Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.925830

55 (2015) 1359–1371
July

Taylor & Francis
Taylor & Francis Group

Application of conventional and statistical experimental methodology to optimize malachite green dye removal from aqueous solutions

Sook-Thing Ong[a], Siew-Teng Ong[a,*], Yung-Tse Hung[b], Yi-Pin Phung[a]

[a]*Faculty of Science, Department of Chemical Science, Universiti Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, Kampar, Perak 31900, Malaysia, Tel. +60 54688888; Fax: +60 54661676; emails: ongst@utar.edu.my, ongst_utar@yahoo.com (S.-T. Ong)*
[b]*Department of Civil and Environmental Engineering, Cleveland State University, Cleveland, Ohio, USA, email: yungtsehung@yahoo.com*

Received 10 July 2013; Accepted 13 May 2014

ABSTRACT

In the present study, the removal of a cationic triphenylmethane dye, malachite green (MG) solution was being investigated by adsorption and photodegradation methods. The adsorbent and photocatalyst used was banana pith (BP) and titanium dioxide (TiO_2), respectively. Plackett–Burman design was applied to identify the most significant factors in the removal of MG. The effect of various operating parameters on removal of MG was studied and a mathematical model showing the influence of each variable was obtained. Response surface methodology was applied to determine the interaction between the factors and their optimum levels for maximum percentage removal of MG. The percentage removal predicted by the model was in good agreement with the experimental values. The optimum conditions for maximum MG removal were identified as pH 8.00 and contact time of 120 min. Under these optimum conditions, the model predicted that the maximum percentage removal of dye by adsorption on BP could be more than 50%, whereas a combination system of photodegradation and adsorption processes could further enhance the percentage removal of MG to above 70%. The results showed that the combination system of adsorption using BP and photocatalytic degradation using TiO_2 was a promising method for the removal of MG from aqueous solution.

Keywords: Malachite green; Banana pith; Adsorption; Photocatalytic degradation; Plackett–Burman; Response surface methodology

---

1. Introduction

Dyes are described by their capability to absorb or emit light in the visible range from 400 to 800 nm. Nowadays, synthetic dyes are widely used in many industries to color their products and the total world colorant production is predicted to be 800,000 ton/y. However, at least 10% of the used dyestuff enters the environment through wastes [1].

The presence of dyes in water not only cause damage to the aesthetic nature of the environment, it also cause serious harm to aquatic life by increasing toxicity, chemical oxygen demand, and hindering photosynthesis process through decrease of light penetration [2]. Dyes may also cause severe damage to human beings such as dysfunction of the kidneys,

---

*Corresponding author.

reproductive system, liver, brain, and central nervous system [3].

Due to the hazardous effect of dyes towards the environment and human health, the removal of synthetic dyestuffs from aqueous solution is crucial [4]. Various methods including coagulation, chemical oxidation, photocatalysis, electrochemical, and adsorption are the techniques that have been examined for dye removal. Among the aforementioned methods, adsorption appeared to be a feasible technique for dye removal due to its low-initial cost, simplicity of design, ease of operation, insensitivity to toxic substances, as well as availability and ability to treat dye in a more concentrated form [5].

Although activated carbon appeared to be an efficient adsorbent for a wide variety of dyes, there are still several problems associated with it such as high-capital investment, weight loss, and reduction in adsorption capacity after each regeneration process. Therefore, considerably research has been carried out in developing low cost, easily available natural wastes for the adsorption of dyes.

One of the low cost adsorbents being investigated is banana pith (BP). Typically, banana stalk was left decompose slowly in a plantation field or disposed into landfill and rivers where it would oxidize and harm the local ecology [6]. It is hoped that by utilizing banana stalk waste as an adsorbent for removal of dye, a potential waste problem would be reduced because the residue would now have some commercial value, thus leading to a zero waste situation.

Apart from adsorption, photocatalytic degradation is another way to remove dye from wastewater. Photocatalytic degradation is one of the advanced oxidation process using heterogeneous photocatalysis for the removal of dyes from aqueous solution. TiO_2 is broadly used as a photocatalyst as it is non-toxic, photochemically stable, low in cost, and does not consume any chemicals product [7–9]. It is well established that when TiO_2 is irradiated with light source that has a wavelength shorter than 380 nm or equivalent energy higher than 3.2 eV, then electron excitation from the valence band to the conduction band occurs and a vacancy or a hole is left in the valence band. Such holes have the effect of positive charges. This, in turn, generates the formation of "holes" on the surface of the semiconductor, which can react with oxygen, water, and hydroxide ion to form the hydroxyl radicals. As such, sunlight was selected as the light source in this study.

Malachite green (MG) is selected as the adsorbate for this research because the available toxicological information reveals that in the tissues of fish and mice, MG is easily reduces to persistable leuco-MG which is a tumor promoter. This might then enters into food chain and cause mutagenic and tetratogenic effects on humans [10]. The removal of MG was studied through adsorption and photocatalytic approaches. The removal efficiencies of both methods were studied singly and through combination means. Besides, statistical experimental methodology was employed. By adopting these statistical techniques, the affecting parameters that influence the uptake can be optimized collectively to fits the experimental domain in the theoretical design through a response function.

2. Materials and methods

2.1. Adsorbate

A cationic basic dye, MG oxalate salt was used as the adsorbate in this research. It was obtained from Sigma–Aldrich Sdn. Bhd. and used without further purification. It has a molecular formula $C_{50}H_{52}N_4O_8{\cdot}C_2H_2O_4$ with molecular weight of 463.50 g/mol. The color index of MG is 42,000 and the maximum wavelength of this dye is 618 nm. Requisite quantity of the dye was dissolved in distilled water to prepare stock solution of 1,000 mg/L. Experimental solutions of the desired concentration were obtained by successive dilutions when necessary.

2.2. Adsorbent

The adsorbent used in this study was BP (Musa spp., subgroup Prata) which was collected at a plantation area near Kampar, Perak, Malaysia. It was washed thoroughly with distilled water after being collected. Then, it was sliced, spread on trays, and oven dried at 55˚C for 48 h. The dried slices were blended and sieved into fine particles and stored in plastic bottle for further use. No other chemical or physical treatments were used prior to adsorption experiments. The immobilization of BP on glass plate (8.00 × 4.00 × 0.20 cm) was carried out by spreading accurately weighed 2.5 g of BP on the surface of glass plates coated with silicone sealant.

