International Food Research Journal 22(6): 2351-2357 (2015)
Journal homepage: http://www.ifrj.upm.edu.my

Optimization study for synthetic dye removal using an agricultural waste of *Parkia speciosa* pod: A sustainable approach for waste water treatment

Ngoh, Y. Y., Leong, Y.-H. and *Gan, C. Y.

Centre for Advanced Analytical Toxicology Services, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Article history

Received: 7 June 2014
Received in revised form: 24 April 2015
Accepted: 20 May 2015

Keywords

Coomassie blue
Dye removal
Biosorption
Optimization
Parkia speciosa

Abstract

Parkia speciosa pod showed extremely high potential in dye (Coomassie Brilliant Blue R-250) removal application especially for waste water treatment. Central composite design (CCD) was successfully employed for experimental design and results analysis. The combined effect of pH (X_1: 5.0-8.0), biosorbent dosage (X_2: 0.05-0.10 g) and contact time (X_3: 30-100 min) on dye adsorption was investigated and optimized using response surface methodology (RSM). Analysis of variance (ANOVA) demonstrated that the contribution of the quadratic model was significant for the responses. The optimum adsorption of 83.4% was obtained with the optimal conditions of pH 5.0, dosage of 0.10 g and the contact time of 70 min. Close agreement was found between both the experimental and predicted values. Therefore, it was suggested that *P. speciosa* pod could be a potential natural dye adsorbent.

Introduction

Synthetic dyes are human-made organic dye. They are used globally in the industries of textiles, plastics, rubber, cosmetics, paper and colouration of products (Asgher and Bhatti, 2012). Annual production is found to be over 7 x 10^5 tons with textile industry individually discharging more than 1.5 x 10^8 m^3 of coloured effluents annually (Feng *et al*., 2011). Production of synthetic dyes is in the trend of increasing due to their inexpensive cost of synthesis, stability, convenient usage and variety of colours choices compared to natural dyes (Aksu and Isoglu, 2006). Extensive use of synthetic dyes has therefore created a major pollution problem. Once being released into the aquatic environment, they are difficult to be decolourized because of their high resistance towards fading on exposure to light (Saad *et al*., 2010). Both human and aquatic life will be greatly affected as synthetic dyes are known to be carcinogenic, mutagenic and toxic. Apart from that, reduction of sunlight transmission will give negative impacts towards aquatic plants (Salleh *et al*., 2011).

Coomassie Brilliant Blue (CBB) belongs to the group of synthetic dye. The name CBB refers to the commercial name of two similar triphenylmethane (Raja, 2012). In this study, Coomassie Brilliant Blue R-250 has been used. The term '250' and the suffix 'R' in 'Brilliant Blue R-250' represents the denotation of the purity of the dye and abbreviation for 'red' as the blue colour of the dye has a slight reddish tint respectively. CBB is widely used in biochemical and clinical laboratories for the purification and quantification of proteins. CBB is employed to stain proteins for protein visualisation in a polyacrylamide gel. It is also used in the quantification of electrophoretically separated protein. Recently, CBB was used in the treatment of spinal injuries in rats (Peng *et al*., 2009) and as a stain to assist surgeons in retinal surgery (Mennel *et al*., 2008). CBB has shown to be toxic and the potential health effects on human beings include irritation of skin, eye and respiratory difficulty. Their target organs are usually eyes, kidney, liver, heart and central nervous system. The pathway of CBB to human beings is by inhalation, ingestion and skin absorption.

The environmental hazard lies in fact that this toxic substance can ultimately get into the drinking water supplies. Therefore, there is a need to remove these dyes immediately and effectively from the polluted water. Many treatments (chemical, biological and physical) such as oxidation process, photochemical, ozonation, microbial cultures, bioremediation, membrane filtration, and ion exchange have been implemented (Salleh *et al*., 2011). Among these, adsorption has been considered as an effective decolourization method due to its simplicity, availability and effectiveness in removing non-biodegradable pollutants (including dyes) from wastewater (Feng *et al*., 2011). Currently, the most promising adsorbent is activated carbon due to its surface area, high adsorption capacity, degree of surface reactivity and microporous structures.

