Desalination and Water Treatment
www.deswater.com

doi: 10/5004/dwt.2012.3072

40 (2012) 260–271
February

Design of experiments for Malachite Green dye removal from wastewater using thermolysis – coagulation–flocculation

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Received 29 June 2011; Accepted 8 November 2011

ABSTRACT

Thermolysis – coagulation–flocculation was used for reduction of colour and chemical oxygen demand (COD) of aqueous basic dye Malachite Green. Statistical design of experiment was used for thermolysis experiments which resulted of 69.57% and 70.59% maximum reduction of COD and color, respectively at the optimum conditions of 95 min treatment time, 82°C treatment temperature, and pH 11.02. $MgCl_2$ was used as coagulant for coagulation–flocculation. About 98% of color and 90% of COD were reduced at a final pH of 10.89 and a coagulant dose of 3 g $MgCl_2$ l^{-1} of dye solution. The optimum conditions for coagulation–flocculation process were determined by varying a single factor while keeping other factors fixed at a specific set of conditions. Coagulation–flocculation after thermolysis at the optimal operating conditions resulted in a reduction of 91.26% COD and 98.78% color at final pH 10.89 but at a much lesser coagulant dosage of 500 mg l^{-1}. Compared to only coagulation–flocculation, combined process of thermolysis followed by coagulation–flocculation produced relatively less floc, since lesser amount of coagulant was required to remove higher color and COD.

Keywords: Design of experiments; Malachite Green; COD; Color; Thermolysis; Coagulation–flocculation

1. Introduction

The rapid growth of textile industry has increased the usage of synthetic complex organic dyes [1]. Due to high requirement of water in textile industry, a large amount of dye wastewater is produced [2]. The color in these wastewaters is due to synthetic dyes left unused due to industrial inefficiencies [3]. Dye wastewater is categorized as not environmental friendly since it is strongly colored, contain large amount of suspended solids, broad fluctuating pH value, and high chemical oxygen which is unacceptable under most country's environmental regulations [4]. Thus, dye wastewater need to be treated before being discharged into the environment. There are various technologies available for the treatment of dye wastewater such as: coagulation–flocculation, adsorption, ion exchange, Fenton oxidation, ozonation, aerobic and anaerobic biological

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treatment, and membrane filtration etc. However, the negative aspects of these technologies are, for example, unable to treat many diverse pollutants, disposal problems or high in operation cost prohibit the particular technology to be applied to the large scale wastewater [4].

Malachite Green, a triphenylmethane basic dye which is dark green crystalline solid, has been widely used in aquaculture, food, health, textile, and other industries [5,6]. It is most widely used for colouring purpose, amongst all other dyes of its category [7]. Like other dyes, the physical and chemical properties of Malachite Green make it difficult to remove from aqueous solutions. If effluent containing Malachite Green is discharged into natural aquatic systems, it can cause harmful effects to the liver, gills, kidneys, intestines and gonads of aquatic life. In addition to have genotoxic and carcinogenic potential, Malachite Green may also exert effects on the immune system and reproductive system, and cause irritation to gastrointestinal tract of its consumer [6]. Besides, according to Kumar et al. [8] and Daneshvar et al. [9], contact of Malachite Green with skin can also cause irritation, redness and pain.

Thermolysis is a chemical process in which heat is used to decompose a substance (complex organic matter + catalyst + H_2O) into other substances (solid residue, smaller organic molecules, water, gas) [10–12].

Gaseous products generated from thermolysis have pungent and foul smell [13]. However these components have not been identified due to difficulty in sampling. In coagulation–flocculation, coagulant and coagulant aids are used to produce flocs together with dye stuffs. The flocs are then removed from the aqueous solution by physical sedimentation and filtration. The examples of coagulants are PAC, alum, $FeSO_4$, $MgCl_2$ and lime [1,14]. It is inadequate to treat dye wastewater with single process due to the complex nature of dye wastewater. Therefore, combined processes have been suggested to overcome the disadvantage of individual unit processes [15]. Thermolysis accompanied with coagulation–flocculation has been proposed as an effective method to treat dye effluent. It can remove almost 100% COD as well as color of textile wastewater at a lower dose of coagulant [11,16]. Therefore, the amount of sludge generated is lesser than the conventional coagulation–flocculation treatment [10,11,16]. The objectives of present study are to optimize the removal efficiency of basic Malachite Green dye using Response Surface Methodology (RSM) for thermolysis followed by coagulation–flocculation process in term of COD reduction and color removal. The effects of different parameters, such as pH, temperature, treatment time and coagulant dosage on performance of the process have been studied.

2. Materials and methods

2.1. Materials

The experimental chemicals used in this study were synthetic dye (Malachite Green, C.I. No. = 42,000, supplied by Bendozen, Malasiya; molecular weight = 329.5; $C_{18}H_{25}N_2Cl$), magnesium chloride (supplied by Systerm ChemAR, Malasiya; 99.5% assay; molecular weight = 203.31; $MgCl_2.6H_2O$), anionic polyacrylamide (coagulant aid, supplied by T.C. Chem. Technology, Malasiya), sulphuric acid (supplied by Bright Chem; 96% assay; molecular weight = 98.08), sodium hydroxide (supplied by Systerm ChemAR, Malasiya; 99% assay) and COD digestion reagent.

2.2. Synthetic dye aqueous solution

Synthetic dye aqueous solution was prepared by dissolving 0.3 g of Malachite Green in distilled water to make 1000 ml solution. Since Malachite Green was not readily dissolved, the solution was stirred and heated for half an hour. After that, the solution was filtered to remove the not dissolved dye. The range for dye which really dissolved in the solution were 175–206 mg l^{-1}. This is the possible range of dye in wastewater.

2.3. Analytical methods

The COD value was assayed using a Hach DR/2010 spectrophotometer, model 45,600, COD analyzer. The Standard Dichromator Closed Reflux Method (APHA-1989) was used. The color measurement was done by the Pt–Co (Hazen) unit method. To determine the color in Pt–Co unit, a light of 455 nm was used in a Hach DR/2010 spectrophotometer. Filtration for all the treated effluent was carried out using Millipore filtration assembly using 0.45 µm filters. Hach's type Sension 3 pH meter was used to measure the pH. A small scale jar test apparatus with six paddle stirrers (Velp Scientifica JLT 6) was used for coagulation–flocculation process.

