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Pulasan Peel for the Removal of Reactive Orange 16.

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ABSTRACT

Adsorption of Reactive Orange (RO) 16 dye was studied utilizing the fruit waste namely the exocarp of Pulasan as a low-cost adsorbent. The effect of experimental conditions like dye concentration, adsorbent dosage, pH and contact time on the removal efficiency of dyes were investigated using design of experiments (DOE). The maximum percentage removal for RO16 on Pulasan was found to be 68.13%. Analysis of variance (ANOVA) showed statistically significant results. Response surface analysis yielded a quadratic model for the removal of dye. The model equation was further solved for optimum value of removal efficiency for RO16 dye. The model-predicted value was experimentally validated, and the error was found to be less than 1%.

Keywords: low-cost adsorbent; fruit waste; adsorption; dyes; response surface methodology; analysis of variance.

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1 INTRODUCTION

Wastewater containing dyes are dangerous to the living things and environment. Water if coloured is unsightly and unpleasant to drink or use for any other cleaning or agricultural purposes. The sources for dye effluents are textile, paper, paint, leather and plastic industries. Textile wastewater shows strong color, abundant suspended solids, elevated temperature, and a wide range of pH fluctuations besides high Chemical Oxygen Demand (COD) concentration. The major harmful waste in textile wastewater is the dyestuff and the resulting color which come from dyeing until finishing steps through the process of imparting desired color to the fabrics (Kim et al., 2003). Dyeing wastewater becomes the largest fraction of the total wastewater in textile processing and if it is discharged into the atmosphere without proper treatment will lead to severe environmental pollution. Several researchers introduced many methods of removing dyes and grouped into three main categories namely, physical, chemical and biological (Gupta et al., 2005) methods. Each method has its own advantages and disadvantages. Filtration is one of the physical methods, including microfiltration, ultrafiltration, nanofiltration, and reverses osmosis which are commonly used in treating water and wastewater (Avlonitis et al., 2008). Usually membranes are used in ultrafiltration and nanofiltration techniques, which are efficient in removing dyes. Clogging of the membrane pores due to dye molecules is the main disadvantage to the filtration system, and hence it finds a limited application in the treatment of textile effluents (Cheremisinoff, 2002). Chemical treatments involves addition of coagulating or flocculating agents, such as aluminum (Al_3^+), calcium (Ca_2^+) or ferric (Fe_3^+) ions, to the dye effluent to induce flocculation or coagulation. Chemical coagulation process is a relatively a cheap process, but a large amount of sludge is generated, thereby reducing the capacity to treat the wastewater (Shi et al., 2007). Biological treatment is extensively used in dye wastewater treatment. A variety of species including bacteria and fungi were used for decolourisation and mineralization of various dyes. Besides being economical, the biological process produces non-toxic end products, but to its disadvantage, it requires a very longer treatment time (Zhang et al., 1998). On the other hand, adsorption is a promising and effective method of dye removal, offering many advantages over other processes. For its high surface area and good adsorption capacity, commercial activated carbon is preferred to remove dyes, but due to its increasing cost of regeneration, it necessary to find alternate low-cost and potential adsorbents. Several researchers explored on utilizing many agricultural waste materials for removing dyes, such as orange peel, saw dust, banana pith, coir pith, barley husk, coconut husk, bagasse, rice hulls, corn cob and paddy straw etc. (Kadirvelu et al., 2003; Annadurai et al., 2002; Crini, 2006; Rajeshwari et al., 2003). But no work was found so far on Pulasan peel as a potential adsorbent. Hence, in this study, suitability of the fruit waste, Pulasan peel as a low-cost adsorbent for the removal of dyes from textile industry wastewater was examined. Pulasan was chosen because it is available in plenty in Malaysia. In a study conducted by Kozai et al., (2005), it was stated that Pulasan was planted in 846 ha in peninsular Malaysia in the year 2001. Around 40-50% of fruit volume contains the shell which is a porous biomass. In order to minimize the fruit waste and to make useful products from waste material, Pulasan peel was considered as a potential adsorbent in this study.

For a batch adsorption process, the important process parameters are initial concentration, adsorbent dosage, pH and contact time. Classical method of experiments to study the effect of these individual parameters as well as the interaction effects on the parameters requires more number of experiments and consumes more time. Hence, a statistical method, response surface methodology (RSM) was used in this study since it is more useful in developing and optimizing the process variables and also in evaluating the relative significance of several affecting parameters.

2 MATERIALS AND METHOD

2.1 Preparation of adsorbent

Pulasan (*Nephelium mutabile)* is a tropical fruit commonly available in Malaysia, Thailand, Indonesia and Philippines. The fruit is ovoid, 5-7.5 cm long, dark red and the outer shell is very thick, which covers about 40-50% of the total volume of fruit. The picture of Pulasan fruit is shown in Figure 1. The fruits obtained from local market were cut to remove the fruit (aril), endocarp and the waste outer layer, exocarp. The exocarp was further cut into small pieces, washed with distilled water and dried in the sunlight initially for about two hours and then kept in the oven overnight at a temperature of 110°C to completely remove the moisture content. The sample was then crushed in the blender into a fine powder. Then the powder sample was sieved through

300 µm. To remove purple colour from Pulasan shell, the powder was rinsed with hexane and ethanol and again dried overnight.

Figure 1: Picture of Pulasan fruit

2.2 Preparation of dye sample

Reactive Orange 16 is a commercial dye, which is widely used in textile industries. The structure of RO16 is shown in Figure 2. After scanning the dye sample in a UV-Vis Spectrophotometer in the range of 400-800 nm, the characteristic wavelength (λ_{max}) of the reactive orange dye was found to be 494 nm. Dye samples of different known concentrations were prepared and corresponding absorbance values at λ_{max} were measured and a standard calibration chart was prepared to find unknown concentration of dyes between 10-60 ppm.