*Corresponding author.
Email: cygan@usm.my
Tel: +604 653 4261; Fax: +604 653 4688

Unfortunately, it does possess disadvantages such as expensive operating costs and reproduction problems (Akar *et al*., 2009). Thus, an effective alternative method which is biosorption using agricultural wastes has been more favorable in the recent years. The advantages of this method include their unique chemical composition, cheap, availability in abundance and biodegradable (Bhatnagar and Sillanpää, 2010). Among the agricultural wastes that have been reported in research include sesame hull (Feng *et al*., 2011), olive pomace (Akar *et al*., 2009), citrus waste (Bhatnagar and Sillanpää, 2010), grass waste (Hameed, 2009), tea waste (Uddin *et al*., 2009), cotton plant wastes (Tunç *et al*., 2009), corncob and barley husk (Robinson *et al*., 2002), date stones and palm trees waste (Belala *et al*., 2011), and yellow passion fruit (Pavan *et al*., 2008).

Parkia speciosa (petai), also known as stink bean is a plant of the genus Parkia from the family of Fabaceae. They are edible legumes that have medicinal properties such as controlling diabetes and carried out anticancer activity deriving from thiazolidine-4-carboxylic acid. Jamaluddin *et al.* reported that their strong pungent smell of mushroom like flavour came from their seeds containing antibacterial cyclic polysulfides (hexathionane, tetrathiane, trithiolane, pentathiepane, pentathiocane and tetrathiepane) (Jamaluddin *et al*., 1995). These beans are commonly found in Southeastern Asia including Malaysia, Singapore, Laos, Southern Thailand and Northeastern India. They are usually found in the long flat pods bearing green seeds and sold in the form of seeds separated from the pods or in the pods (Gan and Latiff, 2011). During the processing (canning of beans), the pod is normally discharged as waste. Hence, as one of the biggest producers of petai, this presents a waste disposal problem for Malaysia. The aim of this study was to evaluate the potentiality of petai pod for the removal of CBB R-250 from aqueous solutions.

In this study, Response Surface Methodology (RSM) was used to optimize the biosorption conditions and the effects being investigated were contact time, biosorbent dosage and pH. RSM is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes. It is very useful in evaluating the relative significance of several affecting factors even in the presence of complex interactions and relations (Moghaddam *et al*., 2010). The main objective of using RSM is to determine the optimum operational conditions of the system or to identify a region that fulfills and satisfies the operating specifications (Chatterjee *et al*., 2012). RSM also offers a few advantages such as cost effective and consuming less time than the classical methods (Crini, 2006). RSM is one of the most popularly used methods in research on biosorption literature (Witek-Krowiak *et al*., 2014). Thus, in the present study, RSM has been applied to optimize the process conditions for the removal of CBB R-250 using petai pod.

Materials and Methods

Materials

Parkia speciosa (15 kg) was purchased from three different local markets (Lipsin market, Batu Lanchang market and Jelutong market) located in Penang, Malaysia. All chemicals (analytical grade) used in the experiment were purchased from Sigma-Aldrich and Fluka company.

Preparation of biosorbent

P. speciosa was rinsed with distilled water and then the seeds were immediately separated from the pods. The latter was lyophilised and milled to the final particle size of 60-mesh.

Adsorption assays

Stock solution of 50 mg/l of blue dye solution was prepared from CBB R-250 (Molecular Formula: C45H44N3O7S2Na, Molecular Weight: 825.99, CAS: 6104-59-2) using distilled water and stirred overnight in order to ensure all the dye dissolved completely. The pH of the dye solution was then adjusted using 0.1 M NaOH or HCl.

Adsorption experiments were carried out by shaking the capped conical flasks at a speed of 200 rpm for a fixed period of time using incubator shaker (IKA KS 4000, Germany) at room temperature. Each variable of the effects was experimented with a set of three conical flasks: (I) sample (containing sample and dye solution), (II) control 1 (containing only dye solution) and (III) control 2 (containing only sample solution).