2.4. Experimental

2.4.1. Thermolysis

pH adjusted (by using NaOH and H_2SO_4) synthetic dye aqueous solution (300 ml) was taken in three-necked glass reactor and. Then, the solution was heated by Rota mantle to desired temperature at constant speed for magnetic stirrer. Design of experiments such as two-level Full Factorial Design and RSM; central composite design (CCD) was applied to optimize the thermolysis process. Minitab version 14 statistical software was used to analyze the results of the process. It was found that parameters such as pH, temperature and treatment time may affect the process. The best working range for all factors was estimated. Then, screening experiment was carried out by using two-level full factorial design to identify the factors which have significant effect. Lastly, optimization experiment was carried out using CCD to identify the optimal conditions.

2.4.2. Coagulation–flocculation

For coagulation–flocculation, six beakers containing 150 ml of dye solution were used with jar test equipment. After pH adjustment, calculated amount of coagulant was added into each beaker. The mixture was then stirred for 3 min at 80 rpm. After addition of 3 ml coagulant aids, again the mixture was stirred at a lower speed for 10 min. The dye solution was then allowed to settle and the settling time was recorded. The supernatant from coagulation was filtered before the COD and color measured. The optimum conditions for coagulation process were determined by varying a single factor while keeping all other factors fixed.

2.5. Experimental design

2.5.1. Two-level full factorial design

Experiments are conducted in order to investigate the effects of one or more factors on a response. Response can be defined as an outcome of an experiment, whereas a factor is an experimental variable that is being investigated. When an experiment consists of two or more factors, the factors can influence the response individually or jointly. Factorial designs involving several factors are important to determine the joint effect of these factors on a response. This design provides the smallest number of treatment combinations with which *k* factors can be studied in a complete factorial arrangement. However, the main objective of factorial design is to discover the insignificant factor and eliminate it throughout out the experiment [17]. The advantage of factorial designs is that this design allows effect of a factor to be estimated at several levels of the other factors, yielding valid conclusion over a range of experimental conditions. Furthermore, a factorial design also can help to avoid misleading conclusions that may be result from undetected interaction among factors [17]. Factorial design which was utilized in this study was 2^3 full factorial design. The independent variables selected were (i) x_1, temperature; (ii) x_2, pH and (iii) x_3, treatment time. The percentage of COD reduction and colour removal were chosen as the dependant response. Table 1 has shown experimental range and levels of independent process variables for full factorial design. The actual design of experiment is shown in Table 2 (Results generated using full factorial design for screening stage).

Table 1
Experimental range and levels of independent process variables for full factorial design

Independent variable	Range and level		
	–1	0	1
Temperature (°C)	70	80	90
pH	3	6	9
Time (min)	50	100	150

2.5.2. Response surface methodology (RSM)

RSM is a collection of mathematical and statistical techniques for analyzing problems in which a dependent variable or response is influenced by several independent variables. The objective of RSM is to find the independent variable conditions that optimize the response [17]. These methods are often employed after screening of independent variables, usually by performing a factorial design [18]. In this study, CCD was used for the RSM in the experimental design. This method is suitable for fitting a quadratic surface and it helps to optimize the significant parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters [19]. Since the result of factorial design shows that the effects of all factors (temperature, pH and treatment time) were significant, thus, these factors were included in RSM. According to a 2^3 full factorial CCD for three variables, a total of 20 experiments were conducted. These 20 experiments consist of eight factorial points (coded to the usual ±1 notation), six axial points (±α, 0, 0), (0, ±α, 0), (0, 0, ±α) and six replicates at the center points (0, 0, 0). Value of α represent the distance of the axial point from center and makes the design rotatable. It was depended on the number of point in the factorial portions of design and can be calculated from the following equation:

$$\alpha = (N_F)^{(1/4)} \tag{1}$$

where N_F is the number of factorial points ($N_F = 2^3$). Thus, according to Eq. (1), α in this study was equal to $(2^3)^{(1/4)} = 1.68179$. Furthermore, center points were used to determine the experimental error and the reproducibility of the data. The low, middle and high levels of each variable were represented by –, 0, and + respectively. Low level is the level where the lowest condition of factors is used and high level is the level where the highest condition of factors is used [4,19,20]. Since the whole experiments were duplicated, total experiments for CCD become 20 × 2 = 40 experiments. The behavior of this experiment is explained by the following quadratic equation:

Table 2
Results generated using full factorial design for screening stage

Run order	Blocks	Temperature	pH	Time	Final pH	Final colour	Final COD	Colour removal (%)	COD removal (%)
1	1	0	0	0	5.50	2900	217	17.14	36.36
2	1	–1	–1	1	3.02	3800	303	9.52	8.18
3	1	–1	–1	1	3.06	4400	304	12.00	9.52
4	1	1	1	–1	6.00	2200	170	45.00	52.25
5	1	–1	–1	–1	3.04	4600	318	8.00	5.36
6	1	–1	–1	–1	3.12	3700	386	7.50	6.31
7	1	1	1	1	6.12	1300	166	69.77	52.84
8	1	–1	1	–1	3.97	4000	210	20.00	56.79
9	1	1	–1	–1	3.11	5300	499	1.85	9.76
10	1	1	–1	1	3.18	4700	415	17.54	24.95
11	1	1	1	1	5.90	1000	150	70.59	54.41
12	1	–1	1	1	5.79	3100	281	35.42	41.82
13	1	0	0	0	5.70	3900	251	15.22	36.29
14	1	1	–1	1	3.22	4200	296	17.65	24.87
15	1	1	1	1	6.06	1200	161	70.00	54.78
16	1	–1	1	–1	3.88	4100	209	19.61	58.94
17	1	1	–1	1	3.15	4100	310	18.00	24.94
18	1	–1	1	1	5.61	3400	285	35.85	41.24
19	1	–1	–1	–1	3.06	4300	309	6.52	6.36
20	1	1	1	–1	6.47	2200	187	45.00	52.54
21	1	–1	–1	1	3.03	3600	372	10.00	9.71
22	1	1	1	–1	5.87	1900	150	44.12	54.41
23	1	–1	1	1	5.83	3300	300	35.29	41.97
24	1	1	–1	–1	3.2	4000	363	0.00	7.87
25	1	1	–1	–1	3.17	5000	378	0.00	8.47
26	1	–1	1	–1	4.04	3800	194	20.83	57.27

$$Y = \beta_0 + \Sigma\ \beta_i X_i + \Sigma\ \beta_{ii} X_i^2 + \Sigma\ \beta_{ij} X_i X_j \qquad (2)$$

where Y is the predicted response, β_0 is the constant coefficient, β_i is the linear effect, β_{ii} is the square effect, β_{ij} represent the interaction effect and X_i, X_j are the coded values of variables [4].