2.3. Photocatalyst

TiO_2 powder was used as the photocatalyst in this study. It was purchased from MERCK with molecular weight of 79.90 g/mol. The TiO_2 suspension was prepared by adding 5.0 g of TiO_2 to 30 mL of 99.9% methanol solution. The resulting mixture was stirred continuously until all the TiO_2 powders were uniformly dispersed. The immobilization of TiO_2 was carried out by coating the inner part of aquarium (21.50 × 15.00 × 12.00 cm) with TiO_2 suspension layer by layer until 3.0 g of TiO_2 was coated. The amount of TiO_2 coated on the aquarium was calculated using the equation given below:

$$\text{Mass of } TiO_2 \text{ coated} = \text{Final mass of aquarium} - \text{Initial mass of aquarium} \quad (1)$$

2.4. Experimental methods

The irradiation experiments of dye solutions were carried out by pouring 2,000 mL of dye at constant pH 5.0 with initial dye concentration of 10 mg/L in the aquarium coated with 3.0 g of TiO_2. The whole setup was placed under the exposure of sunlight for 2 h. Aeration was provided by bubbling air into the reaction solution by an air pump. As for the adsorption study, 2.5 g of BP immobilized on glass plates was placed into the aquarium. For a combination system, the same experimental conditions were applied. At predetermined time intervals, a known volume of dye solution was collected and analyzed with UV–visible spectrophotometer to determine the percentage removal of the dye. The same experimental conditions were employed in throughout the study unless otherwise stated. The percentage removal of dye was calculated according to the equation below:

$$\text{Percentage removal} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

where C_0 and C_t (mg/L) are the concentrations of dye at initial and at time, t, respectively.

2.4.1. Effect of pH

The effect of initial solution pH on dye adsorption was determined by adjusting the pH ranging from 2 to 8. The desired pH was adjusted by adding a few drops of NaOH or HCl of different concentrations prior to the experiment. Two hours of contact time was then provided which was sufficient for the adsorption to reach equilibrium.

2.4.2. Effect of initial dye concentrations and contact time

The effect of initial dye concentrations and contact time on adsorption was carried out by varying the dye concentrations. At predetermined time intervals, 0.5, 1, 5, 15, 30, 60, 90, and 120 min, dye solution was withdrawn from the reservoir and analyzed for its dye concentration.

2.5. Characterization of adsorbent

Scanning electron microscopy (SEM) was carried out on the BP to examine its surface morphology before and after adsorption. Besides, SEM was also carried out to study the surface morphology of TiO_2 before adsorption. Fourier transform infrared (FTIR) analysis was applied on the BP to determine the nature of the functional groups present in BP, using FTIR spectroscope. The spectra of BP before and after adsorption were recorded from 4,000 to 400 cm^{-1}.

2.6. Plackett–Burman design

Plackett–Burman design was applied to identify the significant factor(s) which influences the percentage removal of dye. This technique is useful for constructing designs for various experimental situations and enables the determination of important parameters for further optimization study [9,11]. Experimental design and statistical analysis of data were done using Design Expert Version 7.1.3. Using the design, the effect of operating parameters on dye uptake was studied in a batch system and a mathematical model to show the influence of each variable was obtained. Three variables which were pH, contact time, and initial dye concentration were used in this study and screened in 10 experimental designs. Some of the selected results for removal of dye using adsorption (BP) and combination of adsorption and photodegradation (BP + TiO_2) from the 10 experimental designs were shown in Table 1.

2.7. Optimization of percentage removal of dye using RSM approach

The interaction between the factors and their optimum levels for maximum percentage removal of MG will be determined using response surface methodology (RSM). A factorial central composite design (CCD) model for two variables was used in this study. The variables used were pH and contact time for adsorption system and combination system of adsorption and photodegradation each at three coded levels (−1, 0, +1) as shown in Table 2. Tables 3 and 4 show some of the selected CCD matrix of independent variables and the observed response for adsorption (BP) and combination system of adsorption and photodegradation (BP + TiO_2), respectively. Cubic equation used for optimization of the percentage removal of dye is shown as following:

Table 1
Plackett–Burman design and results for removal of MG in aqueous solutions

		Variables				
System	Experimental run	pH	Dye concentration (mg/L)	Contact time (min)	Observed response (%)	Predicted response (%)
BP	1	2.00	20.00	120.00	26.43	28.97
	2	8.00	10.00	0.50	9.32	16.67
	3	8.00	10.00	120.00	59.53	53.19
	4	8.00	20.00	0.50	6.69	13.05
	5	8.00	20.00	120.00	56.96	49.57
BP + TiO_2	1	2.00	10.00	120.00	37.45	39.87
	2	2.00	20.00	120.00	23.66	31.41
	3	8.00	10.00	120.00	59.60	55.60
	4	8.00	20.00	0.50	1.22	4.19
	5	8.00	20.00	120.00	57.04	47.13

Table 2
Experimental range and levels of independent variables for the removal of MG in aqueous solution

			Range and levels (coded)		
System	Factors	Factor code	−1	0	+1
BP	pH	A	2.00	5.00	8.00
	Contact time (min)	B	0.50	60.25	120.00
BP + TiO_2	pH	A	2.00	5.00	8.00
	Contact time (min)	B	0.50	60.25	120.00

Table 3
The CCD matrix for two independent variables and the observed response for adsorption

	Coded values of variables			
Experimental run	A	B	Observed response (%)	Predicted response (%)
1	0	−1	7.58	12.59
2	0	0	43.56	43.56
3	+1	+1	59.53	62.04
4	0	+1	56.08	51.07
5	+1	−1	9.32	6.81
6	−1	+1	17.61	20.12

$$\begin{aligned} Y = \beta_0 &+ \sum_{i=1}^{2} \beta_i X_i + \sum_{i=1}^{2} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \beta_{iii} X_i^3 \\ &+ \sum_{i=1}^{1} \sum_{j=i+1}^{2} \beta_{ij} X_i X_j \\ &+ \sum_{i=1}^{1} \sum_{j=i+1}^{2} \beta_{ijj} X_i X_j^2 + \sum_{i=1}^{1} \sum_{j=i+1}^{2} \beta_{iij} X_i^2 X_j \end{aligned} \quad (3)$$

where β_0, 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.

3. Results and discussion

3.1. Effect of pH

The influence of pH on MG color removal by BP is shown in Fig. 1. From the results of the effect of pH on percentage removal of MG by adsorption system, it was found that the uptake of MG increases from 17.61 to 49.75% with the increase of pH from 2 to 5. The uptake of MG then increases slowly to the maximum, 59.53% at pH 10.

