International Journal of Applied Environmental Sciences
ISSN 0973-6077 Volume 11, Number 2 (2016), pp. 475-490

http://www.ripublication.com

Statistical analysis of acid blue-113 dye removal using palm tree male flower activated carbon

Kritika Talwar, Srinivas Kini, K. Balakrishna, V.R.C Murty

Manipal Institute of Technology, Manipal, Karnataka-576104, India.

Abstract

Palm tree male flower activated carbon (PTMFAC) was employed as adsorbent for removal of Acid blue-113 (AB) dye from aqueous solution. The interactive effect of five different experimentally controlled environmental factors viz. temperature, initial pH, AB dye concentration, agitation speed and adsorbent dose on removal efficiency was optimized using response surface methodology (RSM) combined with three-level, Five-variable, Box-Behnken design (BBD) to obtain the results. Statistical method was used to evaluate the adequacy of developed model. It was observed that there is consonance in results between values predicted by model (188.07 mg g^{-1})and observed experimental values(188.077 mg g^{-1}). The work indicated that water contaminated with AB dye can be effectively removed by using PTMFAC.

Keywords: Box-Behnken design, Response surface modelling, Adsorption, Process modelling, Acid blue dye, Palm tree male flower activated carbon.

Introduction

Effluents discharged from textile, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries contain residues of dyes. Currently, there exists about 10, 000 different commercial dyes and pigments exist and over $7x10^5$ tones of synthetic dyes are produced annually worldwide [1.]It is estimated that 10-15% of the dyes are lost in the effluent during the dyeing processes [2]. As a result, many governments have established environmental restrictions with regard to the quality of coloured effluents and have impressed upon dye industries to decolorize their effluents before discharging. For treatment of these coloured effluents, adsorption process is one of the effective techniques for removal of color.

Commercially activated carbon is used as adsorbing agent for removal of industrial colored effluents but is associated with greatest drawback of being expensive due to its high cost of manufacturing and regeneration. Some of the naturally occurring adsorbents used for effluent treatment are viz. chitosan, zeolites, fly ash, coal, paper mill sludge, clay minerals, siliceous material, and industrial waste products [3]. These adsorbents have been researched in recent past. Recently number of agricultural wastes also which are by-products of cellulosic origin have also been analyzed to remove dyes from waste water. Some of these agricultural waste tried are coir pith, maize bran, rice, and husk, orange peel, lemon peel, saw dust, barley straw, egg shell, sunflower stalks and pea nut hulls.

In this study Activated Carbon was prepared by using palm tree male flower (PTMF) considering its easy availability and low cost. PTMF applicability as adsorbent for removal of acid blue-113 (AB) was investigated from aqueous solution. It has been established theoretically and experimentally by various researches that activated carbon prepared from agricultural by-products that adsorption process is affected by five process variables i.e. temperature, initial solution pH, initial AB dye solution, agitation speed and PTMFAC concentration. The results in these researches have been analyzed using various tools such as factorial method, response surface method, Box-Behnken, central composite, artificial neural network. For the analysis and study of combined effect of five variables in this study response surface methodology (RSM) combining Box-Behnken Design (BBD) was used.

Material and Methods

In this study acid Blue-113 (Procured from Thomas baker, India.) (C.I. 26360, $C_{32}H_{21}N_5Na_2O_6S_2$, mol. wt. 681.65, IUPAC name disodium;8-anilino-5-[[4-[(3-sulfonatophenyl)diazenyl]naphthalen-1-yl]diazenyl]naphthalene-1-sulfonate with the chemical structure (Fig. 1) was used as dye[4]. All other reagents and chemicals used in the study were of analytical reagent grade. The absorbance values were recorded by using UV spectrophotometer at maximum wavelength of 566nm [5].

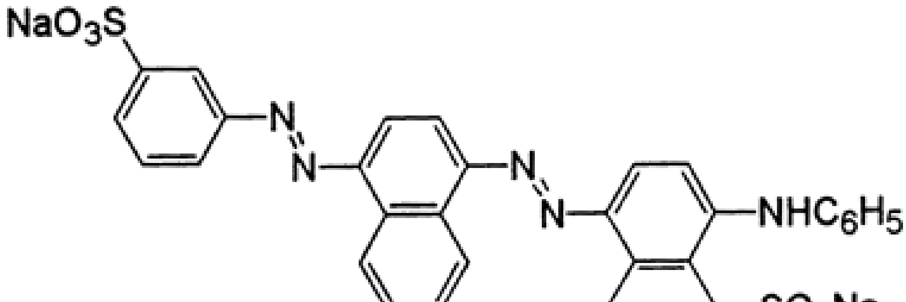

Figure 1: Chemical structure of Acid Blue-113 dye in neutral medium

Adsorbent preparation

Naturally occurring Palm tree male flower (*B. Flabellifer)* [6] was chopped into small pieces and dried at 105^{0}C in hot air oven for 24hrs to minimize its moisture content.

The dried PTMF was then mixed thoroughly with 88% ortho-phosphoric acid (1:1, w/v).The obtained mixture was then carbonized in a muffle furnace at 410^{0}C for 1.5hours.The carbonized sample thus obtained was first washed with water 2-3 times followed by 2% sodium bicarbonate ($NaHCO_3$) for six hours to neutralize its pH (from 2 to 6). The washed neutralized sample was then dried at 60^{0}C in a hot oven for 24 hours and finally grinded and sieved. The PTMFAC thus prepared was stored in air tight container for further experimental use.