Effect of contact time

The effect of contact time on the adsorption capacity of petai pod was investigated at different contact times (30, 60, 90, 120, 150, 180, 210 and 240 min) using a 100 ml solution of 50 mg/l of dye at pH 3 shaken with 1.00 g of biosorbent at room temperature. At the end of each contact period, 10 ml of sample was withdrawn from the conical flask and centrifuged at 4500 rpm for 20 min to remove suspended particles. Supernatant were then being transferred into the microplate. The absorbance of the supernatant solution was estimated to determine the residual dye concentration, measured at λ_{max} = 570 nm spectrophotometrically using M5 Spectramax (Molecular Devices, U.S). The data obtained were used to calculate the percent biosorption (%) by Equation (1).

$$\%Biosorption = \frac{(A-(B-C)\ \times 100}{A} \quad (1)$$

where A is the absorbance of dye; B represents the absorbance of dye and sample; and C is the sample absorbance.

Effect of biosorbent dosage

The experiment on effect of biosorbent dosage was carried out by varying the adsorbent dosage (0.05, 0.10, 0.15, 0.20, 0.25, 0.50, 0.75 and 1.00 g) using a 100 ml solution of 50 mg/l of dye at pH 3.0 for 150 min at room temperature. At the end of the contact period, samples were withdrawn and centrifuged prior to absorbance (570 nm) measurement.

Effect of pH

The experiment on effect of pH was performed by differentiating the pH value (pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0) using a 100 ml solution of 50 mg/l of dye solution shaken with 1.00 g of adsorbent for 150 min at room temperature. At the end of the contact period, samples were withdrawn and centrifuged prior to absorbance (570 nm) measurement.

Experimental design

The biosorption process parameters (i.e. pH *(X_1)*, dosage *(X_2)* and time *(X_3)*) were optimized using RSM. These variables have been considered as factors that may potentially affect the biosorption response function. A Central Composite Design (CCD) was employed in this regard. The range and center point values of these three independent variables displayed in Table 1 were based on the results of single factor study. The experimental design consists of eight factorial runs, six axial runs (α = 1.682) and six central runs (Table 2). Percent biosorption (%) was used as the response for the combination of the independent variables given in Table 2. Three experimental replicates of each condition were performed and the mean values were stated as experimental responses. Experimental runs were randomized to minimize the effects of unexpected variability in the observed responses.

The variables were coded according to the equation:

$$x = (X_i - X_o)/\Delta X \quad (2)$$

where x is the coded value, X_i was the corresponding actual value, X_o was the actual value in the center of the domain, and *ΔX* is the increment of X_i corresponding to a variation of 1 unit of x.

Table 1. Experimental domain of central composite design (CCD)

X_j	Factor levels				
	-1.682	-1	0	1	1.682
pH, X_1	3.98	5	6.5	8	9.02
Dosage (g), X_2	0.033	0.05	0.075	0.10	0.117
Time (min), X_3	6.1	30	65	100	123.9

The mathematical model corresponding to the design is:

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

where *Y* was the dependent variables (i.e. biosorption yield), βo was the model constant, and β_i, β_{ii} and β_{ij} were the model coefficients. They represent the linear, quadratic and interaction effects of the variables. Analysis of the experimental design data and calculation of predicted responses were carried out using Design Expert software (version 6.0, USA). Additional confirmation experiments were subsequently conducted to verify the validity of the statistical experimental design.

Results and Discussion

Effects of single factor variable on dye biosorption response

The effects of contact time on the removal of dyes are illustrated in Figure 1(a). From the experimental results, it can be seen that the percent biosorption increased with the contact time. The percent biosorption increased from 60.9 to 85.6% starting from the 30 to 240 min. This indicates that the removal efficiency is higher as the contact time between the dye and biosorbent is prolonged until equilibrium time is reached. Similar result was also reported by Ravikumar *et al*. (2007).