The pH of the solution affects both the adsorbent surface binding sites and adsorbate speciation in

Table 4
The CCD matrix for two independent variables and the observed response for combination system of adsorption and photodegradation

	Coded values of variables			
Experimental run	A	B	Observed response (%)	Predicted response (%)
1	0	0	60.98	60.98
2	−1	+1	35.57	36.75
3	0	+1	71.99	69.94
4	0	−1	11.33	13.68
5	+1	−1	0.68	0.12
6	−1	−1	0.12	1.47

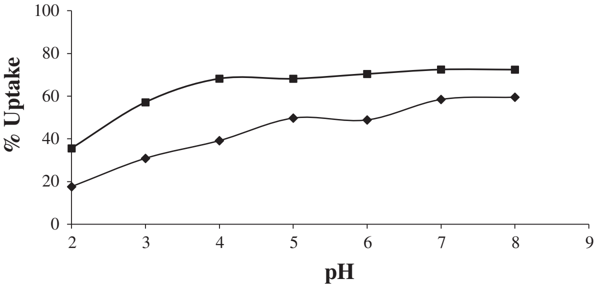

Fig. 1. Effect of pH on removal of MG. ♦, ■—BP, BP + TiO$_2$ (2.5 g of BP; 3.0 g of TiO$_2$; volume of MG: 2,000 mL; concentration of MG: 10 mg/L; contact time: 2 h).

aqueous solution. Since MG is basic in nature, it will release colored dye cations into solution upon dissolution. However, it was reported that the site for uptake of dye was difficult to be identified in view of the fact that there are several potential “ligands” and other functional groups that are capable for the adsorption of cation dye [12]. The results in this experiment revealed that MG has lower percentage removal at low pH and higher percentage removal at high pH. A similar behavior was observed for removal of MG by formaldehyde treated sawdust and sulfuric acid-treated sawdust of *Prosopis cineraria* [5].

At lower pH, the number of negatively charged adsorbent sites decreases and positively charged sites increases. Thus, the adsorption of positively charged MG cations is not favored by the positively charged BP surface due to electrostatic repulsion. On the other hand, at higher pH, surface of BP may become negatively charged. Therefore, the adsorption of positively charged MG cations will be enhanced through electrostatic forces of attraction between the dye cations and the positively charged site of BP. Similar findings were reported in the adsorption of MG by chitosan beads [13] and degreased coffee bean [4]. Higher pH as facilitates a higher uptake of methylene blue by banana stalk wastes [2], Basic blue 3 by durian peel [14], and various basic dyes by sugarcane bagasse [15].

From the results, it is evident that the percentage removal of MG by combination of adsorption and photodegradation system increases rapidly from 35.57 to 68.21% when the pH increases from 2 to 4. Then, it increases gradually to the maximum value which is 72.44% when pH is 8. In an aqueous system, TiO$_2$ is amphoteric. The point of zero charge of TiO$_2$ has been reported as 6.9. Hence, TiO$_2$ surface will remain positively charged when $\text{pH} < 6.9$ and negatively charged when $\text{pH} > 6.9$ [16]. The electrical property of the surface of TiO$_2$ varies with the pH as if the pH is low; the functional groups are protonated and the part of the positively charged surface increases while at high pH, the proportion of negatively charged surface increases due to deprotonation.

Under acidic condition (below pH 6.9), the photodegradation of MG was low due to the electrostatic repulsion and also the low concentration of active hydroxyl radicals. Whereas under alkaline condition, the formation of hydroxyl radical species is favored, thus, the transfer of holes to the adsorbed hydroxyls improved and the number of negatively charged surface sites on the TiO$_2$ also increases. Consequently, more MG cations will be adsorbed due to electrostatic abstractive effect and the photodegradation of MG will be enhanced.

Similar effect of the pH on the adsorption and photocatalytic reaction has been reported for photodegradation of MG on TiO$_2$ nanoparticles [7] and photocatalytic degradation of an azo dye, chrysoidine Y in aqueous suspensions on TiO$_2$ and ZnO [17]. Due to the combination effect of pH on adsorption and photocatalytic degradation, the percentage removal of MG was low in acidic medium and high under alkaline condition.

3.2. Effect of initial dye concentrations and contact time

Fig. 2 shows the effect of initial concentrations of dye and contact time on adsorption of MG. It was found that the percentage removal of MG decreases with an increase in the initial dye concentration. When the initial MG concentration was increased from 10 to 20 mg/L, the percentage removal of MG decreased from 56.08 to 49.52%. This is because, at low initial dye concentration, there will be more unoccupied active sites on the BP surface for the adsorption of MG cations. With increasing MG concentration, the active sites required for adsorption of the dye will be insufficient and lead to the low-percentage removal of MG. This study is similar to the effect of an initial dye concentration on the adsorption process of direct and acid dye by using soy meal hull [18] as well as in the research for removal of basic dye by sunflower seed husk [19].

It was observed that the uptake of MG is rapid at the initial stage of the contact period which is from 0.5 to 60 min and thereafter, it becomes slower until it reaches equilibrium which is at 120 min. This is due to the presence of a large number of vacant surface sites available for sorption of MG during the initial stage which causes the rapid attachment of the dye molecules to the surface of the BP. After a lapse of time, the remaining vacant sites are difficult to be occupied due to repulsive forces between the solute molecules, BP on the solid and bulk phase of MG as well as due to the intraparticle diffusion. A similar trend was observed in the adsorption study of MG by a novel sorbent [10] and the removal of MB dye by adsorption using yellow passion fruit peel [20].

The percentage of MG removal as a function of time by photodegradation using TiO_2 is shown in Fig. 3. Based on the results obtained, it was found that when the initial concentration of dye was low, which was 10 mg/L, the percentage removal of dye was 56.64%. However, when the initial dye concentration was increased to 20 mg/L, the uptake of dye decreased to 46.21%. Although, more MG molecules are adsorbed onto the surface of TiO_2 when the concentration of MG is high, the degradation efficiency of dye is low. This is because the increase in the dye concentration causes the solution to become more intense in color and the path length of the photons entering the solution decreased.