Adsorbent characterization

The BET studies were carried out in a BET analyser (manufactured by smart instruments which complies with ASTM D 4567-03(2004)) for measuring surface area and pore volume respectively. The analysis of particle size was carried in 1064 manufactured by Cilas instruments which comply with ISO 13320 standard for measurement accuracy and repeatability. Proximate analysis was also done for finding moisture, ash, volatile matter and fixed carbon content before and after chemical activation [8, 9].

Table 1: Characteristics of PTMFAC

Surface area	468 m^2/gm	
Pore volume	0.3153 cc/gm	
Mean diameter*	72.08 µm	
Proximate analysis	Before activation	After activation
Moisture content	5.05%	11.6%
Volatile matter	32.9%	7.25%
Ash content	20.86%	1.78%
Fixed carbon content	41.9%	79.73%

(Mean diameter was averaged by dia @10, 50, 90 % which was 7.93, 54.89, 163.07 µm respectively)*

It can be inferred from proximate analysis that (Table 1) fixed carbon content has increased considerably from 41.9% to 79.73% after chemical activation. This is due to bond cleavage and dehydration followed by extensive cross linking binds volatile matter to fixed carbon.

Adsorption experiment

Adsorption experiments were performed on a sample of 100ml of dye solution by changing pH, temperature, amount of adsorbent, concentration of dye and agitation speed. The contact time for all the experiments was kept as five hours (chosen after testing pilot samples where it was noticed this time was sufficient for obtaining saturation in adsorption) The range selected for the variables are tabulated in Table 2.

Table 2: Range for five parameters

Parameter	Low	High
pH	4	9
Temperature (^{0}C)	30	50
Amount of adsorbent(g)	0.1	1
Concentration of dye(mg/L)	25	200
Agitation speed(rpm)	100	200

Table of experiments was created using Design Expert software9 (Version-9.0.6.). Box Benkhen design was employed for RSM studies by varying five parameters. The filtrate form each experiment was analysed using the UV spectrophotometer (At a maximum wavelength of 566nm) and corresponding equilibrium adsorption capacity (Qe) & % removal values were calculated using the equations (1) & (2) respectively [11-13].

$$Qe = \frac{C_o - C_e}{M} \times V \quad (1)$$

Where,
C_o-Initial concentration in mg/L
V-Volume of dye solution in L
C_e-Final equilibrium concentration in mg/L
M-Amount of adsorbent in grams

$$Percentage\ Removal = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

The experimental conditions and responses, Q_e (mg/g) & % removal measured through the batch experiments are presented in Table 3.

Table 3: RSM studies for adsorption of AB on PTMFAC

Std	Run	pH	Amount of adsorbent in grams	Concentration of dye in PPM	Temperature in K	Agitation in RPM	Qe in mg/g	%removal
7	1	6.5	0.55	25	50	150	3.8182	84
8	2	6.5	0.55	200	50	150	36.0129	99.0355
23	**3****	**6.5**	**0.1**	**200**	**40**	**150**	**188.077**	**94.0385**
31	4	6.5	0.55	25	40	200	3.9003	85.806
32	5	6.5	0.55	200	40	200	35.6362	97.999
40	6	6.5	1	112.5	50	150	10.918	97.048
33	7	4	0.55	112.5	40	100	20.3565	99.5204
43	8	6.5	0.55	112.5	40	150	19.6574	96.103
46	9	6.5	0.55	112.5	40	150	19.6574	96.103

36	10	9	0.55	112.5	40	200	19.2392	94.3223
5	11	6.5	0.55	25	30	150	3.6648	85.3408
20	12	6.5	0.55	112.5	50	200	19.225	93.768
21	13	6.5	0.1	25	40	150	21.6923	86.7692
10	14	6.5	1	112.5	40	100	10.9114	96.9902
9	15	6.5	0.1	112.5	40	100	93.269	85.9058
17	16	6.5	0.55	112.5	30	100	19.603	95.8286
11	17	6.5	0.1	112.5	40	200	93.8846	83.4538
29	18	6.5	0.55	25	40	100	3.9289	86.436
1	19	4	0.1	112.5	40	150	112.192	99.7265
13	20	4	0.55	25	40	150	4.3633	95.992
41	21	6.5	0.55	112.5	40	150	19.6574	96.103
19	22	6.5	0.55	112.5	30	200	18.5238	90.5608
28	23	9	0.55	112.5	50	150	19.5452	95.5542
22	24	6.5	1	25	40	150	1.0908	43.63
42	25	6.5	0.55	112.5	40	150	19.6574	96.103
15	26	4	0.55	200	40	150	36.3336	99.9175
2	27	9	0.1	112.5	40	150	73.039	64.9236
45	28	6.5	0.55	112.5	40	150	19.6574	96.103
35	29	4	0.55	112.5	40	200	20.3413	99.4463
16	30	9	0.55	200	40	150	35.4249	97.4183
12	31	6.5	1	112.5	40	200	10.764	95.68
44	32	6.5	0.55	112.5	40	150	19.6574	96.103
30	33	6.5	0.55	200	40	100	35.7055	98.1902
26	34	9	0.55	112.5	30	150	19.6711	82.5145
39	35	6.5	0.1	112.5	50	150	106.577	94.7351
18	36	6.5	0.55	112.5	50	100	19.7975	96.788
25	37	4	0.55	112.5	30	150	20.2586	99.0421
34	38	9	0.55	112.5	40	100	19.7874	96.738
6	39	6.5	0.55	200	30	150	35.8318	98.537
27	40	4	0.55	112.5	50	150	20.3985	99.726
24	41	6.5	1	200	40	150	19.322	96.61
37	42	6.5	0.1	112.5	30	150	87.039	77.368
38	43	6.5	1	112.5	30	150	11.0138	97.79
3	44	4	1	112.5	40	150	11.142	99.04
4	45	9	1	112.5	40	150	10.5318	93.616
14	46	9	0.55	25	40	150	2.9075	63.966