3. Results and discussion

3.1. Screening of independent factors for thermolysis

The extent of performance of thermolysis depends on factors such as treatment time, pH and temperature [10,11]. The influence of these factors was determined by measuring COD reduction and color removal. Screening experiment was performed according to Table 2 (Results generated using full factorial design for screening stage) to determine the effects of factors and their interactions. Triplications of eight runs in one block which contain two center points were performed to determine the standard error of coefficient and experimental error [4]. The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors [20]. The result of colour removal and COD reduction were presented in percentage (%) and were analyzed using Minitab Statistical Software Release 14.1.

3.1.1. Estimated effects and coefficient for full factorial design

Table 3 shows the estimated effects and coefficients for percentage colour removal and COD reduction, respectively. It can be observed that the probability level (p value) for all main factors, which are pH, temperature and treatment time, and the interactions among the factors for both color removal and COD reduction are less

Table 3
Estimated effects and coefficients for color removal and COD reduction (full factorial design)

Term	Color removal				
	Effect	Coef	SE Coef	T	P
Constant		25.836	0.1616	159.86	0.000
Temperature	14.915	7.458	0.1616	46.14	0.000
pH	33.575	16.787	0.1616	103.87	0.000
Time	15.267	7.633	0.1616	47.23	0.000
Temperature* pH	14.665	7.333	0.1616	45.37	0.000
Temperature* time	5.997	2.998	0.1616	18.55	0.000
pH* time	5.127	2.563	0.1616	15.86	0.000
Temperature* pH* time	–0.977	–0.488	0.1616	–3.02	0.008
Ct Pt		–9.656	0.5827	–16.57	0.000
S = 0.791739; R-Sq = 99.91%; R-Sq(adj) = 99.86%.					
	COD reduction				
Constant		31.898	0.1687	189.07	0.000
Temperature	6.552	3.276	0.1687	19.42	0.000
pH	39.413	19.707	0.1687	116.81	0.000
Time	1.075	0.538	0.1687	3.19	0.005
Temperature* pH	–2.685	–1.343	0.1687	–7.96	0.000
Temperature* time	7.507	3.753	0.1687	22.25	0.000
pH* Time	–8.598	–4.299	0.1687	–25.48	0.000
Temperature* pH* time	0.96	0.48	0.1687	2.85	0.011
Ct Pt		4.427	0.6083	7.28	0.000

S = 0.826499; R-Sq = 99.89%; R-Sq(adj) = 99.84%.

than 0.05. This indicates that all the effects and interactions are significant [18]. The center point is useful to obtain the standard error of the coefficients. The probability results show that the center point is significant (p = 0.00). This means that it is detected at a curvature of the factors when the levels are changed from the lower level (–) to the higher level (+), passing through the center point (0) [18]. The model for both color removal and COD reduction present an adjusted determination coefficient (R-Sq adj) of 99.86% and 99.84% respectively, fitting very well with the statistical model [18].

3.1.2. Pareto chart

Pareto chart can be used to evaluate the effect of each factor as well as the interaction among the factors, where any values with an absolute value higher than 2.1 are considered significant [4]. The vertical line in the chart indicates the minimum statistically significant effect magnitude for 95% confidence level [21]. The Pareto chart of standardized effects at P = 0.05 for color removal and COD reduction are presented in Figs. 1 and 2, respectively. Since both figures show that all factors are significant, therefore, no factor is discarded from this study.

3.1.3. Analysis of variance (ANOVA)

The Analysis of Variance (ANOVA) for color removal and COD reduction are shown in Table 4. For both cases, the main factors, two-way interactions and three-way interactions are significant at 5% probability level ($p < 0.05$). Besides, the ANOVA for both color removal and COD reduction showed that this model present a curvature, since the probability for both curvatures are 0.000 [18].

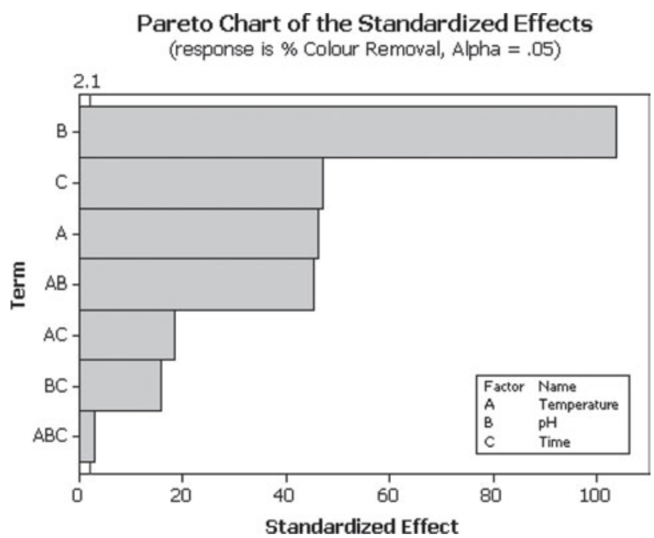

Fig. 1. Pareto chart of standardized effect for percentage of color removal.