The effects of biosorbent dosage on the removal of dyes are shown in Figure 1(b). The percentages of dyes adsorbed increased as the dosage increased over the range of 0.05 - 0.20 g from 40.6 to 82.7%. Meanwhile, a slight decrease (from 82.7% to 78.9%) was observed over as the dosage range increased from 0.20 to 0.80 g. The increment may be attributed to the increased of surface area and the availability of more sorption sites (Gong *et al*., 2005). On the other hand, the decrement may be due to the saturation or equilibrium stage being achieved by the petai pod.

The effects of pH on the removal of dyes are

Table 2. Design and experimental responses of the 20 runs using Central Composite Design (CCD)

Run	pH	Dosage (g)	Time (min)	% biosorption (Experimental)	% biosorpti (Predicted)
1	5.00	0.050	30.0	68.45	64.65
2	8.00	0.050	30.0	36.81	36.72
3	5.00	0.100	30.0	78.72	77.42
4	8.00	0.100	30.0	75.33	72.97
5	5.00	0.050	100.0	83.18	81.62
6	8.00	0.050	100.0	45.21	42.59
7	5.00	0.100	100.0	89.57	85.74
8	8.00	0.100	100.0	70.31	70.19
9	3.98	0.075	65.0	91.33	95.67
10	9.02	0.075	65.0	57.91	59.11
11	6.50	0.033	65.0	39.42	42.32
12	6.50	0.117	65.0	73.63	76.27
13	6.50	0.075	6.1	53.90	56.50
14	6.50	0.075	123.9	65.49	68.43
15	6.50	0.075	65.0	64.80	64.61
16	6.50	0.075	65.0	63.45	64.61
17	6.50	0.075	65.0	65.00	64.61
18	6.50	0.075	65.0	67.01	64.61
19	6.50	0.075	65.0	65.82	64.61
20	6.50	0.075	65.0	62.54	64.61

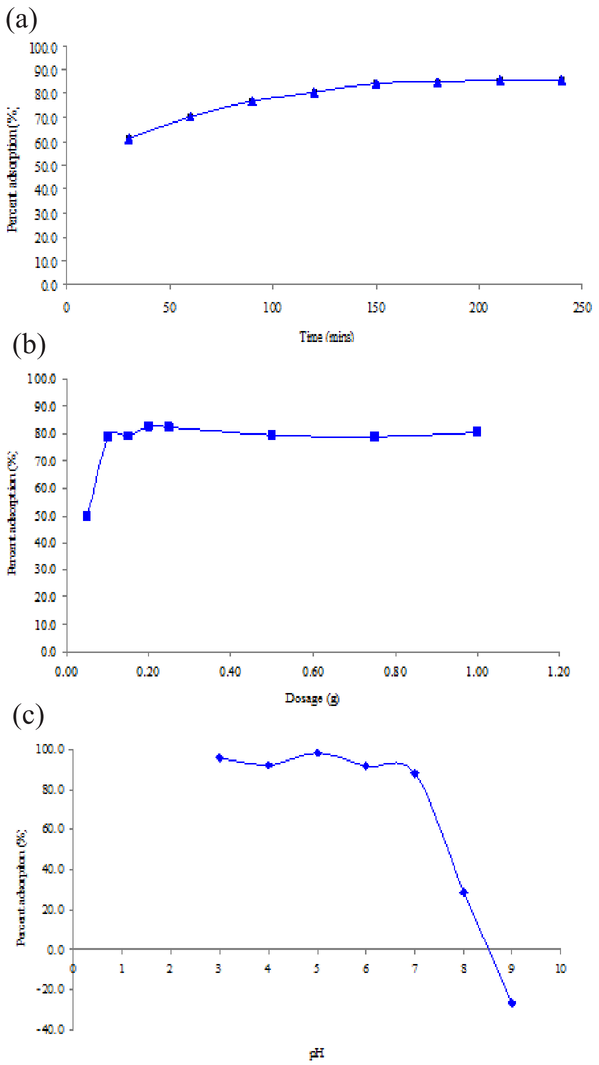

Figure 1. Effect of (a) time, (b) dosage and (c) pH on removal of Coomassie Brilliant Blue using petai pod