***Represents optimum conditions for maximum adsorption capacity*

Results and Discussion

The model parameters and statistical significance of the regression coefficients for various models was tested using the analysis of variance (ANOVA) and the t test statistics [15]. The results are depicted in Table 3

Table 3: Model summary analysis was obtained for adsorption capacity of PTMFAC on AB dye

Source	Std. Dev	R-Squared	Adjusted R-Squared	Predicted R-Squared	Adeq. Precision	PRESS***	Remarks
Linear	23.10	0.6452	0.6008	0.5173	4.607	29028.46	
2FI	22.64	0.7442	0.6163	0.3213	9.098	40813.72	
Quadratic	9.35	0.9464	0.9036	0.7858	21.503	12884.16	Suggested
Cubic	2.38	0.9991	0.9958	0.9399	19.635	3614.41	Aliased

*** *PRESS-Predicted Residual Sum of Squares*

The linear and 2FI model were rejected due to low R^2 and low adequate precision value. A ratio greater than 4 for Adequate precision (Measures signal to noise ratio) is desirable, which is the main reason for rejecting linear and 2FI models.
Even though R^2 & Adjusted R^2 value obtained for cubic model are better than quadratic model, the quadratic model is chosen, considering the interaction of factors. The interaction between the factors will be significant is based on past research [16-19]. A ratio of 21.503 for quadratic model indicates an adequate signal and thus this model is used to navigate the design space. This was suggested by the software also. This can also be seen from Table 4 where one of the interaction factors (BC) has become significant.
Thus the ANOVA results were obtained for RSM quadratic model for adsorption of AB dye as depicted in Table 4:

Table 4: ANOVA results of response surface quadratic model for adsorption of AB dye

Source	Coefficient	Sum of Squares	df	Mean squares	F-value	p-value	Remarks
Model	19.66	56917.76	20	2845.89	22.09	< 0.0001	significant
A-pH	-2.83	127.92	1	127.92	0.99	0.3286	
B-Amt of adsorbent	-43.13	29762.84	1	29762.84	231.00	< 0.0001	significant
C-Conc. of dye	23.56	8882.02	1	8882.02	68.94	< 0.0001	significant
D-Temp	1.29	26.75	1	26.75	0.21	0.6526	
E-agitation speed	-0.12	0.21	1	0.21	1.651E-003	0.9679	
AB	9.64	371.39	1	371.39	2.88	0.1020	
AC	0.14	0.075	1	0.075	5.808E-004	0.9810	
AD	-0.066	0.018	1	0.018	1.371E-004	0.9908	
AE	-0.13	0.071	1	0.071	5.512E-004	0.9815	
BC	-37.04	5487.36	1	5487.36	42.59	< 0.0001	significant
BD	-4.91	96.37	1	96.37	0.75	0.3953	
BE	-0.19	0.15	1	0.15	1.130E-003	0.9735	
CD	6.925E-003	1.918E-004	1	1.918E-004	1.489E-006	0.9990	
CE	-0.010	4.141E-004	1	4.141E-004	3.214E-006	0.9986	
DE	0.13	0.064	1	0.064	4.982E-004	0.9824	

A^2	-0.53	2.44	1	2.44	0.019	0.8916	
B^2	34.13	10167.26	1	10167.26	78.91	< 0.0001	significant
C^2	1.32	15.19	1	15.19	0.12	0.7342	
D^2	1.587E-003	2.199E-005	1	2.199E-005	1.707E-007	0.9997	
Residual		3221.04	25	128.84			
Lack of fit		3221.04	20	161.05			
Pure error		0.000	5	0.000			
Cor Total		60138.80	45				

The Model F-value of 22.09 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. In this case Amount of adsorbent (B), Concentration of dye(C), BC, B^2 are significant model terms.

Response surface quadratic equation

ANOVA analysis of the batch studies result into a quadratic equation (3). Significant factors are distinctively shown.

$$Q_e = 19.66 - 2.83A - \mathbf{43.13B} + \mathbf{23.56}C + 1.29D - 0.12E + 9.64AB + 0.14AC - 0.066AD - 0.13AE - \mathbf{37.04}BC - 4.91BD - 0.19BE + 6.925e - 003CD - 0.010CE - 0.53A^2 + \mathbf{34.13}B^2 + 1.32C^2 + 1.587e - 003D^2 - 0.58E^2 \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

The measured and the model predicted values of the response variable were used to calculate the coefficient of determination (R^2), Adjusted and predicted R^2 (refer Table 3). The results obtained indicate good correlation (188.07 mg g^{-1}, experimental & 188.077 mg g^{-1}, predicted) as evident from Figure1.

