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Full Length Research Paper

Optimization of basic and reactive dye uptakes in binary dye solution using statistical experimental methodology

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In the present study, the optimum adsorption conditions for the uptake of methylene blue (MB) and reactive orange 16 (RO16) in binary dye solution by ethylenediamine tetraacidic acid (EDTA) modified rice hulls was studied. By using the Plackett-Burman design, the significant variables in affecting the MB and RO16 uptake in binary dye solution were identified as pH and contact time. The combined effects of interaction between the variables were determined using response surface methodology (RSM). The model predicted that at optimum conditions: pH 6.77 and contact time of 205.58 min, the MB uptake greater than 95% could be obtained. As for RO16, the RSM indicated that pH 3.17 and contact time of 205.59 min were optimal for maximum percent dye uptake. These predicted values were also experimentally validated to confirm the reliability of the models.

Key words: EDTA modified rice hulls, methylene blue, reactive orange 16, plackett burman, response surface methodology, optimization.

INTRODUCTION

Ecotoxicological effects and the non-biodegradable characteristics of dyes have led to an increasing focus on the treatment processes to remove the dye content from wastewater. Dye can be considered as the first pollutant to be identified, because its presence, even at a very low concentration, is sufficient to impart noticeable colour to the effluent. Thus, the discharge of dyes not only decreases the transmission of sunlight into the water bodies but also perturbs the ecosystem of streams (Attia et al., 2006; Ong et al., 2007). Besides, some dyes and their degradation products are carcinogenic and mutagenic (Pavan et al., 2007).

A number of established techniques and materials have been successfully utilized in the treatment of wastewater containing dyes such as precipitation, filtration, chemical coagulation and flocculation, oxidation and adsorption (Kadirvelu et al., 2003; Slokar et al., 1998). However, adsorption has been considered as the most efficient method for the removal of various dyes (Amin, 2008). A range of natural materials, for instance, peanut hull, tea dust leaves, paddy straw, wood products, coir pith and sugarcane bagassee that have the capability to remove dyes had been used as an alternative for activated carbon since there are many problems connected with the cost and regeneration process of the used activated carbon (Ong et al., 2010a; Amin, 2008; Kadirvelu et al., 2003; Ponnusami et al., 2007).

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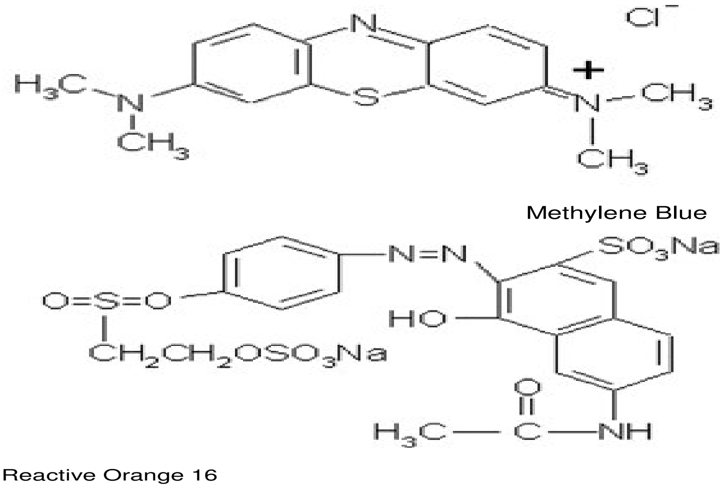

Figure 1. Structure of methylene blue and reactive orange 16.

Most of the studies indicated that the modified adsorbents are efficient in binding either the cationic or anionic species but not both. However, a mixture of different types of dyes is usually found in the industrial effluents. Therefore, there is a need to have adsorbents capable of removing different types of dyes that are commonly present together. Conventional methods of studying a process by maintaining other variables involved at an unspecified constant level does not describe the combined effect of all the variables (Ravikumar et al., 2006). Response Surface Methodology (RSM) which is an efficient experimental strategy to determine optimal conditions for a multivariable system (Alam et al., 2009) was used to overcome this limitation. The application of RSM in textile effluent treatment process might result in improvement of decolourization process by reducing process variability and time (Tavares et al., 2009). This application has been extensively studied on biotechnology namely optimization of medium composition, fermentation and food process (Beg et al., 2003; Chang et al., 2002; Singh et al., 2008; Taveres et al., 2005; Weuster-Botz, 2000).