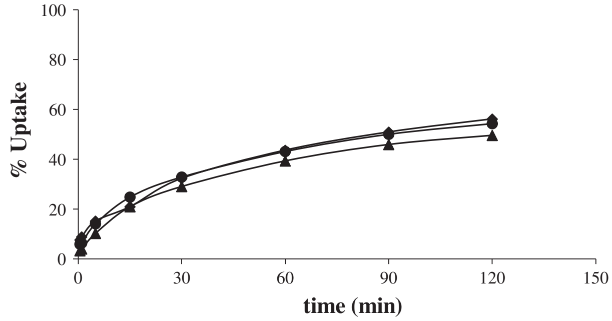

Fig. 2. Effect of initial concentrations of dye and contact time on adsorption of MG. ♦, ●, ▲—10, 15 and 20 mg L^{-1} of MG (2.50 g BP; 2,000 mL; natural pH of dye solution: 5.3).

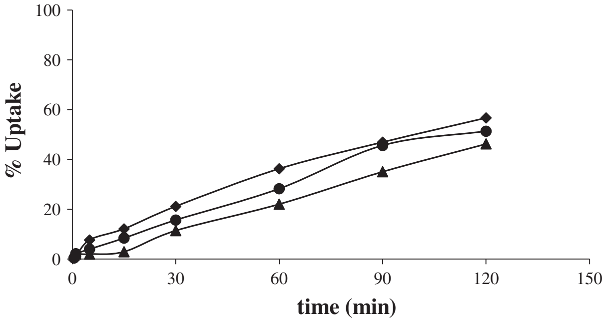

Fig. 3. Effect of initial concentrations of dye and contact time on photodegradation of MG. ♦, ●, ▲—10, 15 and 20 mg L^{-1} of MG (3.0 g of TiO_2; 2,000 mL; natural pH of dye solution: 5.3).

Therefore, fewer photons will reach the catalyst surface and the production of hydroxyl radicals will be reduced which cause the number of radicals that attack the dye compound decreased. As a result, the photodegradation efficiency dropped and the uptake of dye decreased. This finding is similar to the photodegradation of Reactive black-5 dye using TiO_2 impregnated ZSM-5 [21]. The adverse effect of increasing initial concentration towards photodegradation of azo dye acid red 18 [22] has also been reported previously.

As for the exposure effect, it was found that the percentage removal of MG increases with irradiation time. This was due to the fact that more hydroxyl radicals were generated when exposure time is longer. Subsequently, the relative number of hydroxyl radical that attacked the dye compound increased and thus the percentage removal of dye increased with time. This study is similar to the investigation of photodegradation of indigo carmine dye using TiO_2 impregnated activated carbon [23], MB using immobilized TiO_2 [24] and MG using immobilized TiO_2 [25].

Fig. 4 shows the effect of initial concentrations of dye and contact time on adsorption and photodegradation of MG. The results are similar to that observed

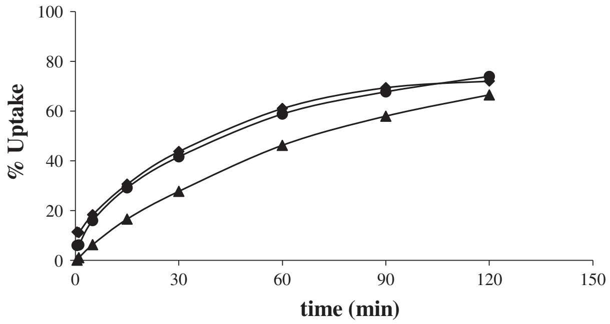

Fig. 4. Effect of initial concentrations of dye and contact time on adsorption and photodegradation of MG. ♦, ●, ▲—10, 15 and 20 mg L^{-1} of MG (2.50 g of BP; 3.0 g of TiO_2; 2,000 mL; natural pH of dye solution: 5.3).

in the system which involved the adsorption and photodegradation only due to the same aforementioned reasons. However, it was observed that the uptake of MG by the combination system was higher (>60%) than the other two systems. The enhancement was due to the adsorption and photodegradation processes that were carried out at the same time. After adsorption, the concentration of dye will be decreased and hence, more photons can reach the catalyst surface as the path length for the photons to enter the solution increases. This will cause more hydroxyl radicals to be produced for the degradation activity of the dye compound. Therefore, the percentage removal of dye will be improved.

3.3. FTIR analysis

The FTIR spectra of BP before and after adsorption were shown in Figs. 5 and 6, respectively. The analysis of IR spectra for BP is shown in Table 5, and these values were compared with the peaks reported by Hameed [2]. It was found that the frequency of the peaks was quite similar to the reported values. A strong adsorption was observed in the region of 3,600–3,200 cm^{-1} and this indicates the existence of free and intermolecular bonded hydroxyl groups. The peaks observed around 2,900 cm^{-1} can be assigned to stretching vibration of C–H group. Peak around 1,630 cm^{-1} corresponded to C=C groups. The presence of lignin structure in BP was shown by the strong band observed at 1,051 cm^{-1}. The peak at 610 cm^{-1} was due to the bending modes of aromatic compounds.

3.4. SEM analysis

Figs. 7 and 8 show the SEM images of BP before and after adsorption at 20,000× magnifications. From Fig. 7, it was clear that BP belongs to a non-porous material due to the absence of pores and cavities. The section analysis from Fig. 7 showed that the pores smaller than 1 μm were observed on the surface of BP and those pores are very suitable sites for the adsorption of MG. The figures show that, before dye adsorption, BP surfaces were rough. After dye adsorption, a significant change is observed in structure of BP. It can be seen that the

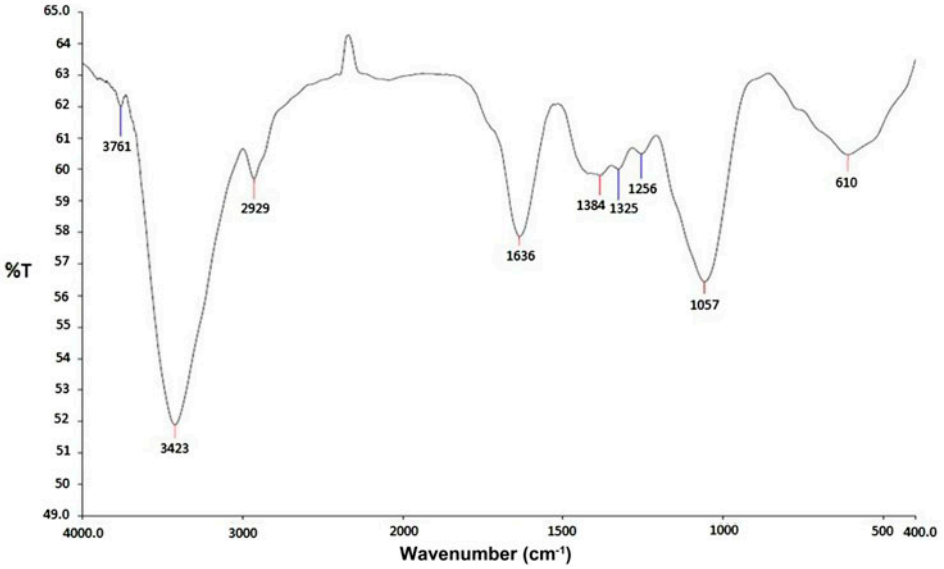

Fig. 5. FTIR spectrum of BP before the adsorption of MG.