Response surface quadratic model

This tested equation (Equation (3)) and predicted values are matched with actual values as shown in Figure 1. And the results obtained show good agreement.
Thus, Equation (3) can be universally applied for all the batch conditions within the range mentioned.

Three dimensional surface plots

Three dimensional surface plots obtained using Design expert software are represented in figure 2-11:

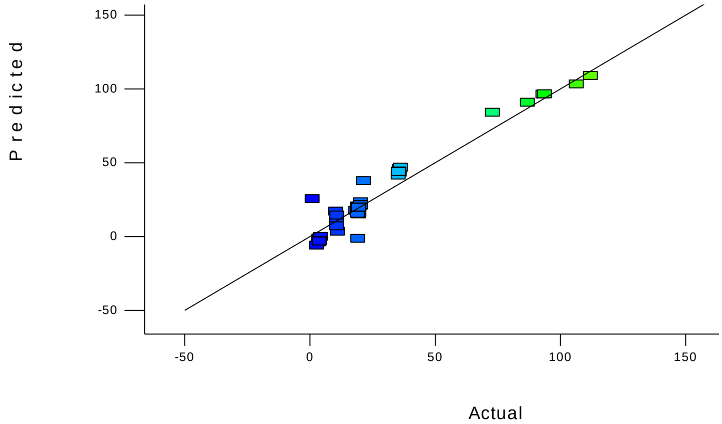

Figure 2: Plot of the actual and model predicted adsorption (mg g^{-1}) of the AB dye on PTMFAC

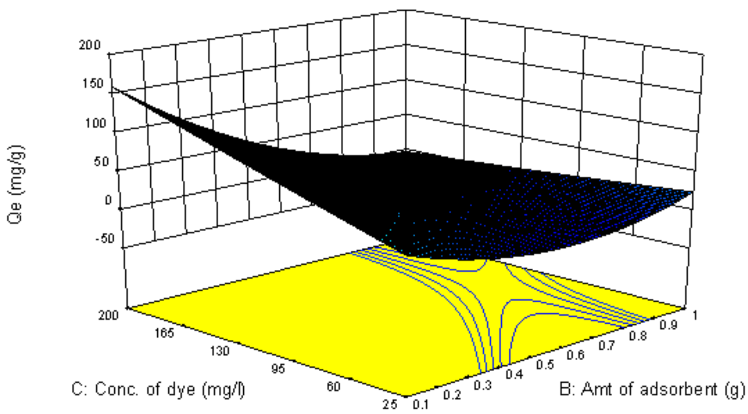

Figure 3: Effect of amount of adsorbent and concentration of dye on adsorption capacity of PTMF (pH 6.5, 150rpm, 40^0C)

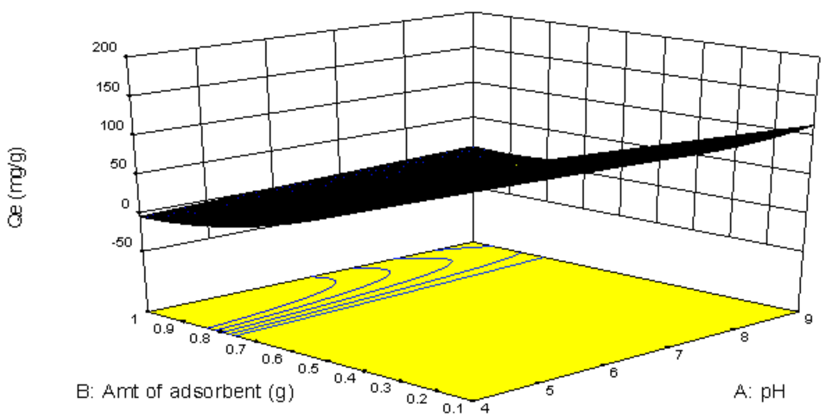

Figure 4: Effect of pH and amount of adsorbent on adsorption capacity of PTMF (112.5ppm, 40^0C, 150 rpm)

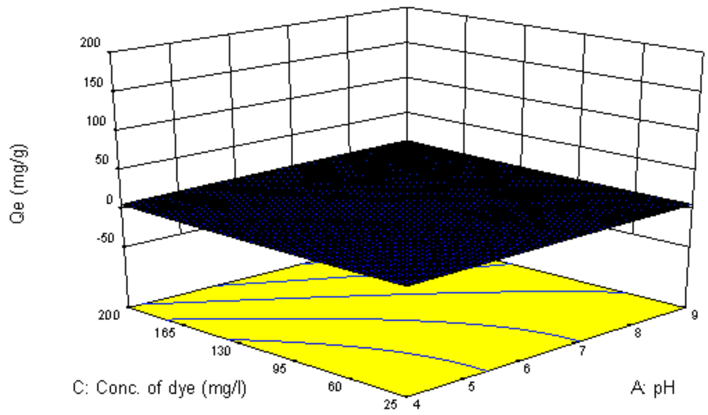

Figure 5: Effect of pH and Concentration of dye on adsorption capacity of PTMF (0.55gm, 40^0C, 150 rpm)