In our previous study, EDTA (ethylenediamine tetraacetic acid) modified rice husk has demonstrated its potential to be a low-cost adsorbent to remove both Methylene Blue (MB) and Reactive Orange 16 (RO16) in binary dye solution (Ong et al., 2010b). Therefore, in this continued effort, we tried to investigate the interaction between the variables and optimized the dyes uptake by using statistical experimental approach.

MATERIALS AND METHODS

Sorbent

The rice husk was collected from a local rice mill. It was washed thoroughly with water and then sun dried. The dried rice husk was ground to size of 1 mm using a grinder and labeled as Natural Rice Husk (NRH). The modification with EDTA was attempted by varying temperature and the ratio of EDTA to rice husk. Based on the experimental result, it was found that the optimum conditions for the modification of rice husk were by treating 8 g of grinded rice husk with 0.5 g of EDTA and soaked in 300 ml of 1.0 M sodium hydroxide (NaOH) for 3 h at 70°C. The treated rice husk was filtered and washed with excess water and dried in an oven at 60°C and the material was labeled as ERH.

Sorbates

Synthetic dye solutions of MB and RO16 in binary dye solution were used in this study without further purification. All dyes used were purchased from Sigma-Aldrich Pte. Ltd. (United Stated of America). Standard dye solutions of 1000 mg/L were prepared as stock solutions and subsequently diluted when necessary. All the dye structures are shown in Figure 1.

Plackett Burman design

Plackett Burman Design was used to identify which variable(s) has a significant effect on the percentage uptake of the dyes. Six variables (pH, contact time, sorbent dosage, initial dye concentration, agitation rate and temperature) were used in this study and screened in 12 experimental designs. The designs and the percentage uptake for both MB and RO16 in binary dye solution are shown in Table 1. All experimental designs were carried out in duplicate and the mean value of the percentage uptake was taken as response. Experimental design and statistical analysis of data were done by using Design Expert Version 7.1.3.

Response surface methodology (RSM)

A factorial Central Composite Design (CCD) model for two variables with replicates was used in this study. The variables used were pH and contact time for MB and RO16 binary each at five coded levels (-α, -1, 0, +1, +α) as shown in Table 2. All experiments were conducted in duplicate and the mean value of percentage uptake was used as response. Cubic equation used for optimization

Table 1. Plackett-Burman design and results for the uptake of MB and RO16.

Dyes	Experimental run	Variables						Observed response (%)	Predicted response (%)
		pH	Contact time	Sorbent dosage	Initial concentration	Temperature	Agitation rate		
	1	10	5	0.05	15	30	200	93.11	91.54
	2	10	5	0.2	25	70	50	94.25	96.69
	3	10	240	0.05	15	70	50	98.44	96.43
	4	2	5	0.05	15	30	50	72.56	75.83
	5	2	5	0.05	25	70	50	80.71	78.91
	6	2	5	0.2	15	70	200	83.63	81.83
	7	10	240	0.05	25	70	200	97.68	99.05
MB	8	2	240	0.2	25	30	50	87.13	84.94
	9	10	5	0.2	25	30	200	96.77	96.23
	10	10	240	0.2	15	30	50	97.74	98.04
	11	2	240	0.05	25	30	200	82.15	82.87
	12	2	240	0.2	15	70	200	84.46	86.26
	1	10	5	0.05	15	30	200	31.34	36.71
	2	10	5	0.2	25	70	50	35.47	38.17
	3	10	240	0.05	15	70	50	40.74	40.61
	4	2	5	0.05	15	30	50	73.21	69.31
	5	2	5	0.05	25	70	50	68.50	78.91
	6	2	5	0.2	15	70	200	73.97	74.19
	7	10	240	0.05	25	70	200	46.10	43.71
RO16	8	2	240	0.2	25	30	50	80.00	82.85
	9	10	5	0.2	25	30	200	46.47	42.26
	10	10	240	0.2	15	30	50	48.50	47.16
	11	2	240	0.05	25	30	200	79.17	80.39
	12	2	240	0.2	15	70	200	82.39	82.18

Table 2. Experimental range and levels of independent variables for MB and RO16 in binary dye solution.