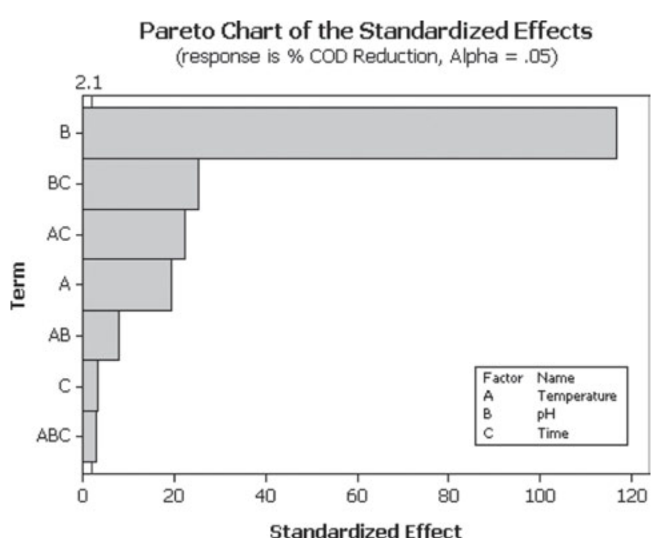

Fig. 2. Pareto chart of standardized effect for percentage of COD reduction.

Table 4
Analysis of variance (ANOVA) for color removal and COD reduction (full factorial design)

Source	DF	Seq SS	Adj SS	Adj MS	F	P
	Color removal					
Main effects	3	9496.9	9496.85	3165.62	5050.03	0.000
Two-way interactions	3	1663.8	1663.83	554.61	884.76	0.000
Three-way interactions	1	5.7	5.72	5.72	9.13	0.008
Curvature	1	172.1	172.13	172.13	274.59	0.000
Residual error	17	10.7	10.66	0.63	–	–
Pure error	17	10.7	10.66	0.63	–	–
Total	25	11349.2	–	–	–	–
	COD reduction					
Main effects	3	9584.9	9584.94	3194.98	4677.17	0.000
Two-way interactions	3	824.9	824.94	274.98	402.55	0.000
Three-way interactions	1	5.5	5.53	5.53	8.09	0.011
Curvature	1	36.2	36.18	36.18	52.96	0.000
Residual error	17	11.6	11.61	0.68	–	–
Pure error	17	11.6	11.61	0.68	–	–
Total	25	10463.2	–	–	–	–

DF, degree of freedom; Seq SS, sequential sum of squares; Adj SS, adjusted sum of squares; F, factor F; P, probability.

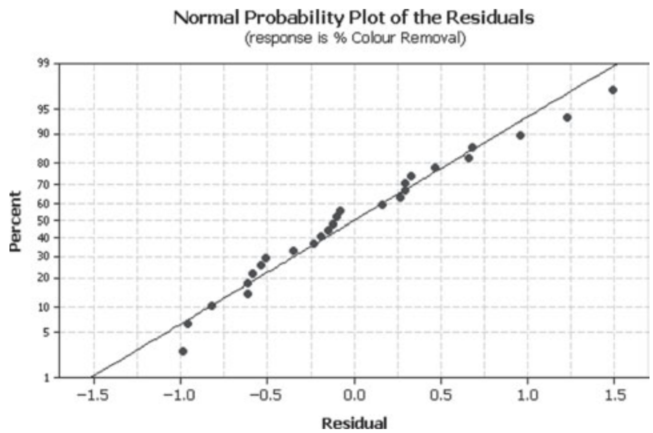

Fig. 3. Normal probability plot of the residuals for percentage of color removal.

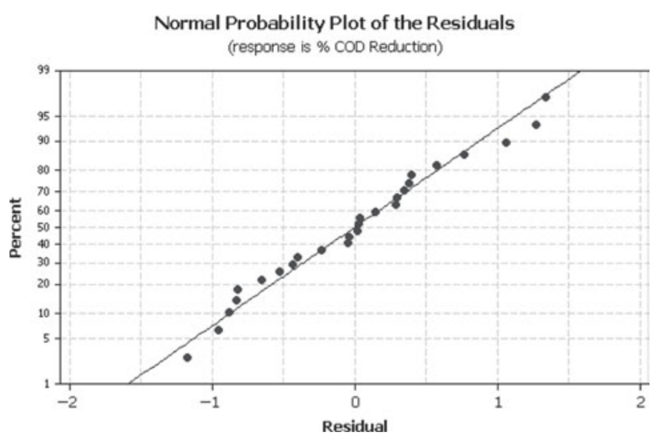

Fig. 4. Normal probability plot of the residuals for percentage of COD reduction.

3.1.4. Normal probability plot of residuals

Figs. 3 and 4 show the normal probability plot of residuals for both color removal and COD reduction, respectively. The data are normally distributed, since the plots resemble a straight line. After performing screening process, it was found that all factors have significant effect on responses. Therefore, no factor was discarded from this stage.

3.2. Optimization for thermolysis

After performing screening of factors using full factorial design, a central composite response surface design was conducted to obtain the relationship between the factors and response and to optimize the response. This experiment contains 20 base runs and duplicates were performing; therefore, there were overall 40 runs. The range and level was used according to Table 5. Results generated from this design are shown in Table 6.

3.2.1. Development of regression model equation

The regression coefficient, t and p-value for all the linear, quadratic and interaction effects of the parameters for color removal and COD reduction are given in Table 7. It is observed that the coefficients for the linear, quadratic and interaction effect for both COD reduction and color

Table 5
Experimental range and levels of independent process variables for central composite design

Independent variable	Range and level				
	$-\alpha$	–1	0	1	α
Temperature (°C)	63.2	70	80	90	96.8
pH	0.95	3	6	9	11.05
Time (min)	16	50	100	150	184