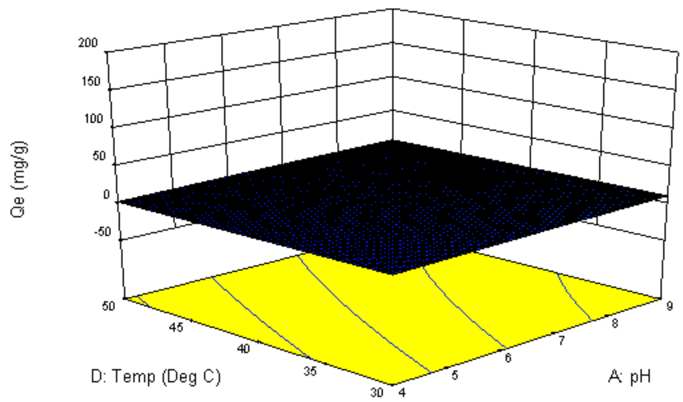

Figure 6: Effect of pH and temperature on adsorption capacity of PTMF (0.55gm, 112.5ppm, 150 rpm)

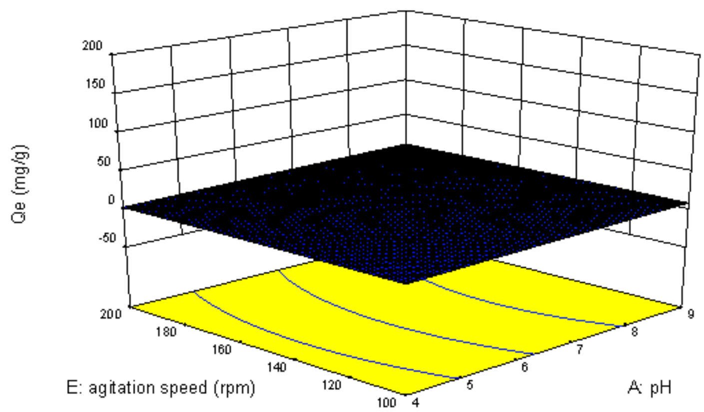

Figure 7: Effect of pH and agitation speed on adsorption capacity of PTMF (0.55gm, 112.5ppm, 40^0C)

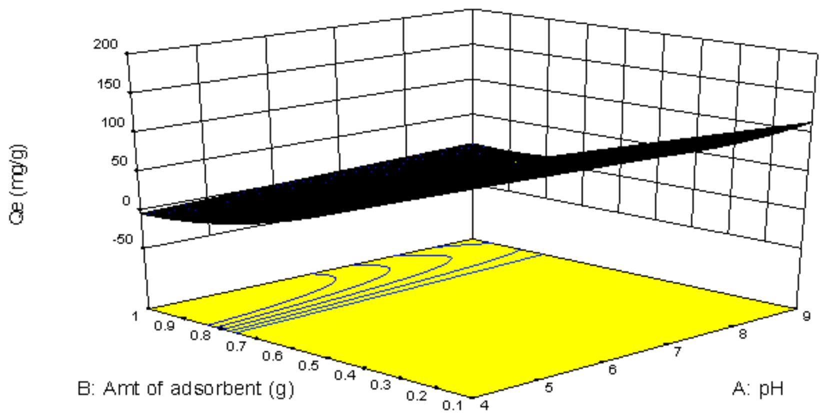

Figure 8: Effect of pH and amount of adsorbent on adsorption capacity of PTMF (112.5ppm, 40^0C, 150 rpm)

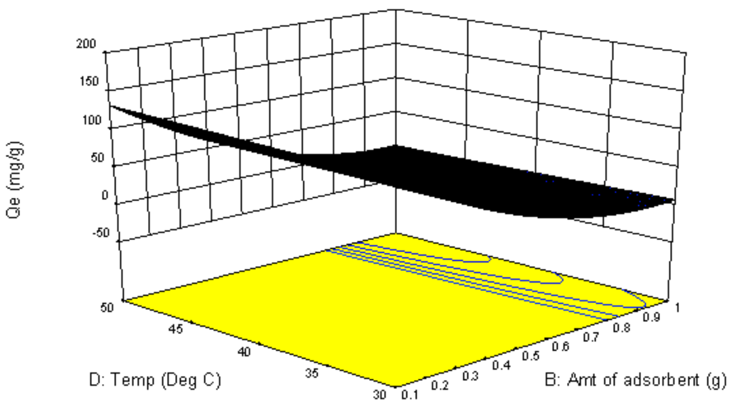

Figure 9: Effect of amount of adsorbent and temperature on adsorption capacity of PTMF (pH 6.5, 150rpm, 112.5ppm)