presented in Figure 1(c). From the plot, it can be observed that high percent biosorption value of more than 80% occurred at pH range of 3.0-7.0. As the value of pH increased (pH 8.0-9.0), the percent biosorption decreased. The percent biosorption dropped around 27% and darker colour was induced in the solution. This phenomenon was caused by the oxidation of phytochemicals that solubilized in the buffer. The highest percentage of biosorption was achieved at pH 5.0 with the value of 98.3%. A possible explanation of this phenomenon may be due to the fact that dyes adsorb poorly when they are ionized. This leads to a situation whereby the adjacent molecules of the dyes on the hybrid adsorbent surface will repel with each other to a significant degree because of their same electrical charge. In conjunction, this explains the concept of better adsorption being performed by non-ionized form of cationic compared to their ionized form. This is further supported by Ravikumar *et al.* (2007) who agreed that cationic species adsorbs better at low pH.

Optimization of biosorption

According to RSM analysis on three biosorption process variables (i.e. pH (X_1), dosage (X_2) and time (X_3)), a set of 20 runs of optimization experiment was conducted. The response of interest was percent biosorption (%). The results of 20 runs using CCD design are presented in Table 2 that includes the design and experimental responses. The percent biosorption seemed to be varied depending on the conditions studied. It could be observed that the adsorption ranged from 36.8 to 91.3%. The maximum biosorption (91.3 %) was obtained in run 9 under the experimental conditions of X_1 = pH 3.98, X_2 = 0.075 g and X_3 = 65 min.

The results obtained from the eight-factorial RSM model fitted well to the empirical quadratic model (Equation 3). The analysis of variance

Table 3. ANOVA analysis for response surface quadratic model

Source	Sum of Squares	DF	Mean Square	*F*-value	*P*-value
Model	3938.893	9	437.6548	39.89842	< 0.0001
X_1	1613.989	1	1613.989	147.1379	< 0.0001
X_2	1390.711	1	1390.711	126.7829	< 0.0001
X_3	171.8986	1	171.8986	15.67099	0.0027
X_1^2	294.094	1	294.094	26.81083	0.0004
X_2^2	50.94155	1	50.94155	4.644042	0.0566
X_3^2	8.309768	1	8.309768	0.757553	0.4045
X_1X_2	275.6552	1	275.6552	25.12986	0.0005
X_1X_3	61.605	1	61.605	5.616166	0.0393
X_2X_3	37.41125	1	37.41125	3.410564	0.0945
Residual	109.6923	10	10.96923		
Lack of Fit	96.80308	5	19.36062	7.510402	0.0535
Pure Error	12.8892	5	2.57784		
R^2	0.972906				
Adj R^2	0.948521				
CV	5.026228				

(ANOVA) assesses the significance of each studied response and identifies the important factors in a multi-significant model. The results of ANOVA are shown in Table 3. The significance of each coefficient was determined using the F-test and p-value. The corresponding variables would be more significant if the absolute F-value becomes greater and the p-value becomes smaller (Amani-Ghadim *et al*., 2013). The contribution of quadratic model was significant. The fitted quadratic model for percent biosorption in coded variables is given in Equation 4. It can be observed that the variable with the largest effect on percent biosorption was linear term of pH *(X_1)* and dosage *(X_2)* followed by quadratic term of pH *(X_1^2)*, interaction term of X_1X_2, linear term of time *(X_3)* and interaction term of X_1X_3. However, X_2^2, X_3^2 and X_2X_3 were found insignificant (p>0.05). These results clearly stated that the change of pH, dosage and time had significant effects (p<0.05) on the percent biosorption of dye.

$$\%Biosorption = 64.61 - 10.87x_1 + 10.09x_2 + 3.55x_3 + 4.52x_1^2 - 1.88x_2^2 - 0.76x_3^2 + 5.87x_1x_2 - 2.78x_1x_3 - 2.16x_2x_3 \quad (4)$$