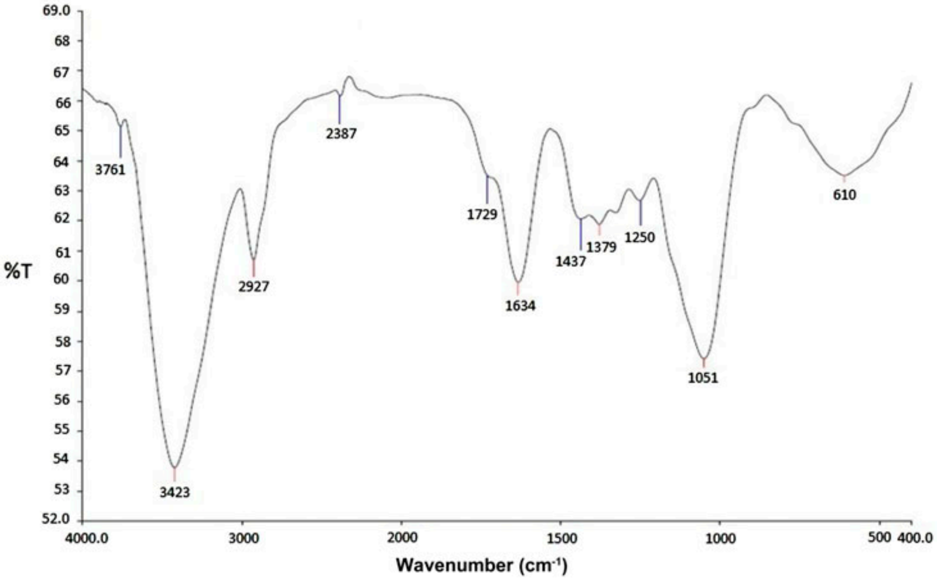

Fig. 6. FTIR spectrum of BP after the adsorption of MG.

Table 5
Analysis of IR spectra for BP

	Frequency (cm^{-1})	
Assignment	Before	After
O–H stretch	3,423	3,423
C–H stretch	2,929	2,927
C=C stretch	1,636	1,634
C–$(CH_3)_2$	1,384	1,437
	1,325	1,379
C–O stretch	1,256	1,250
C–O–C stretch	1,057	1,051
C–OH twist	610	610

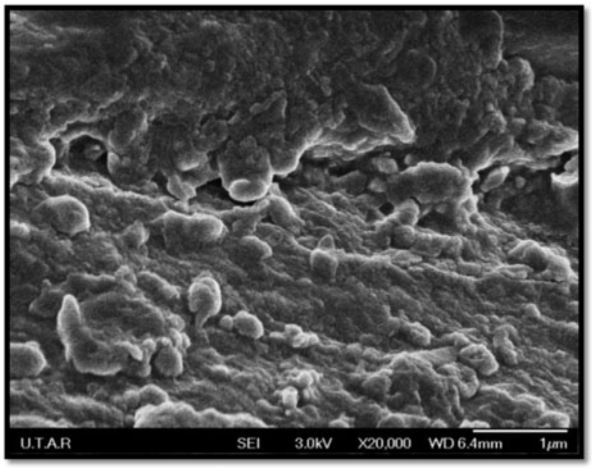

Fig. 7. SEM micrograph of BP before adsorption.

BP surface became smoother because it is covered by dye molecules. Besides, comparison of maximum adsorption capacity for MG by different adsorbents was tabulated and shown in Table 6. Fig. 9(a) and (b) show the surface of TiO_2 before and after adsorption process, respectively. It is observed that there was little difference between these two micrographs and this is because dye molecules were only adhere on the surface of the TiO_2 but the morphology of the photocatalyst was retained.

3.5. Evaluation of important variables for dyes removal

The important factors that cause a significant effect on percentage removal of MG were identified using Plackett–Burman. The analysis of variance (ANOVA) table for removal of MG using adsorption system and using combination system of adsorption and photodegradation was presented in Tables 7 and 8, respectively. From results, it was found that the model *F*-value of 21.41 for adsorption system and 30.33 for combination system implies that both of the models are significant. For both systems, the Prob>*F* value for pH and contact time was less than 0.05 which indicates the model terms are significant for MG uptake.

Since the Prob>*F* values of adsorption system and combination system were greater than 0.05 for initial dye concentration, which were 0.5704 and 0.1209, respectively, this factor was insignificant for the influences of removal of MG. This result agreed well with the studies reported in which the removal of dyes are depended on the pH of the solution and contact time

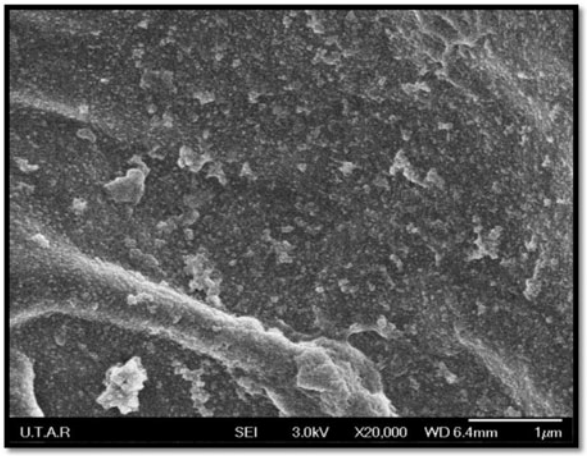

Fig. 8. SEM micrograph of BP after adsorption.

[1,35]. Thus, the important factors which affected the percentage removal of dye in conventional batch study were pH and contact time.

3.6. *Verification of Plackett–Burman design models*

Function of desirability was applied using Design-Expert Version 7.1.3 to validate the models. The experimental conditions were chosen based on the highest desirability. All the experimental conditions, experimental and predicted percentage removal was shown in Table 9. It is apparent that the experimental values obtained agreed well with the predicted values for both models. The percentage errors between the actual and predicted values were 11.92 and 7.20%, respectively, for adsorption system and combination system.