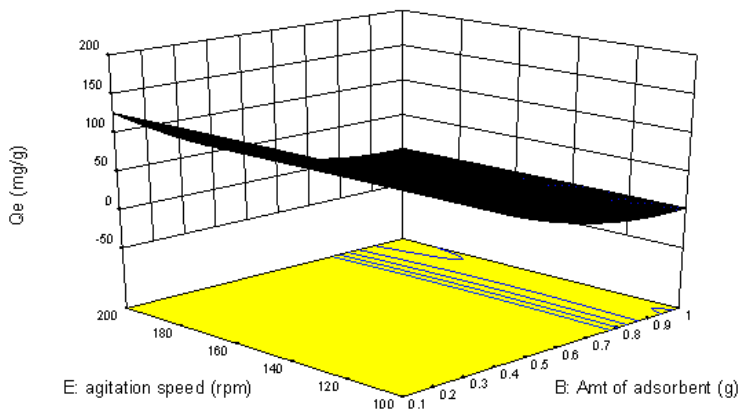

Figure 10: Effect of amount of adsorbent and agitation speed on adsorption capacity of PTMF (pH 6.5, 40^0C, 112.5ppm)

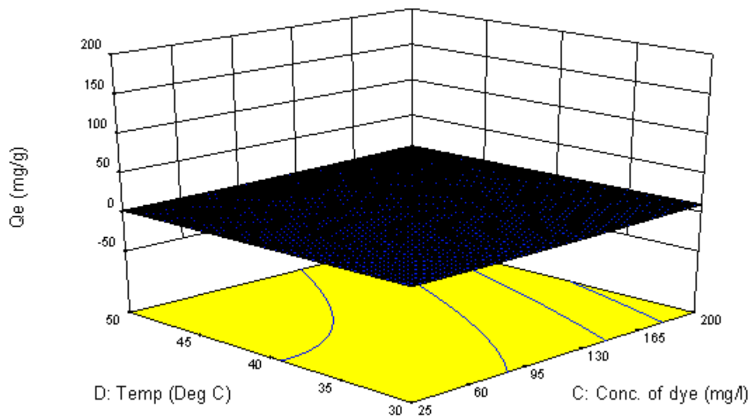

Figure 11: Effect of concentration and temperature on adsorption capacity of PTMF (pH 6.5, 0.55g, 150rpm)

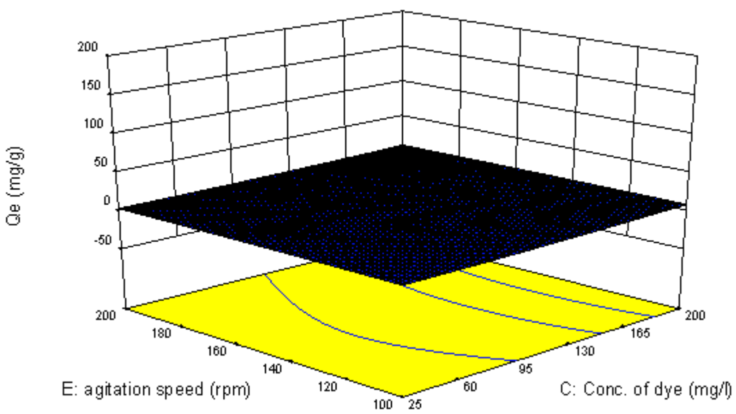

Figure 12: Effect of concentration and agitation on adsorption capacity of PTMF (pH 6.5, 0.55g, 40^0C)

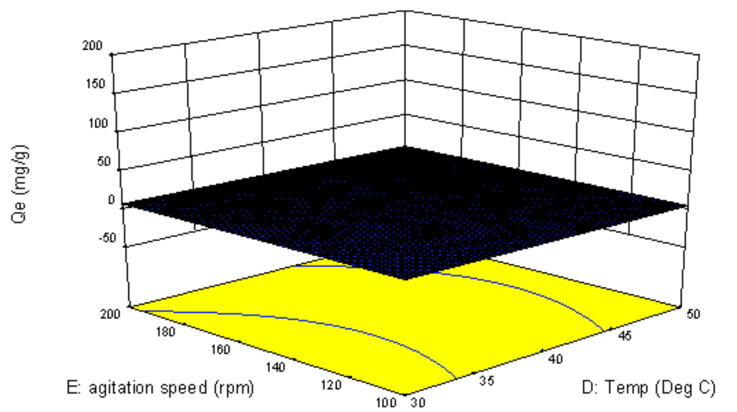

Figure 13: Effect of temperature and agitation on adsorption capacity of PTMF (pH 6.5, 0.55g, 112.5ppm)

Effect of concentration of dye and amount of adsorbent

It can be observed from Table 4 that concentration of dye and amount of adsorbent are significant with p-value of < 0.0001 and it has major effect on adsorption capacity (Figure 3). The adsorption capacity increases with the dye concentration and attains a peak value of 188.077mg g^{-1}. It can be proposed that increase in initial concentration of dye leads to an increase in mass gradient between the dye solution and adsorbent. This acts as a driving force leading to transfer of dye molecules from bulk to particle surface [20]. Similarly it can be proposed that with increase in amount of adsorbent higher number of adsorption sites are available which increases the adsorption capacity. With time due to overlapping or aggregation of adsorbent, additionally the aggregation of adsorbent particle at high mass may lead to decreases in surface area and increases in diffusion path length. [21, 22]

Effect of pH, temperature and agitation speed

It can be observed from table 4 that parameters pH, temperature and agitation are less significant and have p-value of 0.3286, 0.6526 and 0.9679 respectively. From 3-D plots in Figure 4-13 it can be seen that there is negligible effect of these parameters with both concentration and amount of adsorbent.