The lack of fit test measured the failure of the model to represent the data in the experimental domain at points which were not included in the regression. The result showed that the lack of fit p-value of 0.0535 (p>0.05) indicating the experimental data fitted well to the model and adequate for predicting the percent biosorption. The value of the determination coefficient R^2 was 0.973 while the value of adjusted determination coefficient R^2_{adj} was 0.949, indicating a high degree of correlation between the experimental and predicted values. Coefficient of variation (CV) is a standard deviation expressed as a percentage of the mean. The lower the CV, the smaller residuals relative to the predicted value was. In this study, the CV value being obtained was 5.03, suggesting a good precision and high reliability of the experiment performed.

Dye biosorption response

A graphical representation of regression equation is represented by three-dimensional (3D) response surface. It is very useful in the application of visualizing the relationship between responses and experimental levels of each variable as well as the type of interactions between the two tested variables. Three-dimensional plots for percent biosorption as the function of dosage and time at different pH conditions are given in Figure 2(a)-(c).

The percent biosorption as a function of dosage and time at pH 5.0 is shown in Figure 2(a). An increase in the contact time from 30 to 100 min demonstrated an increase on the response. This trend applies also to the effect of dosage in the range of 0.05 - 0.10 g. At this pH condition, highest % biosorption (86.12%) was observed at dosage of 0.10 g and time of 100 min. Figure 2(b) shows the response as a function of dosage and time at pH 6.5. An increase in the contact time from 30 to 100 min illustrated a slight increase (from 46.1 to 59.8%) on the response. A more drastic increase (46.1-73.0%) was observed in

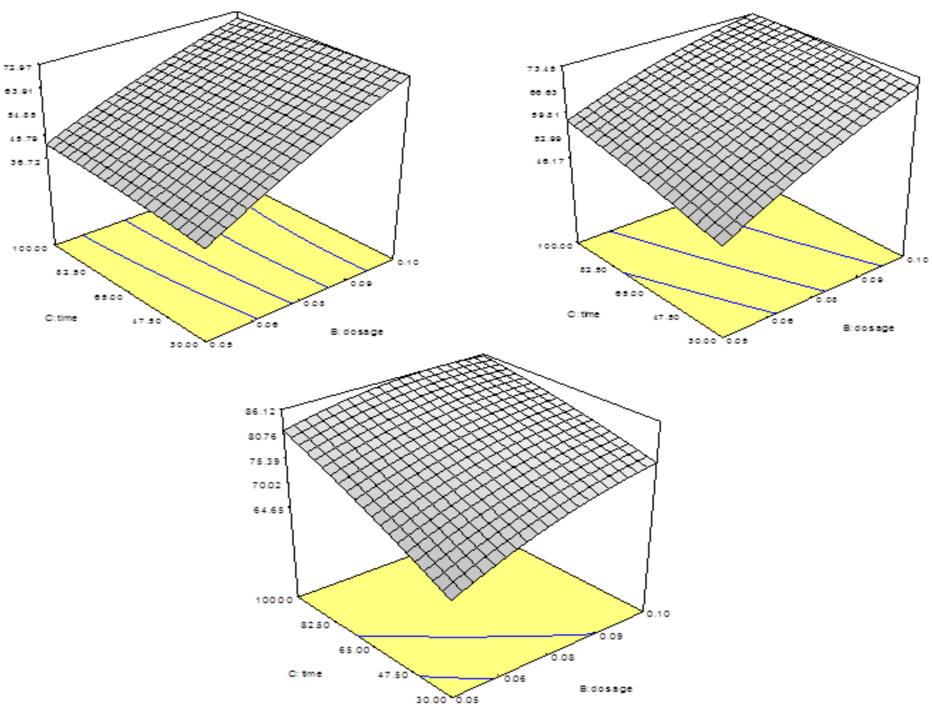

Figure 2. Three-dimensional response surfaces as a function of time and dosage at (a) pH 5.0, (b) pH 6.5 and (c) pH 8.0

the effect of dosage from 0.05 - 0.10 g. At higher pH condition (pH 8.0), contact time from 30 to 100 min only exhibited a small increment (36.7 - 45.7%) on the % biosorption [Figure 2(c)]. However, a more apparent increase was observed with the increment of the dosage.