Dyes	Factors	Factor code	Range and levels (coded)				
			-1.414	-1	0	+1	+1.414
	pH	A	2.00	3.17	6.00	8.83	10.00
MB	Contact time (min)	B	5.00	39.41	122.50	205.59	240.00
	pH	A	2.00	3.17	6.00	8.83	10.00
RO16	Contact time (min)	B	5.00	39.41	122.50	205.59	240.00

Table 3. Regression analysis (ANOVA) of Plackett-Burman for the uptake of MB in binary dye solution.

Source	Degree of freedom	Sum of square	Mean square	*F*-value	Prob>F
Model	6	744.09	124.01	15.34	0.0044
pH	1	635.84	635.84	78.66	0.0003
Contact time	1	58.83	58.83	7.28	0.0429
Temperature	1	7.86	7.86	0.97	0.3694
Initial dye concentration	1	6.38	6.38	0.79	0.4150
Agitation rate	1	4.05	4.05	0.50	0.5107
Sorbent dosage	1	31.14	31.14	3.85	0.1069
Residual	5	40.41	8.08		
Total	11	784.5			

Table 4. Regression analysis (ANOVA) of Plackett-Burman for the uptake of RO16 in binary dye solution.

Source	Degree of freedom	Sum of square	Mean square	*F*-value	Prob>F
Model	6	3910.27	651.71	37.73	0.0005
pH	1	3626.86	3626.86	209.95	< 0.0001
Contact time	1	191.52	191.52	11.09	0.0208
Temperature	1	11.06	11.06	0.64	0.4599
Initial dye concentration	1	2.58	2.58	0.15	0.7153
Agitation rate	1	14.13	14.13	0.82	0.4073
Sorbent Dosage	1	64.13	64.13	3.17	0.1120
Residual	5	86.37	17.27		
Total	11	3996.64			

of the percentage uptake of dye is shown as following:

$$Y=\beta_o+\sum_{i=1}^{2}\beta_i X_i+\sum_{i=1}^{2}\beta_{ii} X_i^2+\sum_{i=1}^{2}\beta_{iii} X_i^3+\sum_{i=1}^{1}\sum_{j=i+1}^{2}\beta_{ij} X_i X_j + \sum_{i=1}^{1}\sum_{j=i+1}^{2}\beta_{ijj} X_i X_j^2+\sum_{i=1}^{1}\sum_{j=i+1}^{2}\beta_{iij} X_i^2 X_j \quad (1)$$

Where, β_o, β_i, β_{ii}, β_{iii}, β_{ij}, β_{ijj} and β_{iij} are the constant coefficients, and X_i, and X_j are the independent variables. All the experimental design and statistical analysis of the data were done by using design expert version 7.1.3.

RESULTS AND DISCUSSION

Evaluation of variables affecting percentage uptake of dye

The important variables that have a significant effect on the dye uptake were determined using Plackett Burman. The analysis of variance (ANOVA) table for MB and RO16 binary were presented in Tables 3 and 4, respectively. The model F-value of 15.34 for MB and 37.73 for RO16 implies that the model is significant. From Table 3, the Prob>F value for pH and contact time was less than 0.05 which indicates the model terms are significant for MB uptake. As for RO16, the same variables, pH and contact time showed a Prob>F values of <0.0001 and 0.0208, respectively. It thus appears that both of these variables are significant in the uptake of RO16. This result agreed well with most of the reported works whereby the uptake of dyes by solid substrates depends on the contact time and pH of the solution (Ong et al., 2007; Hammed et al., 2007; Onal et al., 2006).