Table 6
Randomized design table and result for central composite design

Run order	Blocks	Temperature	pH	Time	Final pH	Final color	Final COD	Color removal (%)	COD removal (%)
1	1	1	1	1	6.12	1300	166	69.77	52.84
2	1	−1	1	1	5.79	3100	281	35.42	41.82
3	1	0	−α	0	0.96	3500	485	10.26	3.39
4	1	1	1	−1	6	2200	170	45.00	52.25
5	1	−1	1	−1	3.97	4000	210	20.00	56.79
6	1	1	−1	1	3.18	4700	415	17.54	24.95
7	1	1	−1	−1	3.2	4000	363	0.00	7.87
8	1	0	0	α	6.37	2900	300	38.30	23.27
9	1	0	0	0	5.5	2900	217	17.14	36.36
10	1	0	0	0	5.7	3900	251	15.22	36.29
11	1	α	0	0	5.38	3100	236	22.50	41.15
12	1	0	−α	0	0.96	3300	307	10.81	2.85
13	1	0	0	0	5.5	4400	255	16.98	35.11
14	1	−1	−1	−1	3.12	3700	386	7.50	6.31
15	1	0	0	−α	5.81	4200	314	10.64	21.50
16	1	1	1	−1	5.87	1900	157	44.12	52.28
17	1	0	0	0	5.53	3700	245	15.91	35.86
18	1	0	0	0	5.82	3100	265	16.22	36.30
19	1	0	0	−α	5.6	3500	300	10.26	21.05
20	1	0	α	0	8.22	1200	154	69.23	69.32
21	1	−1	−1	1	3.03	3600	375	10.00	8.98
22	1	0	α	0	8.35	1100	150	69.44	69.57
23	1	0	0	0	5.6	3800	285	15.56	35.96
24	1	1	−1	−1	3.17	5000	380	0.00	7.99
25	1	1	1	1	5.9	1000	155	70.59	52.89
26	1	0	0	0	5.66	3000	232	16.67	36.09
27	1	α	0	0	5.66	3200	232	21.95	40.97
28	1	−α	0	0	5.41	4200	264	0.00	32.82
29	1	−α	0	0	5.6	3700	220	0.00	32.93
30	1	0	0	0	5.68	3000	238	16.67	35.50
31	1	−1	−1	−1	3.06	4300	309	6.52	6.36
32	1	−1	1	−1	4.04	3800	194	20.83	57.27
33	1	1	−1	1	3.15	4100	310	18.00	24.94
34	1	0	0	0	5.77	3300	243	17.5	36.05
35	1	0	0	α	6.36	2400	292	38.46	23.16
36	1	0	0	0	5.69	3400	268	17.07	35.11
37	1	0	0	0	5.38	3200	262	15.79	35.94
38	1	−1	1	1	5.83	3300	300	35.29	41.97
39	1	−1	−1	1	3.02	3800	303	9.52	8.18
40	1	0	0	0	5.8	3300	250	15.38	35.40

removal are highly significant since p-value is equal to 0.000. Eqs. (3) and (4) shows the quadratic regression model equation for color removal (Y_1) and COD reduction (Y_2), respectively:

$$Y_1(\%\text{ color removal}) = 16.344 + 7.128x_1 + 17.197x_2 + 7.912x_3 - 1.861x_1^2 + 8.329x_2^2 + 2.842x_3^2 + 7.246x_1x_2 + 3.213x_1x_3 + 2.505x_2x_3 \quad (3)$$

$$Y_2(\%\text{ COD reduction}) = 35.8343 + 2.7774x_1 + 19.6099x_2 + 0.5849x_3 + 0.3790x_1^2 + 0.1368x_2^2 - 4.8262x_3^2 - 1.4694x_1x_2 + 3.8131x_1x_3 - 4.2244x_2x_3 \quad (4)$$

Table 7
Estimated regression coefficient for color removal and COD reduction (central composite design)

Term	Color removal			
	Coef	SE Coef	T	P
Constant	16.344	0.2531	64.578	0.000
Temperature	7.128	0.1679	42.449	0.000
pH	17.197	0.1679	102.411	0.000
Time	7.912	0.1679	47.116	0.000
Temperature* temperature	–1.861	0.1635	–11.386	0.000
pH* pH	8.329	0.1635	50.952	0.000
Time* time	2.842	0.1635	17.385	0.000
Temperature* pH	7.246	0.2194	33.027	0.000
Temperature* time	3.213	0.2194	14.642	0.000
pH* time	2.505	0.2194	11.417	0.000
S = 0.8776, R-Sq = 99.8%, R-Sq(adj) = 99.8%.				
	COD reduction			
Constant	35.8343	0.12654	283.194	0.000
Temperature	2.7774	0.08395	33.082	0.000
pH	19.6099	0.08395	233.58	0.000
Time	0.5849	0.08395	6.967	0.000
Temperature* temperature	0.379	0.08173	4.637	0.000
pH* pH	0.1368	0.08173	1.674	0.000
Time* time	–4.8262	0.08173	–59.053	0.000
Temperature* pH	–1.4694	0.10969	–13.396	0.000
Temperature* time	3.8131	0.10969	34.762	0.000
pH* time	–4.2244	0.10969	–38.512	0.000

S = 0.4388, R-Sq = 100.0%, R-Sq(adj) = 99.9%.

where Y is predicted response, x_1, x_2 and x_3 are coded values of the respective treatment system factors: temperature (x_1), pH (x_2) and treatment time (x_3) respectively. For both equations, positive sign in front of the terms indicate synergistic effect, whereas the negative sign indicates antagonistic effect [19]. The quality of polynomial model is expressed by the coefficient of determination, R^2. A high R^2 value, close to 1, is desirable and ensures a satisfactory adjustment of the quadratic model to the experimental data [19]. The R^2 value for Eq. (3) is 0.998 and 1 for Eq. (4). This indicates that both regression model for color removal and COD reduction provides an excellent relation between the significant variables and the response. In addition, the high value of the adjusted determination coefficient (R-Sq adj) for both color removal and COD reduction show that both model are highly significant.