Comparison of adsorption with other adsorbents for AB

Comparison between adsorption capacity of PTMFAC and other adsorbents is represented in Table 5. Comparing our results for PTMFAC with the others it can be concluded that PTMFAC has a considerably high adsorption capacity for AB dye

Table 5: Maximum adsorption capacity of different adsorbents using AB dye

Adsorbent	**Maximum adsorption capacity (mg g^{-1})**	**References**
Rice husk	155	[27]
Soy meal hull	114.94	[28]
Hazelnut shell	60.2	[29]
Chitosan/cyclodextrin	77.4	[30]
DTMA-bentonite	74.5	[31]
Carbonaceous adsorbent	119	[32]
Modified silica	45.8	[33]
Palm tree male flower	210.09	This study

Conclusion

The present study shows that Phosphoric acid treated palm tree male flower (PTMFAC) can be used as a potential adsorbent for elimination of Acid blue-113 from aqueous solution. Concentration of dye and amount of adsorbent are major factors affecting adsorption capacity whereas pH, temperature and agitation speed have negligible effect. Equilibrium data fitted very well with Langmuir isotherm, confirming monolayer adsorption with maximum adsorption capacity of 210 mg g^{-1}. Palm tree male flower is inexpensive and abundantly available material can be used as an alternative for costly adsorbent for dye removal in waste treatment. Thus activated carbon obtained from naturally occurring palm tree male flower has an ample scope for industrial treatment of effluent.

Acknowledgment
The authors acknowledge the resources provided by Manipal University to carry out research that resulted in the article.

References

[1] Mohammed M.A., Shitu A. and Ibrahim A., 2014, “Removal of Methylene Blue Using Low Cost Adsorbent: A Review” Research Journal of Chemical Sciences
[2] M. Nourouzi, S. Keshani, and L. Chuah Abdullah, April 2014, “Neural Network Application in Fixed Bed Column Adsorption”, International Journal of Innovation, Management and Technology, Vol. 5, No. 2.
[3] Y. Yang • X. Lin • B. Wei • Y. Zhao • J. Wang, 2013, “Evaluation of adsorption potential of bamboo bio char for metal-complex dye: equilibrium, kinetics and artificial neural network modelling” Int. J. Environ. Sci. Techno Journal. Springer
[4] Kayan B., Gozmen B., 2012, “Degradation of Acid Red 274 using H2O2 in subcritical water: Application of response surface methodology”, Journal of Hazardous Materials, 201-202, 100-106
[5] Avlontis, S. A., Poulios, I., Sotiriou, D., Pappas, M., Moutesidis, K., 2008, “Simulated cotton dye effluents treatment and reuse by Nano filtration.” Desalination 221, 259-267.
[6] Zhou, Y., Liang, Z., 2008, “Decolonization and COD removal of secondary yeast wastewater effluents by coagulation using aluminum sulphate, Desalination”, 301-311
[7] Lee, J-W., Choi, R., Shim, W.-G., Moon, 2006, “Evaluation of the performance of adsorption and coagulation processes for the maximum removal of reactive dyes”, Dyes Pigments 69, 196-203.
[8] Maezawa, A., Nakodi, H., Suzuki, K., Furusawa, T., Suzuki, Y., Uchida, S., 2007, “Treatment of dye wastewater by using photo-catalytic oxidation with sonication”, Ultrasound Sonochem 14, 615-620.
[9] Hunger, K., 2003, “Handbook of water and wastewater treatment technologies, Wiley-VCH, Weinheim; 2nd edition”, 20-35.
[10] Faouzi, A., M., Nasr, B., Abdellataif, G., 2007, “Electrochemical degradation of anthraquinone dye Alizarin Red S by anodic oxidation on boron-doped diamond”, Dyes Pigments 73, 86-89.
[11] Cohen, J., 2006, “Multiple regression as a general data-analytic system”, Psychological Bulletin, 70, 426-443

[12] Yadav Deepti, 2015, "Utilization of Corn Cob Activated Carbon for Adsorptive Removal of MB Dye from Aqueous Solution: Application of RSM approach in Optimization of Removal Process", International journal of research in chemistry and environment, 48-58

[11] George Box, Donald Behnken. 1960, "Some new three level designs for the study of quantitative variables", Technometrics Volume 2, 455-475.

[12] K.Y. Foo, B.H. Hameed, 2009, "Utilization of biodiesel waste as a renewable resource for activated carbon: application to environmental problems", Renew. Sust. Energy Rev. 13 (9), 2495-2504.

[13] A.L. Macfarlane, R. Prestidge, M.M. Farid, J.J.J. Chen, 2009, "Dissolved air flotation: a novel approach to recovery of organo solv lignin", Chem. Eng. J. 148 (1), 15-19.

[14] R. Bürger, F. Concha, F.M. Tiller, 2000, "Applications of the phenomenological theory to several published experimental cases of sedimentation processes", Chem. Eng. J. 80 (1-3), 105-117.