The dependence of dye uptake on contact time may be attributed to the three phases of dye sorption, which are boundary layer sorption, intraparticle diffusion and sorption equilibrium. Whereas for the effect of pH, it has been postulated that the uptake of these dyes by ERH is essentially due to electrostatic interaction (Ong et al., 2010b). Therefore, at low pH, the electrostatic attractions between negatively charged dye anions and positively charged sorption sites resulting in an increase in dye uptake. As the pH increased, the number of positively charged sorption sites decreased and this phenomenon now favoured the sorption of positively charged dye.

Verification of Plackett Burman design model

Function of desirability was applied to validate the

Table 5. Plackett-Burman model validation for MB and RO16 in binary dye solution.

Dye system	Factors						Percentage Uptake (%)	
	pH	Contact time	Sorbent dosage	Initial concentration	Agitation	Temperature	Predicted	Experimental
MB	9.87	212.61	0.19	21.39	108.99	36.29	98.7463	96.87
RO16	2.01	216.54	0.20	16.93	192.83	35.67	82.9834	82.29

Table 6. Regression analysis (ANOVA) for the uptake of MB in binary dye solution.

Source	Degree of freedom	Sum of square	Mean square	F-value	P
Model	7	534.80	76.40	294.02	< 0.0001
A	1	134.48	134.48	517.53	< 0.0001
B	1	192.08	192.08	739.20	< 0.0001
AB	1	2.10	2.10	8.09	0.0361
A^2	1	67.23	67.23	258.73	< 0.0001
B^2	1	24.03	24.03	92.49	0.0002
A^2B	1	21.84	21.84	84.05	0.0003
AB^2	1	4.95	4.95	19.05	0.0073
Residual	5	1.30	0.26		
Lack of fit	1	0.55	0.55	2.95	0.1611

R^2: 0.9976, Adjusted R^2: 0.9942, Predicted R^2: 0.9320, Adequate precision: 51.265 and C.V.: 0.56%.

models. The experimental conditions were chosen based on the highest desirability. All the experimental conditions, predicted and experimental percentage uptake were presented in Table 5. It is apparent that the experimental values agreed well with the predicted values with a relatively small percentage error which is approximately 1.9 and 0.7% for MB and RO16, respectively.

Data analysis by RSM

Characterization of the individual and interactive effects of pH and contact time on the MB and RO16 uptake in binary dye solution was done by using RSM. The modified cubic model describes the correlation between the 2 variables, pH and contact time, and the percentage uptake of MB in binary dye solution is as follow:

$$\%Uptake = 93.78 + 5.8A + 6.93B - 0.72AB - 3.11A^2 - 1.86B^2 - 3.30A^2B - 1.57AB^2 \quad (2)$$

Where A = pH and B = Time

The 2 significant variables in affecting the percentage uptake of RO16 were pH and contact time. The modified cubic model for RO16 is as follow:

$$\%Uptake = 36.24 - 2.28A + 1.89B - 0.92AB + 3.49A^2 + 0.54B^2 - 8.09A^2B + 4.65AB^2 \quad (3)$$

Where pH = A and B = Time.

The ANOVA tables for MB and RO16 in binary dye solution were shown in Tables 6 and 7, respectively. From the tables, the model F-value for both MB and RO16 binary were 294.02 and 10082.03, respectively. These values indicate that the models were significant. There is only a 0.01% of chance that a model F-value this large could occur due to noise. As for the value of coefficient of determination (R^2), 0.9976 was obtained for MB and 0.9999 for RO16. The closer the R^2 to unity, the better it predicts the response (Chauhan et al., 2006). Both R^2 values were in reasonable agreement with adjusted R^2 of 0.9942 for MB binary dye solution, 0.9998 for RO16 in binary dye solution and this is to ensure that a satisfactory adjustment of a cubic model to the experimental data. Moreover, the Prob>F values obtained indicate the pH and contact time are significant model terms in the uptake of MB and RO16 in binary dye solution since it is less than 0.0001 (Tables 6 and 7).