3.7. *Data analysis by RSM*

Characterization of the individual and interactive effects of pH and contact time on the percentage removal of MG by adsorption system and combination system was studied using RSM. The modified cubic models describing the correlation between the two factors and the percentage removal of MG were shown as followed:

Removal of MG using adsorption system:

$$\begin{aligned}\%\,\text{Removal} = {} & -22.43164 + 12.48442\,\text{A} + 0.48436\,\text{B} \\ & + 0.046709\,\text{AB} - 1.11028\,\text{A}^2 - 3.28566 \\ & \times 10^{-3}\,\text{B}^2\end{aligned} \tag{4}$$

Removal of MG using combination system of adsorption and photodegradation:

$$\begin{aligned}\%\,\text{Removal} = {} & -27.37695 + 16.13190\,\text{A} + 0.86716\,\text{B} \\ & + 0.050642\,\text{AB} - 1.60639\,\text{A}^2 - 5.41167 \\ & \times 10^{-3}\,\text{B}^2\end{aligned} \tag{5}$$

where A = pH and B = contact time.

The ANOVA tables for the removal of MG by adsorption system and combination system were shown in Tables 10 and 11, respectively. The model *F*-value of 55.61 and *P* of 0.0002 indicates model for uptake of dye using adsorption was significant. Model for uptake of dye of combination effect was significant ($p < 0.0001$) with *F*-value of 478.71. Both of the coefficients of determination (R^2) for adsorption system were 0.9823 while that of combination system were 0.9979. Both of these values were relatively high and

Table 6
Comparison of maximum adsorption capacity for MG by different adsorbents

Adsorbent	Maximum adsorption capacity (mg/g)	Reference
Activated carbon from pine sawdust	370.37	[26]
Carbonaceous material	75.08	[27]
Chitosan bead	93.55	[13]
Freshwater macrophyte alligator weed	185.54	[12]
Groundnut shell waste	222.22	[28]
Neem sawdust	3.42	[29]
Oil palm trunk fiber	149.35	[30]
Rattan sawdust	62.71	[31]
Rice straw-derived char	148.71	[32]
Sawdust carbon	74.50	[33]
Sugarcane dust	4.88	[34]
Banana pith	5.285	Current work

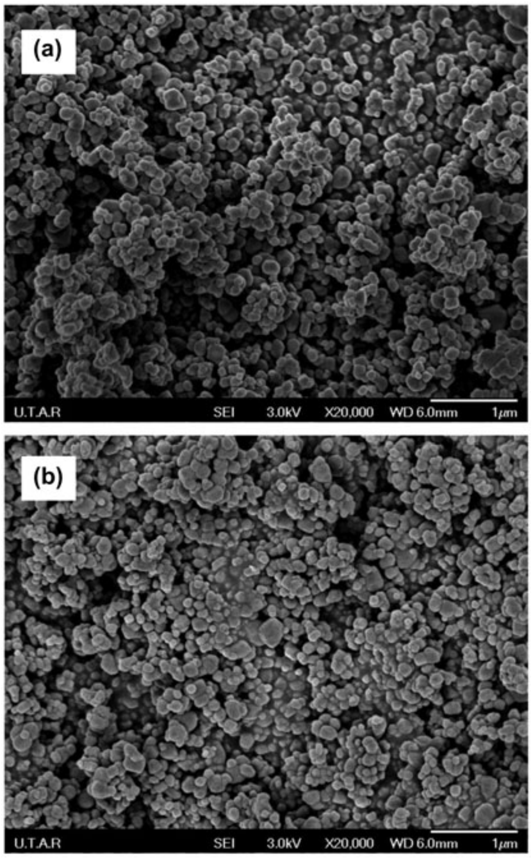

Fig. 9. SEM micrograph of TiO_2 (a) before adsorption and (b) after adsorption.

very close to unity. This shows the good prediction of the response and there were good agreements between the observed and predicted values of both models.

The predicted multiple correlation coefficient (predicted R^2) value of 0.9958 is reasonable agreement with the adjusted multiple correlation coefficient (adjusted R^2) value of 0.8874 for combination effect. However, the predicted R^2 value of 0.9647 for adsorption system did not agree well with its adjusted R^2 value which was 0.0462. The coefficient of variance (CV) of both models was 11.58 and 4.03%, respectively. When the CV value is higher, the precision and reliability of the experiments are lower; hence, the model for combination system was more reliable and precise. Adequate precision shows the signal to noise ratio. Since the adequate precision for both systems was of 22.201 and 55.504 which were greater than 4, adequate signals were shown.

Both models can be used to navigate the design space. To study the interaction between the two variables and their optimum levels, response surface plot for both systems was plotted. Figs. 10 and 11 show the 3D surface plot for interaction between pH and contact time of adsorption system and combination system, respectively. From both of the 3D plot, it was found that maximum percentage removal of MG was attained when both pH and contact time were at maximum level. The optimum operational values were reported as pH 8 and 120 min of contact time for both of the systems. The model predicted 62.04% removal for adsorption system and 72.44% removal for the combination system at these operational conditions.

3.8. Verification of RSM models

Experiments were conducted based on the experimental conditions with the highest desirability generated by Design Expert Version 7.1.3 for verification of the model equations for both systems. All the experimental conditions, predicted and experimental percentage removal were presented in Table 12. From the experimental results obtained, the percentage removal of dye was 59.53% for adsorption system and 72.44% for combination system. Both of the results do not deviate far from the predicted results with percentage errors of 4.04 and 1.60% for adsorption system and combination system, respectively. Thus, it can be concluded both models as valid.