[15] G.B. Zhu, Y.Z. Peng, B. Ma, Y. Wang, C.Q. Yin, 2009, "Optimization of anoxic/oxic step feeding activated sludge process with fuzzy control model for improving nitrogen removal", Chem. Eng. J. 151 (1-3), 195-201.

[16] H. Delmas, C. Creanga, C. Julcour-Lebigue, A.M.Wilhelm, 2009, "AD-OX: a sequential oxidative process for water treatment—adsorption and batch CWAO regeneration of activated carbon", Chem. Eng. J. 152, 189-194.

[17] N. Miladinovic, L.R. Weatherley, 2008, "Intensification of ammonia removal in a combined ion-exchange and nitrification column", Chem. Eng. J. 135 (1-2), 15-24

[18] K.Y. Foo, B.H. Hameed, 2009, "Recent developments in the preparation and regeneration of activated carbons by microwaves", Adv. Colloid Interface Sci. 149, 19-27.

[19] D. Kalderis, D. Koutoulakis, P. Paraskeva, E. Diamadopoulos, E. Otal, J.O. del Valle, C. Fernández-Pereira, 2008, "Adsorption of polluting substances on activated carbons prepared from rice husk and sugarcane bagasse", Chem. Eng. J. 144 (1), 42-50.

[20] F. Gimbert, N. Morin-Crini, F. Renault, P.M. Badot, G. Crini, 1998, "Adsorption isotherm models for dye removal by cationized starch-based material in a single component system: error analysis", J. Hazard. Mater. 157, 34-46.

[21] O. Altin, H.O. Ozbelge, T. Dogu, 1998, "Use of general purpose adsorption isotherms for heavy metal-clay mineral interactions", J. Colloid Interface Sci. 198, 130-140.

[22] A. Gunay, E. Arslankaya, I. Tosun, 2007, "Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics", J.Hazard. Mater. 146, 362 371.

[23] M. Horsfall, A.I. Spiff, 2005, "Equilibrium sorption study of Al3+, Co2+ andAg2+ in aqueous solutions by fluted pumpkin (Telfairia occidentalis HOOK) waste biomass", Acta Chim. Slov. 52, 174-181.

[24] S. Kundu, A.K. Gupta, 2006, “Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization”, Chem. Eng. J. 122, 93-106.

[25] K. Vijayaraghavan, T.V.N. Padmesh, K. Palanivelu, M. Velan, 2006, “Biosorption of nickel(II) ions onto Sargassum wightii: application of two-parameter and three parameter isotherm models”, J. Hazard. Mater. B133, 304-308.

[26] M.M. Dubinin, 1960, “The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface”, Chem. Rev. 60, 235-266.

[27] Malik, P.K..2003, “Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of acid blue” Dyes Pigments 56, 239-249.

[28] Mittal A., Kaur D., Mittal J.2008, “Applicability of waste materials-bottom ash and deoiled soya meal-as adsorbents for the removal and recovery of a hazardous dye, acid blue”, J Colloid Interface Science, 326

[29] F. Ferrero, 2007, “Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust”, J. Hazard. Mater. 142, 144-152.

[30] Ravi Kumar, M.N.V, 2000, “A review of chitin and chitosan applications”, React. Funct. Polym., 46, 1-27.

[31] O¨zcan, A.S., Erdem, B., O¨ zcan, A., 2004, “Adsorption of acid blue113 from aqueous solutions onto Na-bentonite and DTMA-bentonite.”, J. Colloid Int. Sci., 280, 44-54.

[32] Stephan Inbaraj, B. and Sulochana N., 2002, “Basic dye adsorption on a low cost carbonaceous sorbent-kinetic and equilibrium studies”, Indian J. Chemi. Technol., 201-8

[33] Krysztafkiewicz, A., Binkowski, S., Jesionowski, T., 2001, “Adsorption of dyes on a silica surface”, Appl. Surf. Sci., 199, 31-39.

[34] J.C.Y. Ng, W.H. Cheung, G. McKay, 2003, “Equilibrium studies for the sorption of lead from effluents using chitosan”, Chemosphere 52, 1021-1030.

[35] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, 2005, “Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon-kinetic study and equilibrium isotherm analyses”, Colloid Surf. A 264, 17-28.

[36] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, 2005, “Removal of Congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses”, Chemosphere 61, 492-501.

[37] A. Jumasiah, T.G. Chuah, J. Gimbon, T.S.Y. Choong, I. Azni, 2005, “Adsorption of basic dye onto palm kernel shell activated carbon: sorption equilibrium and kinetics studies”, Desalination 186, 57-64.

[38] Y.S. Ho, W.T. Chiu, C.C. Wang, 2005, “Regression analysis for the sorption isotherms of basic dyes on sugarcane dust”, Bioresour. Technol. 96, 1285-1291.

[39] D. Mohan, K.P. Singh, G. Singh, K. Kumar, 2002, "Removal of dyes from wastewater using fly ash, a low-cost adsorbent", Ind. Eng. Chem. Res. 41, 3688-3695

[40] Grag, V.K., Raksh Kumar and Renuka Gupta, 2004, "Removal of malachite green dye from aqueous solution by adsorption using agroindustries waste: A case study of Phosopis cineraria". Dyes & Pigments, Ind. Eng. Chem. Res. 41, 62, 1-10.