Coefficient of variance (C.V.) indicates the precision and reliability of the experiment which favours lower percentage value. For both MB and RO16 in binary dye solution, the C.V. values are 0.56 and 0.72%, respectively. The not significant in lack-of-fit for MB and RO16 implies that the tested model is valid. Adequate precision is an indicator for the signal to noise ratio and this ratio is desirably higher than 4. As for MB in binary, the adequate precision is 51.265 whereas for RO16 in binary is 299.284. Figure 2 shows the 3D plot of the interaction between the variables of pH and contact time for MB. Higher percentage uptake was observed when

Table 7. Regression analysis (ANOVA) for the uptake of RO16 in binary dye solution.

Source	Degree of freedom	Sum of square	Mean square	F-value	P
Model	7	5409.51	772.79	10082.03	< 0.0001
A	1	2093.05	2093.05	27306.52	< 0.0001
B	1	1431.13	1431.13	18670.91	< 0.0001
AB	1	3.42	3.42	44.65	0.0011
A^2	1	83.55	83.55	1103.05	< 0.0001
B^2	1	2.00	2.00	26.10	0.0037
A^2B	1	130.90	130.90	1707.76	< 0.0001
AB^2	1	43.24	43.24	564.16	< 0.0001
Residual	5	0.38	0.077		
Lack of fit	1	0.21	0.21	4.91	0.0910

R^2: 0.9999, Adjusted R^2: 0.9998, Predicted R^2: 0.9975, Adequate precision: 299.284 and C.V.: 0.72%.

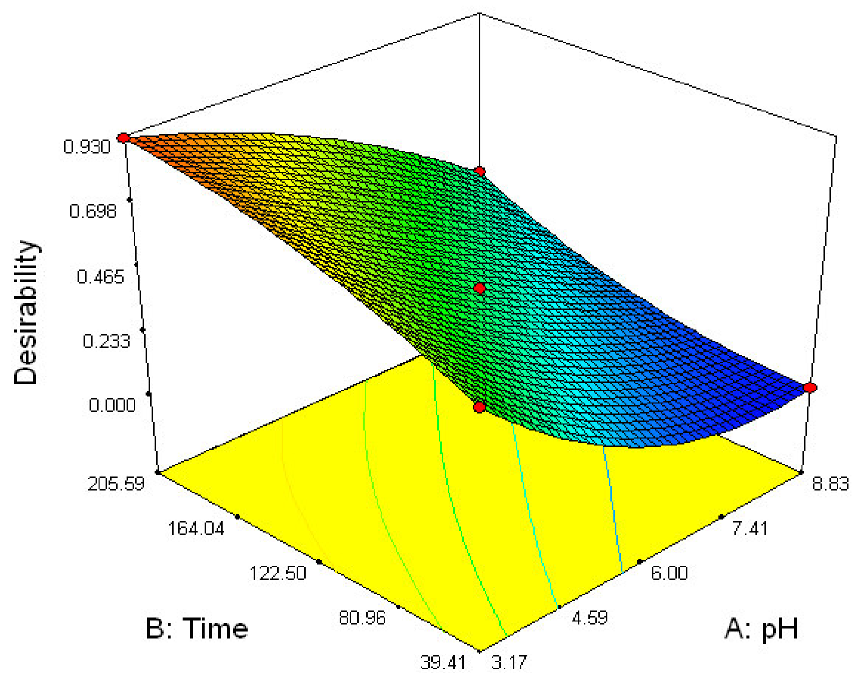

Figure 2. 3D surface plot for uptake of MB in binary dye solution as a function of pH and contact time.

the pH and contact time were at its higher point. At low pH, the surface of the sorbent was surrounded by hydronium ions (H^+) which prevented the MB dye molecules from approaching the binding sites. With increasing pH, the carboxyl groups are predominantly deprotonated and resulted in sorption sites that were available for binding with MB (Ong et al., 2010b; Ong et al., 2010c). The increase in contact time between dye molecules and sorbent allows complete interaction and attainment of interaction. Hence, percentage uptake of MB in binary dye solution increases when contact time increased. The optimum conditions of the variables for MB in binary dye solution were pH 6.77 and 205.58 min.