3.2.2. Effect of interactive variables

To investigate the interaction between three factors towards the response, three dimensional surface plots and two dimensional contour plots were drawn. Fig. 5 (pH and temperature) shows the relative effect of pH and temperature when the remaining variable (treatment time) was keep constant. Vertical axis for that contour plot represent pH while temperature represented by horizontal axis. The highest percentage of color removal was 80% when the condition for both pH and temperature were at high level. From the second contour plot in Fig. 5 (time and temperature), the highest percentage of color removal (40%) was achieved when the condition for both time and temperature were at high level. From the third contour plot in Fig. 5 (time and pH), the highest percentage of color removal (80%)

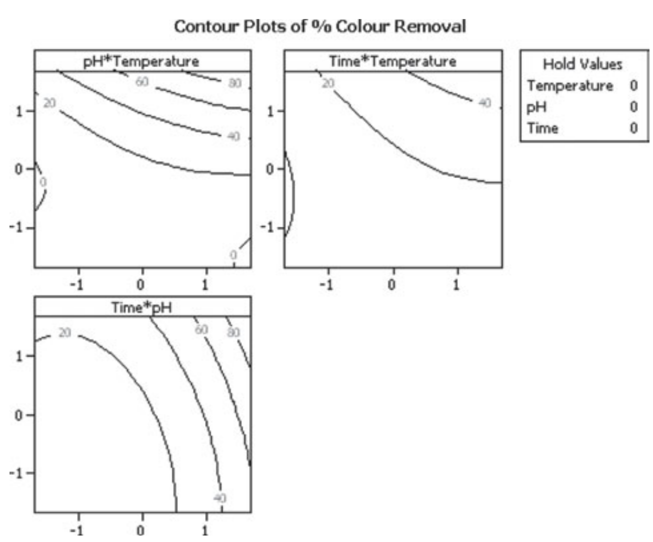

Fig. 5. Contour plot for color removal.

was attained when the condition for both time and pH were at high level.

3.2.3. Optimum response for color removal and COD reduction

The optimum condition for color removal and COD reduction are shown in Fig. 6. The optimum response for color removal and COD reduction are 70.59% and 69.57%, respectively. To attain the optimum response, temperature and pH are fixed at high level, which are 0.1785 (82°C) and 1.6718 (11.02) respectively; whereas time is fixed at low level, which is −0.0935 (95 min).

The result from Fig. 6 indicated that high pH (11.02) maximize the color removal and COD reduction. When a basic dye is treated with alkali, it will decompose with the liberation of the dye base which is colourless. Besides, many of the dye bases are sparingly soluble in water. Therefore, if alkaline is added to a basic dye solution, a flocculent precipitate of the base will appear [22]. During thermolysis, it is anticipated that the pH of the solution undergoes continuous change. Therefore, at the end of the thermolysis, the final pH of the solution may be different from initial pH [13,23]. Randomized design and result for CCD are shown in Table 6. The reduction in pH at the end of the treatment possibly is due to decomposition of bigger organic molecules which transform them into lower carboxylic acids [10]. However, there are also some exceptions. For final pH which is higher than initial pH, it may be due to the formation of hydroxyl ion by reaction with water. As mention earlier, time taken to attain desired temperature is heating time, whereas treatment time refers to time that needed to maintain the desired temperature. The heating time increases with an increase in the treatment temperature [13]. In this study, the heating periods required for raising the temperature of the solution from the ambient temperature to the treatment temperatures are 20 min for 63.2°C; 25 min for 70°C; 31 min for 80°C; 38 min for 90°C; and 45 min for 96.8°C.

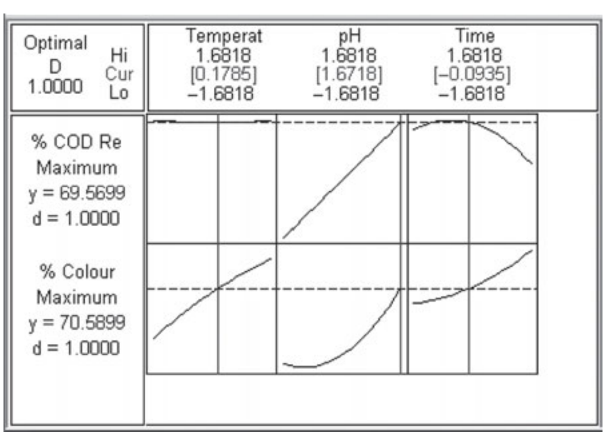

Fig. 6. Optimum responses for color removal and COD reduction.

At 95 min of treatment time for thermolysis can attain optimum response. Because from the transient heating to the 95 min of treatment time, precipitation and thermal degradation of organic molecules were occurred and large molecules of organic matter were broken into smaller molecules. At 95 min of treatment time, the reaction was optimum, therefore, yielding optimum responses. Further increase in treatment time did not give any significant effect as the thermolysis of the smaller molecules is relatively difficult [13].

3.3. Coagulation–flocculation

3.3.1. Effect of pH

The effect of pH on COD reduction and color removal by coagulation–flocculation was studied. $MgCl_2$ was used as coagulant. The optimum pH range for this process was determined by varying the solution pH at a constant coagulant dosage (3000 mg l^{-1}). Table 8 shows the result in coagulation–flocculation process. Color removal and COD reduction are increased as the final pH value of the solution increases from 7.78 to 10.89. This is because magnesium ions in $Mg(OH)^+$ form reduces the negative charges on the dye particles to form $Mg(OH)_2$ precipitates on the dye particle surface [24]. The color removal and COD reduction was decreased as the pH increased beyond 10.89. This was probably due to the increased in solubility of the magnesium precipitate and the formation of hydrolysis products such as $Mg(OH)^+$, $Mg_2(OH)_3^+$, and $Mg(OH)_4^{4+}$ [25].

3.3.2. Effect of $MgCl_2$ dosage

The effect of coagulant dosage was investigated by varying the dosage of $MgCl_2$ keeping other conditions constant. Final pH was kept at 10.89. Color removal and COD reduction were increased with the $MgCl_2$ dosage (Table 9).

It can be seen that a minimum dosage of $MgCl_2$ of 3000 mg l^{-1} was required to achieve more than 98% color removal and 90% COD reduction. However, further increased in the $MgCl_2$ dosage could only achieve slight improvement in color removal and COD reduction since almost all the dyes was removed at this stage. Besides, excessive $MgCl_2$ will result in forming of too much floc which in turn will prolong the floc settling time [14]. It also reveals that the COD reduction rate was increased slower than the color removal rate with increasing $MgCl_2$ dosage. This was probably due to the oxidation of organic compounds which was not as rapid as decolorization [24].