All three plots showed that different % biosorption patterns with the interactions between an increase of dosage and time. The difference lies in the numerical value of the maximum percent biosorption being achieved with approximation of 86.12%, 73.45% and 72.97% representing Figures 2(a), (b) and (c), respectively at the condition of 100 min and dosage of 0.10 g. From the plots, it can be observed that percent biosorption was much higher at the condition of pH 5.0.

In this study, it is found that lower pH favours in removing CBB R-250 using petai pod. This is in agreement with the work of Raja (2012). As for the effect of dosage and time, increment may be due to the presence of a greater surface for adsorption that increased the availability of more adsorption sites as well as the time of exposure. This results in the uptake of more dye molecules to be adsorbed, thus having a higher percentage of removal (Moussavi and Khosravi, 2011).

Verification of predictive models

Based on the above findings, optimal point for the variables inside the valid region (experimental region) were generated in consideration of the efficiency, feasibility and cost of the experiment. This optimal condition (pH of 5.0, dosage of 0.10 g and time of 70 min) with desirability of 0.9006 obtained the % biosorption of 83.4% which was closed to the predicted value (82.9%). Thus, the RSM is a suitable method to optimize the best operating conditions to maximize the dye adsorption using *P. speciosa* pod.

Conclusions

The present study clearly demonstrated the applicability of *P. speciosa* pod for the removal of CBB dye in aqueous solution, especially when the process parameters are optimized. Quadratic models derived from RSM were successfully predicting all the responses. ANOVA showed that there was a significant effect on the CBB dye adsorption capacity with the change of pH, biosorbent dosage and contact time. Verification has been done whereby maximal dye adsorption has been predicted and confirmed experimentally. No significant difference between the predicted and experimental values. Therefore, RSM as an effective method for optimization of CBB dye removal from aqueous solution was proven.

Acknowledgement

This work was supported by Ministry of Education Malaysia under ERGS Grant (203/CAATS/6730103).

References

Akar, S.T., Özcan, A.S., Akar, T., Özcan, A. and Kaynak, Z. 2009. Biosorption of a reactive textile dye from aqueous solutions utilizing an agro-waste. Desalination 249: 757-761.

Aksu, Z. and Isoglu, I.A. 2006. Use of agricultural waste sugar beet pulp for the removal of *Gemazol turquoise* blue-G reactive dye from aqueous solution. Journal of Hazardous Materials B137: 418-430.

Amani-Ghadim, A.R., Aber, S., Olad, A. and Ashassi-Sorkhabi, H. 2013. Optimization of electrocoagulation process for removal of an azo dye using response surface methodology and investigation on the occurrence of destructive side reactions. Chemical Engineering and Processing 64: 68-78.

Asgher, M. and Bhatti, H.N. 2012. Evaluation of thermodynamics and effect of chemical treatments on sorption potential of Citrus waste biomass for removal of anionic dyes from aqueous solutions. Ecological Engineering 38: 79-85.

Belala, Z., Jeguirim, M., Belhachemi, M., Addoun, F. and Trouvé, G. 2011. Biosorption of basic dye from aqueous solutions by Date Stones and Palm-Trees Waste: Kinetic, equilibrium and thermodynamic studies. Desalination 271: 80-87.

Bhatnagar, A. and Sillanpää, M. 2010. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment – A review. Chemical Engineering Journal 157: 277-296.

Chatterjee, S., Kumar, A., Basu, S. and Dutta, S. 2012. Application of Response Surface Methodology for Methylene Blue dye removal from aqueous solution using low cost adsorbent. Chemical Engineering Journal 181-182: 289-299.

Crini, G. 2006. Non-conventional low-cost adsorbents for dye removal: A review. Bioresource Technology 97: 1061-1085.