Table 7
Regression analysis (ANOVA) of Plakett–Burman for the uptake of MG in aqueous solution using adsorption system

Source	Degree of freedom	Sum of square	Mean square	*F*-value	Prob > *F*
Model	3	5,414.79	1,771.60	21.41	0.0004
pH	1	1,273.29	1,273.29	15.39	0.0044
Initial dye concentration	1	39.28	39.28	0.47	0.5104
Contact time	1	4,002.23	4,002.23	48.36	0.0001
Residual	8	662.06	82.76		
Total	11	5,976.85			

Table 8
Regression analysis (ANOVA) of Plakett–Burman for the removal of MG in aqueous solution using combination system

Source	Degree of freedom	Sum of square	Mean square	F-value	Prob > F
Model	3	6,488.59	2,162.86	30.33	0.0001
pH	1	741.83	741.83	10.40	0.0121
Initial dye concentration	1	214.80	214.80	3.01	0.1209
Contact time	1	5,531.96	5,531.96	77.56	≤0.0001
Residual	8	570.57	71.32		
Total	11	7,059.15			

Table 9
Plackett–Burman model validation for adsorption and combination system

	Factors			Percentage removal (%)	
System	pH	Initial concentration	Contact time	Predicted	Experimental
BP	8.00	10.00	120.00	53.1917	59.53
BP + TiO_2	8.00	10.00	120.00	55.5950	59.60

Table 10
Regression analysis (ANOVA) for the removal of MG by adsorption system

Source	Degree of freedom	Sum of square	Mean square	F-value	P
Model	5	4,190.50	838.10	55.61	0.0002
A	1	633.78	633.78	42.06	0.0013
B	1	2,220.68	2,220.68	147.36	<0.0001
AB	1	280.40	280.40	18.61	0.0076
A^2	1	133.13	133.13	8.83	0.0311
B^2	1	196.56	196.56	13.04	0.0154
Residual	5	75.35	15.07		
Lack of fit	1	75.35	75.35		

Note: R^2: 0.9823, Adjusted R^2: 0.9647, Predicted R^2: 0.0462, Adequate precision: 22.201 and CV: 11.58%.

Table 11
Regression analysis (ANOVA) for the removal of MG by combination of adsorption and photodegradation system

Source	Degree of freedom	Sum of square	Mean square	F-value	P
Model	5	7,942.32	1,588.46	478.71	<0.0001
A	1	350.25	350.25	105.55	0.0002
B	1	4,696.72	4,696.72	1,415.44	<0.0001
AB	1	329.60	329.60	99.33	0.0002
A^2	1	278.69	278.69	83.99	0.0003
B^2	1	533.23	533.23	160.70	<0.0001
Residual	5	16.59	3.32		
Lack of fit	1	16.59	16.59		

Note: R^2: 0.9979, Adjusted R^2: 0.9958, Predicted R^2: 0.8874, Adequate precision: 55.504 and CV: 4.03%.

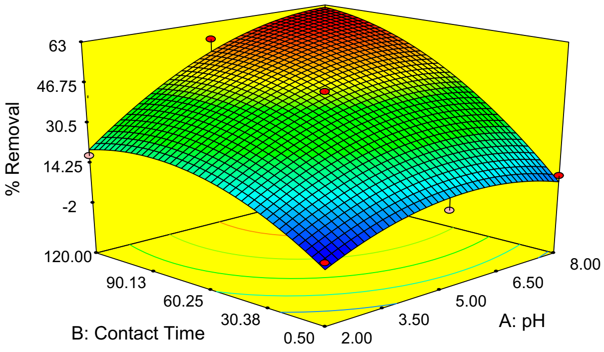

Fig. 10. 3D surface plot for removal of MG in aqueous solution by adsorption as a function of contact time and pH of solution.

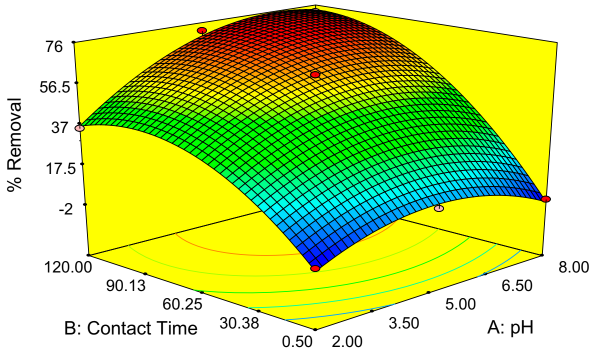

Fig. 11. 3D surface plot for removal of MG in aqueous solution by adsorption and photodegradation as a function of contact time and pH of solution.

Table 12
RSM model validation for adsorption and combination system

	Factors		Percentage removal (%)	
System	pH	Contact time	Predicted	Experimental
BP	8.00	120.00	62.0358	59.53
BP + TiO_2	8.00	120.00	73.6158	72.44

4. Conclusion

The present work identified that BP could be used as potential adsorbent for the removal of MG from aqueous solution. The photocatalytic degradation of MG using TiO_2 could further enhance the percentage removal of MG from aqueous solution. The percentage removal of MG increased with the increased pH of dye solution. The removal of dye increased with contact time but decreased with initial concentration of dye. Plakett–Burman design successfully identify that the most significant factors which influence the percentage removal of dye were pH and contact time but not initial concentrations of MG. Using RSM, optimum conditions for maximum MG removal were determined which were pH 8.0 and contact time of 120 min. Under these optimum conditions, the maximum percentage removal of dye by adsorption on BP was 59.53%. In the presence of photocatalyst, TiO_2, the maximum percentage removal of MG increased to 72.44% at the optimum conditions due to the combination effects of photodegradation and adsorption processes. The model employed provided good quality of predictions in term of dye uptake and correlation coefficients.

Acknowledgments

The authors are thankful for the support by the International Foundation for Science, Stockholm, Sweden and the Organisation for the Prohibition of Chemical Weapons, The Hague, The Netherlands via grant number W/4386-1 and teaching assistantship for E.C. Khoo by Universiti Tunku Abdul Rahman (UTAR).

References

[1] S.T. Ong, E.C. Khoo, P.S. Keng, S.L. Hii, S.L. Lee, Y.T. Hung, S.T. Ha, Plackett–Burman design and response surface methodological approach to optimize basic dyes removal using sugarcane bagasse, Desalin. Water Treat. 25 (2011) 310–318.

[2] B.H. Hameed, D.K. Mahmoud, A.L. Ahmad, Sorption equilibrium and kinetics of basic dye from aqueous solution using banana stalk waste, J. Hazard. Mater. 158 (2008) 499–506.

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

[4] M.H. Baek, C.O. Ijagbemi, S.J. O, D.S. Kim, Removal of malachite green from aqueous solution using degreased coffee bean, J. Hazard. Mater. 176 (2010) 820–828.

[5] V.K. Garg, R. Kumar, R. Gupta, Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: A case study of *Prosopis cineraria*, Dyes Pigm. 62 (2004) 1–10.

[6] K. Sathasivam, M.R.H.M. Mas Haris, Adsorption kinetics and capacity of fatty acid-modified banana trunk fibers for oil in water, Water, Air, Soil Pollut. 213 (2010) 413–423.