The 3D plot in Figure 3 shows that the maximum percentage uptake for RO16 in binary dye solution was observed as the pH at it minimum point and contact time at its maximum point. When pH increased, this lead to the deprotonation of surface groups and the presence of excess OH^-, results in the electrostatic repulsion between the dye molecules and negatively charged sites. The increase in contact time between dye molecules and sorbent allows complete interaction and attainment of interaction. Therefore, the optimum conditions for the uptake of RO16 in binary dye solution were pH 3.17

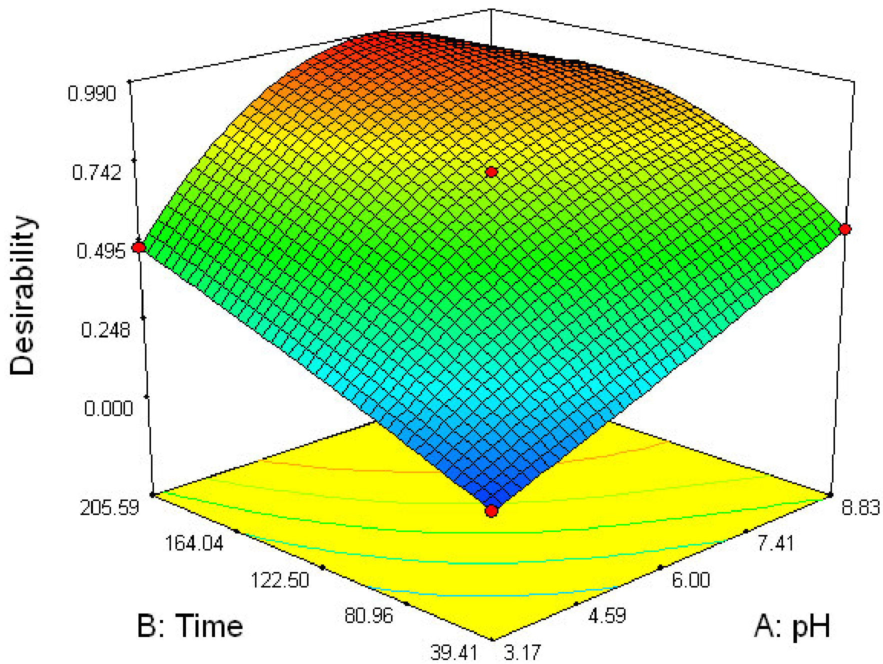

Figure 3. 3D surface plot for uptake of RO16 in binary dye solution as a function of pH and contact time.

and 205.59 min.

Verification of RSM model

Experiments were conducted based on the experimental conditions with the highest desirability generated by design expert v 7.1.3 in order to check the validity of the model equations for both MB and RO16 in binary dye solution. The experimental results obtained agreed well with the predicted value with percentage errors of 0.199 and 0.231% for MB and RO16, respectively. The model F-value of 294.02 for MB and 10082.03 for RO16 indicated that both models were significant and valid.

Conclusion

The usage of an experimental design permitted the rapid screening of a large experimental domain for optimisation of conditions for the uptake of both MB and RO16 in binary dye solution using EDTA rice hulls. Plackett Burman identified the significant variables in affecting the uptake of both dyes were pH and contact time. RSM was used to determine the interaction between the optimum conditions of the variables for maximum percentage uptake of MB and RO16 in binary dye solution. The optimum conditions for dyes uptake in binary dye solution were: pH 6.77 and 205.58 min for MB and pH 3.17 and 205.59 min for RO16.

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REFERENCES

Alam MZ, Mansor MF, Jalal KCA (2009). Optimization of decolorization of methylene blue by lignin peroxidase enzyme produced from sewage sludge with phanerocheate chrysosporium. J. Hazard. Mater. ,162: 708-715.

Amin NK (2008). Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith. Desalination, 223: 152-161.

