *Environ. Technol*. 22 [**2001**] 721–729.
[17] I.A. Balcioglu, I. Arslan, M.T. Sacan, *Environ. Technol.* 22 [**2001**] 813–822.
[18].Safarikova M, Ptackova L, Kibrikova I, Safarik I [**2005**] *Chemosphere* 59[6]:831–835
[19].Yang YY, Li ZL, Wang G, Zhao XP, Crowley DE, Zhao YH [**2012**] *PLoS ONE* 7[3]:e33551

[20].Debrassi A, Baccarin T, Demarchi CA, Nedelko N, SlawskaWaniewska A, Dluzewski P, Bilska M, Rodrigues CA [**2012**] *Environ Sci Pollut* R 19[5]:1594–1604
[21].Shen DZ, Fan JX, Zhou WZ, Gao BY, Yue QY, Kang Q [**2009**] *J Hazard Mater* 172[1]:99–107
[22].Forgacs E, Cserha´ti T, Oros G [**2004**] *Environ Int* 30[7]:953–971
[23].Chen DZ, Zhang JX, Chen JM [**2010**] *Int J Environ Sci Technol* 7[2]:235–242
[24].Mittal A, Thakur V, Gajbe V [**2012**] *Environ Sci Pollut* R 19[6]: 2438–2447
[25].Mahmoud DK, Salleh MAM, Karim W, Idris A, Abidin ZZ [**2012**] *Chem Eng J* 181:449–457
[26].Qiu YP, Zheng ZZ, Zhou ZL, Sheng GD [**2009**] *Bioresource Technol* 100[21]:5348–5351
[27].Xu RK, Xiao SC, Yuan JH, Zhao AZ [**2011**] *Bioresource Technol* 102[22]:10293–10298