Final COD of treated solution was recorded and shown in Table 9. Results show that COD reduction by

Table 8
Effect of pH in coagulation–flocculation process using $MgCl_2$ as coagulant (initial color concentration: 3300 PtCo, initial COD concentration: 306 mg l^{-1})

Initial pH	Final pH	Final color (PtCo)	Final COD (mg l^{-1})	Color removal (%)	COD reduction (%)	Settling time	Conditions of floc
10.26	7.78	780	83	76.36	72.88	NA*	Lesser floc
11.02	9.45	257	55	92.21	82.03	07 min 30 s	Less floc
12.44	10.24	94	46	97.15	84.97	04 min 25 s	Large in amount, small in size
12.7	10.6	79	39	97.61	87.25	01 min 45 s	Large in amount, small in size
13.01	10.89	56	29	98.30	90.52	01 min 13 s	Large in amount, small in size
13.6	11.02	257	63	92.21	79.41	03 min 13 s	Large in amount, small in size

NA* = Not available (due to solution's high turbidity).

Table 9
Effect of coagulant dosage, $MgCl_2$ (mg l^{-1}) in coagulation–flocculation (initial color: 3700 PtCo, initial COD: 339 mg l^{-1})

Dosage (mg l^{-1})	Initial pH	Final pH	Final color (PtCo)	Final COD (mg l^{-1})	Color removal (%)	COD reduction (%)	Settling time	Conditions of floc
1000	11.16	10.89	133	54	96.41	84.07	55 s	Large in amount, small in size
2000	11.8	10.87	84	47	97.73	86.14	3 min 22 s	Large in amount, small in size
3000	13.01	10.9	68	33	98.16	90.27	5 min 18 s	Large in amount, small in size
4000	13.16	10.88	59	32	98.41	90.56	6 min	Large in amount, small in size
5000	13.3	10.88	51	31	98.62	90.86	6 min 40 s	Large in amount, small in size
6000	13.4	10.9	50	31	98.65	90.86	8 min	Large in amount, small in size

$MgCl_2$ in the optimal conditions is highly sufficient to meet Malaysia's standard discharge limit (50 mg l^{-1}) established by the Environmental Quality Act 1974.

3.3.3. Coagulant aid

Anionic polyacrylamide was used as coagulant aid to improve the coagulation–flocculation process and to reduce flocs settling time. This can be done by aggregation of flocs formed by the cationic coagulants to increase floc density and subsequently increase the flocs settling velocity. However, overdose of coagulant aid will cause a repulsive force between the dye particles due to excessive accumulation of negative charges on the particle surface. As a result, restabilization of the suspension will be happen [24].

3.4. Combination of thermolysis followed by coagulation–flocculation

Since the optimum color removal and COD reduction for dye solution that treated by thermolysis are only 70.59% and 69.57% respectively, further treatment is needed in order to reduce the color and COD of the treated solution to meet Malaysia's standard discharge limit. In this study, supernatant obtained from thermolysis at optimum conditions was subsequently treated with $MgCl_2$ at optimized conditions mentioned above (except coagulant dosage). The effect for combination of thermolysis followed by coagulation–flocculation is shown in Fig. 7.

It can be seen that coagulation–flocculation has significant effect on color removal and COD reduction when it is applied after thermolysis. An increase in color removal of about 28% (70.59–98.80%) was achieved when coagulation–flocculation was applied to the thermally pretreated solution. Similarly, COD reduction was increased about 20% (69.57–91.27%) when coagulation–flocculation was applied to the supernatant of thermolysis.

The optimum dosage of $MgCl_2$ that needed to treat supernatant of thermolysis is 500 mg l^{-1}. This show that lower amount of $MgCl_2$ is needed to treat the supernatant of thermolysis. Compare to treatment of fresh dye solution using coagulation–flocculation independently, combination of thermolysis followed by coagulation–flocculation process on basic dye produce relatively small amount of floc. Besides, the final COD concentration of supernatant obtained from combined process at optimum condition is 29 mg l^{-1}, which is highly sufficient to meet Malaysia's standard discharge limit (50 mg l^{-1}) established by the Environmental Quality Act 1974.

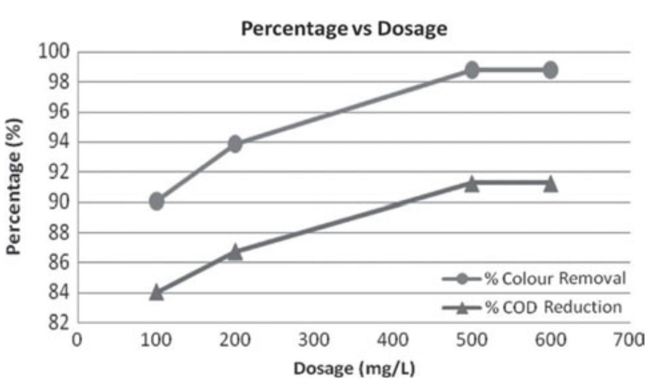

Fig. 7. Effect of thermolysis followed by coagulation–flocculation on color removal and COD reduction. (initial color: 4100 PtCo, initial COD: 332 mg l^{-1}, for thermolysis treatment time: 95 min, pH: 11.02, temperature: 82°C, for coagulation–flocculation final pH ≈10.89.)

4. Conclusions

The experiments of thermolysis, coagulation–flocculation and combination of these two were carried out for COD reduction and color removal of dye solution. The design of experiments was used to carry the experiments. Thermolysis alone is not very effective in colour removal and COD reduction of Malachite Green dye solution. The maximum colour removal and COD reduction in Malachite Green dye solution by thermolysis were 70.59% and 69.57% respectively. This can be attained by optimum conditions at 82°C, treatment time is 95 min and pH is 11.02. The results from experiment of design was indicated that treatment time, pH and temperature have significant effect on decolorization and COD reduction of Malachite Green dye solution in thermolysis process. Treatment of fresh Malachite Green dye solution using coagulation–flocculation was more effective than thermolysis. A minimum dosage of $MgCl_2$ of 3000 mg l^{-1} at final pH 10.89 was required to achieve more than 98% colour removal and 90% COD reduction. However, further increase in the $MgCl_2$ dosage could only achieve slight improvement in color removal and COD reduction, which was less than 1%. The optimal color removal and COD reduction was able to achieve by combine treatment of thermolysis at 82°C, 95 min and pH 11.02 followed by coagulation–flocculation at pH 10.89 and 500 mg l^{-1} on Malachite Green dye solution are 98.80% and 91.27% respectively. For Malachite Green dye solution, the treatment efficiency of combined process is approximately same with the treatment efficiency of coagulation–flocculation process. However, the amount of floc which was produced by combined process is relatively less than coagulation–flocculation.