Attia AA, Girgis BS, Fathy NA (2006). Removal of methylene blue by carbons derived from peach stones by H_3PO_4 activation: Batch and column studies. Dyes and Pigments, 76: 282-289.

Beg QK, Sahai V, Gupta R (2003). Statistical media optimization and alkaline protease production from Bacillus mojavensis in a bioreactor. Pr. Biochem., 39: 203-209.

Chang YN, Huang JC, Lee CC, Shih IL, Yzeng YM (2002). Use of response surface methodology to optimize culture medium for production of lovastatin by Monascus ruber. Enzyme Microb. Technol. ,30: 889-894.

Chauhan K, Trivedi U, Patel KC (2006). Application of response surface methodology for optimization of lactic acid production using date juice. J. Microb. Biotechnol., 16: 1410-1415.

Hammed BH, Ahmad AL, Latiff KNA (2007). Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. Dyes and Pigments, 75: 143-149.

Kadivelu K, Kavipriya M, Karthika C, Radhika M, Vennilamani N, Pattabhi S (2003). Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. Biores. Technol., 87: 129-132.

Onal Y, Akmil-Bascar C, Eren DC, Sarıcı-Ozdemir C, Depci T (2006). Adsorption kinetics of malachite green onto activated carbon prepared from Tuncbilek lignite. J. Hazard. Mater., B128: 150-157.

Ong ST, Keng, PS, Chong AW, Lee SL, Hung YT (2010c). Tartaric acid modified rice hull as a sorbent for methylene blue removal. Am. J. Env. Sci., 6: 244-248.

Ong ST, Khoo EC, Hii SL, Ha ST (2010a). Utilization of sugarcane bagasse for removal of basic dyes from aqueous environment in single and binary systems. Desalination and Wat. Treatment J. 20: 86-95.

Ong ST, Lee CK, Zainal Z (2007). Removal of basic and reactive dyes using ethylenediamine modified rice hull. Biores. Technol., 98: 2792-2799.

Ong ST, Lee WN, Keng PS, Lee SL, Hung YT, Ha ST (2010b). Equilibrium studies and kinetics mechanism for the removal of basic and reactive dyes in both single and binary systems using EDTA modified rice husk. Int. J. Phys. Sci., 5: 582-595.

Pavan FA, Lima EC, Dias SLP, Mazzocato AC (2007). Methylene blue biosorption from aqueous solutions by yellow passion fruit waste. J. Hazard. Mater., 150: 703-712.

Ponnusami V, Vikram S, Srivastava SN (2007). Guava (*Psidium guajava*) leaf powder: Novel adsorbent for removal of methylene blue from aqueous solutions. J. Hazard. Mater., 152: 276-286.

Ravikumar K, Ramalingam S, Krishnan S, Balu K (2006). Application of response surface methodology to optimize the process variables for Reactive Red and Acid Brown dye removal using a novel adsorbent. Dyes and Pigments, 70: 18-26.

Singh G, Ahuja N, Batish M, Capalash N, Sharma P (2008). Biobleaching of wheat straw-rich soda pulp with alkalophilic laccase from γ-proteobacterium JB: Optimization of process parameters using response surface methodology. Biores. Technol., 99: 7472-7479.

Slokar YM, Le M, Marechal A (1998). Methods of decoloration of textile wastewaters. Dye and Pigments, 37: 335-356.

Tavares APM, Cristovao RO, Loureiro JM, Boaventura RAR, Macedo EA (2009). Application of statistical experimental methodology to optimize reactive dye decolourization by commercial laccase. J. Hazard. Mater., 162: 1255-1260.

Taveres APM, Coelho MAZ, Agapito MSM, Countinho JAP, Xavier AMRB (2005). Selection and optimization of culture medium for exopolysaccharide production by Coriolus (Trametes) versicolor. J. Microbiol. Biotechnol., 21: 1499-1507.

Weuster-Botz D (2000). Experimental design for fermentation media development: statistical design or global random search. J. Biosci. Bioeng., 90: 473-483.