[7] C.C. Chen, C.S. Lu, Y.C. Chung, J.L. Jan, UV light induced photodegradation of malachite green on TiO_2 nanoparticles, J. Hazard. Mater. 141 (2006) 520–528.

[8] K. Rajeshwar, J.G. Ibanez, Electrochemical aspects of photocatalysis: Application to detoxification and disinfection scenarios, J. Chem. Educ. 72 (1995) 1044–1049.

[9] Y. Li, X. Li, J. Li, J.W., J. Yin, TiO_2-coated active carbon composites with increased photocatalytic activity prepared by a properly controlled sol–gel method, Mater. Lett. 59 (2005) 2659–2663.

[10] O. Hamdaoui, F. Saoudi, M. Chiha, E. Naffrechoux, Sorption of malachite green by a novel sorbent, dead leaves of plane tree: Equilibrium and kinetic modeling, Chem. Eng. J. 143 (2008) 73–84.

[11] J. Tyssedal, Plackett–Burman Designs, Encyclopedia of Statistics in Quality and Reliability, John Wiley, Chichester, 2008.

[12] X.S. Wang, Invasive freshwater macrophyte alligator weed: Novel adsorbent for removal of malachite green from aqueous solution, Water, Air, Soil Pollut. 206 (2010) 215–223.

[13] Z. Bekçi, C. Özveri, Y. Seki, K. Yurdakoç, Sorption of malachite green on chitosan bead, J. Hazard. Mater. 154 (2008) 254–261.

[14] S.T. Ong, S.Y. Tan, E.C. Khoo, S.L. Lee, S.T. Ha, Equilibrium studies for basic blue 3 adsorption onto durian peel (Durio zibethinus Murray), Desalin. Water Treat. 45 (2012) 161–169.

[15] S.T. Ong, E.C. Khoo, S.L. Hii, S.T. Ha, Utilization of sugarcane bagasse for removal of basic dyes from aqueous environment in single and binary systems, Desalin. Water Treat. 20 (2010) 86–95.

[16] S.T. Ong, P.S. Keng, W.T. Liw, S.L. Wan, Y.T. Hung, Photodegradation of congo red and reactive yellow 2 using immobilized TiO_2 under sunlight irradiation, World Appl. Sci. J. 9 (2010) 303–307.

[17] M. Qamar, M. Saquib, M. Muneer, Semiconductor-mediated photocatalytic degradation of an azo dye, chrysoidine Y in aqueous suspensions, Desalination 171 (2004) 185–193.

[18] M. Arami, N.Y. Limaee, N.M. Mahmoodi, N.S. Tabrizi, Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull, J. Hazard. Mater. 135 (2006) 171–179.

[19] S.T. Ong, P.S. Keng, S.L. Lee, M.H. Leong, Y.T. Hung, Equilibrium studies for the removal of basic dye by sunflower seed husk (*Helianthus annuus*), Int. J. Phys. Sci. 5 (2010) 1270–1276.

[20] F.A. Pavan, A.C. Mazzocato, Y. Gushikem, Removal of methylene blue dye from aqueous solutions by adsorption using yellow passion fruit peel as adsorbent, Bioresour. Technol. 99 (2008) 3162–3165.

[21] O.K. Mahadwad, P.A. Parikh, R.V. Jasra, C. Patil, Photocatalytic degradation of reactive black-5 dye using TiO_2 impregnated ZSM-5, Bull. Mater. Sci. 34 (2011) 551–556.

[22] S. Mozia, M. Tomaszewska, A.W. Morawski, Photocatalytic degradation of azo-dye acid red 18, Desalination 185 (2005) 449–456.

[23] A.K. Subramani, K. Byrappa, S. Ananda, K.M. Lokanatha Rai, C. Ranganathaiah, M. Yoshimura, Photocatalytic degradation of indigo carmine dye using TiO_2 impregnated activated carbon, Bull. Mater. Sci. 30 (2007) 37–41.

[24] S.T. Ong, W.S. Cheong, Y.T. Hung, Photodegradation of commercial dye, methylene blue using immobilized TiO_2, 4th International Conference on Chemical, Biological and Environmental Engineering, 43, 2012, pp. 109–113.

[25] P.W. Lee, S.T. Ong, Y.T. Hung, S.L. Lee, Photodegradation of malachite green by immobilization of titatium dioxide, TiO_2 on glass plates, Asian J. Chem. 25 (2013) 755–758.

[26] C. Akmilbasar, Y. Onal, T. Kilicer, D. Eren, Adsorptions of high concentration malachite green by two activated carbons having different porous structures, J. Hazard. Mater. 127 (2005) 73–80.

[27] V.K. Gupta, S.K. Srivastava, D. Mohan, Equilibrium uptake, sorption dynamics, process optimization, and column operations for the removal and recovery of malachite green from wastewater using activated carbon and activated slag, Ind. Eng. Chem. Res. 36 (1997) 2207–2218.

[28] R. Malik, D.S. Ramteke, S.R. Wate, Adsorption of malachite green on groundnut shell waste based powdered activated carbon, Waste Manage. 27 (2007) 1129–1138.

[29] S.D. Khattri, M.K. Singh, Colour removal from synthetic dye wastewater using a bioadsorbent, Water, Air, Soil Pollut. 120 (2000) 283–294.

[30] B.H. Hameed, M.I. El-Khaiary, Batch removal of malachite green from aqueous solutions by adsorption on oil palm trunk fibre: Equilibrium isotherms and kinetic studies, J. Hazard. Mater. 154 (2008) 237–244.

[31] B.H. Hameed, M.I. El-Khaiary, Malachite green adsorption by rattan sawdust: Isotherm, kinetic and mechanism modeling, J. Hazard. Mater. 159 (2008) 574–579.

[32] B.H. Hameed, M.I. El-Khaiary, Kinetics and equilibrium studies of malachite green adsorption on rice straw-derived char, J. Hazard. Mater. 153 (2008) 701–708.

[33] V.K. Garg, R. Gupta, A. Bala Yadav, R. Kumar, Dye removal from aqueous solution by adsorption on treated sawdust, Bioresour. Technol. 89 (2003) 121–124.

[34] S.D. Khattri, M.K. Singh, Colour removal from dye wastewater using sugarcane dust as an adsorbent, Adsorpt. Sci. Technol. 17 (1999) 269–282.

[35] S.T. Ong, W.N. Lee, P.S. Keng, S.L. Lee, Y.T. Hung, Optimization of basic and reactive dye uptakes in binary dye solution using statistical experimental methodology, Int. J. Phys. Sci. 5 (2010) 2171–2178.