References

[1] H. Wang, X.W. Zheng, J.Q. Su, Y. Tian, X.J. Xiong and T.L. Zheng, Biological decolorization of the reactive dyes reactive black 5 by a novel isolated bacterial strain *Enterobacter* sp. EC3, J. Hazard. Mater., 171 (2009) 654–659.

[2] J.H. Mo, Y.H. Lee, J. Kim, J.Y. Jeong and J. Jegal, Treatment of dye aqueous solutions using nanofiltration polyamide composite membranes for the dye wastewater reuse, Dyes Pigm., 76 (2008) 429–434.

[3] M. Asgher, N. Azim and H.N. Bhatti, Decolorization of practical textile industry effluents by white rot fungus Coriolus versicolor IBL-04, Biochem. Eng. J., 47 (2009) 61–65.

[4] C.L. Lim, M. Norhashimah, T.T. Teng and I. Norli, Treatment of Terasil Red R Dye wastewater using H_2O_2/pyridine/Cu(II) system, J. Hazard. Mater., 168 (2009) 383–389.

[5] G.H. Jang, I.S. Park, S.H. Lee, T.L. Huh and Y.M. Lee, Malachite Green induces cardiovascular defects in developing zebrafish (*Danio rerio*) embryos by blocking VEGFR-2 signaling, Biochem. Biophys. Res. Commun., 382 (2009) 486–491.

[6] L.T. Li, Q. Hong, X. Yan, G.H. Fang, S.W. Ali and S.P. Li, Isolation of a Malachite Green-degrading *Pseudomonas* sp. MDB-1 strain and cloning of the Tmr2 gene, Biodegradation, 20 (2009) 769–776.

[7] V.K. Gupta, A. Mittal, L. Krishnan and V. Gajbe, Adsorption kinetics and column operations for the removal and recovery of Malachite Green from wastewater using bottom ash, Sep. Purif. Technol., 40 (2004) 87–96.
[8] K.V. Kumar, S. Sivanesan and V. Ramamurthi, Adsorption of Malachite Green onto *Pithophora* sp., a fresh water algae: equilibrium and kinetic modeling, Process Biochem., 40 (2005) 2865–2872.
[9] N. Daneshvar, M. Ayazloo, A.R. Khataee and M. Pourhassan, Biological decolorization of dye solution containing Malachite Green by Microalgae Cosmarium sp., Bioresour. Technol., 98 (2007) 1176–1182.
[10] P. Kumar, B. Prasad, I.M. Misha and S. Chand, Catalytic thermal treatment of desizing wastewaters, J. Hazard. Mater., 149 (2007) 26–34.
[11] P. Kumar, B. Prasad, I.M. Misha and S. Chand, Decolorization and COD reduction of dyeing wastewater from a cotton textile mill using thermolysis and coagulation, J. Hazard. Mater., 153 (2008) 635–645.
[12] A. Garg, I.M. Mishra and S. Chand, Thermochemical precipitation as a pretreatment ster for the chemical oxygen demand and colour removal from pulp and paper mill effluent, Ind. Eng. Chem. Res., 44 (2005) 2016–2026.
[13] P.K. Chaudhari, I.M. Mishra and S. Chand, Effluent treatment for alcohol distillery: catalytic thermal pretreatment (catalytic thermolysis) with energy recovery, Chem. Eng. J., 136 (2008) 14–24.
[14] B.H. Tan, T.T. Teng and A.K.M. Omar, Removal of dyes and industrial dye wastes by magnesium chloride, Water Res., 34 (2000) 597–601.
[15] T.Y. Kim, I.H. Baek, Y.D. Jeoung and S.C. Park, Manufacturing activated carbon using various agricultural wastes, J. Ind. Eng. Chem., 9 (2003) 254–260.
[16] P. Kumar, B. Prasad, I.M. Misha and S. Chand, Treatment of composite wastewater of a cotton textile mill by thermolysis and coagulation, J. Hazard. Mater., 151 (2009) 770–779.
[17] D.C. Montgomery, Design and Analysis of Experiment, 2nd edition. John Wiley & Sons, New York, 1976, pp. 446–470.
[18] B.H. Hameed, I.A.W. Tan and A.L. Ahmad, Optimization of basic dye removal by oil palm fibre-based activated carbon using response surface methodology, J. Hazard. Mater., 158 (2008) 324–332.
[19] S.S. Moghaddam, M.R.A. Moghaddam and M. Arami, Coagulation/flocculation process for dye removal using sludge from water treatment plant: optimization through response surface methodology, J. Hazard. Mater., 175 (2009) 651–657.
[20] F.A. Paven, Y. Gushikem, A.C. Mazzocato, S.L.P. Dias and E.C. Lima, Statistical design of experiments as a tool for optimizing the batch conditions to methylene blue biosorption on yellow passion fruit and mandarin peels, Dyes Pigm., 72 (2007) 256–266.
[21] V. Ponnusami, V. Krithika, R. Madhuram and S.N. Srivastava, Biosorption of reactive dye using acid-treated rice husk: factorial design analysis, J. Hazard. Mater., 142 (2007) 397–403.
[22] E.R. Trotman, Dyeing and Chemical Technology of Textile Fibres, 4th edition, Charles Griffin & Company, London, 1970, pp. 368–372.
[23] P.K. Chaudhari, I.M. Mishra and S. Chand, Catalytic thermal treatment (catalytic thermolysis) of a biodigester effluent of an alcohol distillery plant, Ind. Eng. Chem. Res., 44 (2005) 5518–5525.
[24] P.W. Wong, T.T. Teng and N.A.R. Nik Norulaini, Efficiency of the coagulation-flocculation method for the treatment of dye mixtures containing disperse and reactive dye, Water Qual. Res. J. Can., 42 (2007) 54–62.
[25] P.Y. Ooi, T.T. Teng and A.K.M. Omar, Removal of dyes by aqueous mixed coagulants, AJChE, 5 (2005) 52–64.