Feng, Y.F., Yang, F., Wang, Y.Q., Ma, L., Wu, Y.H., Kerr, P.G. and Yang, L.Z. 2011. Basic dye adsorption onto an agro-based waste material – Sesame hull (*Sesamum indicum* L.). Bioresource Technology 102: 10280-10285.

Gan, C.Y. and Latiff, A.A. 2011. Antioxidant Parkia speciosa pod powder as potential functional flour in food application: Physicochemical properties' characterization. Food Hydrocolloids 25: 1174-1180.

Gong, R., Ding, Y., Li, M., Yang, C., Liu, H. and Sun, Y. 2005. Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution. Dyes Pigments 64: 187- 192.

Hameed, B.H. 2009. Grass waste: A novel sorbent for the removal of basic dye from aqueous solution. Journal of Hazardous Materials 166: 233-238.

Jamaluddin, F., Mohamed, S. and Lajis, Md.N. 1995. Hypoglycaemic effect of Stigmast-4-en-3-one, from Parkia speciosa empty pods. Food Chemistry 54: 9-13.

Mennel, S., Meyer, C.H., Schmidt, J.C., Kaempf, S. and Thumann, G. 2008. Trityl dyes patent blue V and brilliant blue G - clinical relevance and *in vitro* analysis of the function of the outer blood-retinal barrier. Developments in Ophthalmology 42: 101-114.

Moghaddam, S.S., Moghaddam, M.R.A. and Arami, M. 2010. Coagulation/ flocculation process for dye removal using sludge from water treatment plant: Optimization through response surface methodology. Journal of Hazardous Materials 175: 651-657.

Moussavi, G. and Khosravi, R. 2011. The removal of cationic dyes from aqueous solutions by adsorption onto pistachio hull waste. Chemical Engineering Research and Design 89: 2182-2189.

Pavan, F.A., Mazzocato, A.C. and Gushikem, Y. 2008. Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent. Bioresource Technology 99: 3162-3165.

Peng, W., Cotrina, M.L., Han, X., Yu, H., Bekar, L., Blum, L. Takano, T. and Tian, G.F. 2009. Systemic administration of an antagonist of the ATP-sensitive receptor P2X7 improves recovery after spinal cord injury. Proceedings of the National Academy of Sciences USA 106, p. 12489-12493.

Raja, S. 2012. Decolorisation of synthetic dye by Guava *(Psidiumguajava)* leaf powder-A statistical approach. Journal of Chemical and Pharmaceutical Research 4(6): 3239-3244.

Ravikumar, K., Krishnan, S., Ramalingam, S. and Balu, K. 2007. Optimization of process variables by the application of response surface methodology for dye removal using a novel sorbent. Dyes Pigments 72: 66-74.

Robinson, T., Chandran, B. and Nigam, P. 2002. Removal of dyes from an artificial textile dye effluent by two agricultural waste residues, corncob and barley husk. Environment International 28: 29-33.

Saad, S.A., Isa, K.Md. and Bahari, R. 2010. Chemically modified sugarcane bagasse as a potentially low-cost biosorbent for dye removal. Desalination 264: 123-128.

Salleh, M.A.M., Mahmoud, D.K., Karim, W.A.W.A. and Idris, A. 2011. Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. Desalination 280: 1-13.

Tunç, Ö., Tancı, H. and Aksu, Z. 2009. Potential use of cotton plant wastes for the removal of Remazol Black B reactive dye. Journal of Hazardous Materials 163: 187-198.

Uddin, Md.T., Islam, Md.A., Mahmud, S. and Rukanuzzaman, Md. 2009. Adsorptive removal of methylene blue by tea waste. Journal of Hazardous Materials 164: 53-60.

Witek-Krowiak, A., Chojnacka, K., Podstawczyk, D., Dawiec, A., Pokomeda, K. 2014. Application of response surface methodology and artificial neural network methods in modelling and optimization of biosorption process. Bioresource Technology 160: 150-160 .