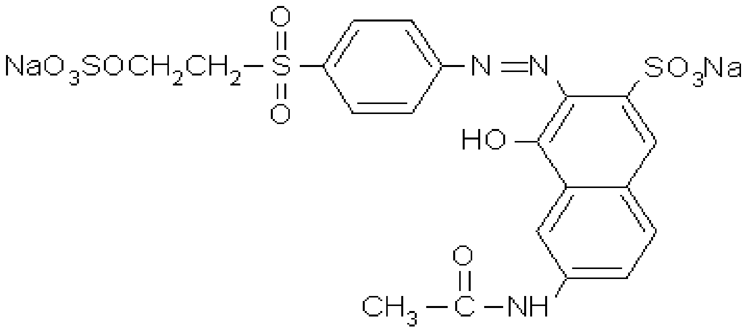

Figure 2: Structure of Reactive Orange 16

2.3 Response Surface Methodology

To get the maximum information with less numbers of designed experimental conditions, design of experiment is carried out. This statistical approach is used to minimize time and cost in conducting several experiments. Once the range of parameters is chosen for the study, experimental design table is generated using the software to carry out the experiments. The results of the experiments are then analysed using the same software. In this study, the statistical software package, Minitab, Version 14 was used and the factors screened were dye concentration, dosage of the adsorbent, pH and the contact time for the dye removal. The range of process conditions was selected based on the literature and the values used in this study are shown in Table 1.

Table 1: Parameters used in this study

Parameter	Range
Concentration (ppm), x_c	20 - 50
Adsorbent dosage (g), x_d	0.5 -1.0
pH, x_p	4 - 10
Contact time (min), x_t	15- 45

In the modeling and analysis of problems, recently, RSM is used to study one or more specific responses of a process on several other influencing factors with a view to optimize the response(s). The analyses of results yield the surface plots and contour plots to visualize the shape of the response surface. From these response surface plots one can interpret easily the interaction effects of factors, tendency towards maximization or minimization of responses. The experimental design table was generalized by the central composite design for the four parameters which yielded 31 experimental conditions. Experiments were conducted with these generated conditions and the corresponding removal efficiencies (Response) of dye were found out. The experimental conditions together with the response values are given in Table 2.

Table 2: Central composite design table and the response for RO16 on Pulasan

Run	x_c (ppm)	x_d (mg)	x_p pH	x_t (min)	% dye removal
1	20	0.5	4	15	1.79
2	50	0.5	4	15	2.76
3	20	1	4	15	8.27
4	50	1	4	15	7.58
5	20	0.5	10	15	8.94
6	50	0.5	10	15	9.37
7	20	1	10	15	10.05
8	50	1	10	15	15.53
9	20	0.5	4	45	0.23
10	50	0.5	4	45	4.90
11	20	1	4	45	8.94
12	50	1	4	45	12.85
13	20	0.5	10	45	14.74
14	50	0.5	10	45	8.65
15	20	1	10	45	20.10
16	50	1	10	45	19.90
17	5	0.75	7	30	39.39
18	65	0.75	7	30	4.31
19	35	0.25	7	30	6.37
20	35	1.25	7	30	19.90
21	35	0.75	1	30	30.87
22	35	0.75	13	30	68.13
23	35	0.75	7	0	0.00
24	35	0.75	7	60	3.82
25	35	0.75	7	30	16.20
26	35	0.75	7	30	15.94
27	35	0.75	7	30	16.20
28	35	0.75	7	30	16.07
29	35	0.75	7	30	16.33
30	35	0.75	7	30	16.20
31	35	0.75	7	30	16.07

3 RESULTS AND DISCUSSION

From Table 2, it is observed that various combinations of parameters could yield the removal of RO16 as maximum as 68.13% which is quite high when compared with the control experiment carried out by Abdullah et al., (2010) in treating RO16 with a commercial activated carbon. The main effects of each parameter on RO16 dye removal using Pulasan are given in Figure 3. From the figure, it is found that the increase in concentration of dye leads to decrease in the removal of dye for the entire range of concentration studied. This indicates that low concentration can give higher removal percentage. Similar results were found by Pavan et al. (2005) for the removal of methylene blue dye on yellow passion fruit and mandarin peels. The overall effect of adsorbent dosage showed a shallow increase in the removal of dye. This also is in agreement with the observation by Rajeshwari et al. (2003) for the removal of acid violet dye on orange peel and Jagannathan and Kumar for the removal of acid violet dye using Mangosteen peel. Maximum adsorption of RO16 using Pulasan as adsorbent occurred at dosage 0.75 mg where the minimum of percentage removal was at 0.25 mg of adsorbent. Because of the minimum surface area, the adsorption process only occurred in a less rate of adsorption. The overall effect of pH in the removal showed a different pattern. In the acidic pH up to 4 the removal of dye is found to decrease with increase in pH and from pH 4 to 10 showed almost no effect, while pH larger than 10, the removal is increasing drastically. It is for the reason that the working pH of the reactive dyeing process is generally high (pH > 11) to fix the colour on the cellulosic fabrics (Lee et al., 2012) which is also in consistent with the adsorption of dyes in cellulosic biomass, Pulasan peel. Similar results were obtained by Pavan et al. (2005) for the removal of methylene blue dye on yellow passion fruit and mandarin peels. The overall effect of contact time clearly showed that up to 30 min, removal of dye increased and beyond 30 min, the removal of dye decrease.

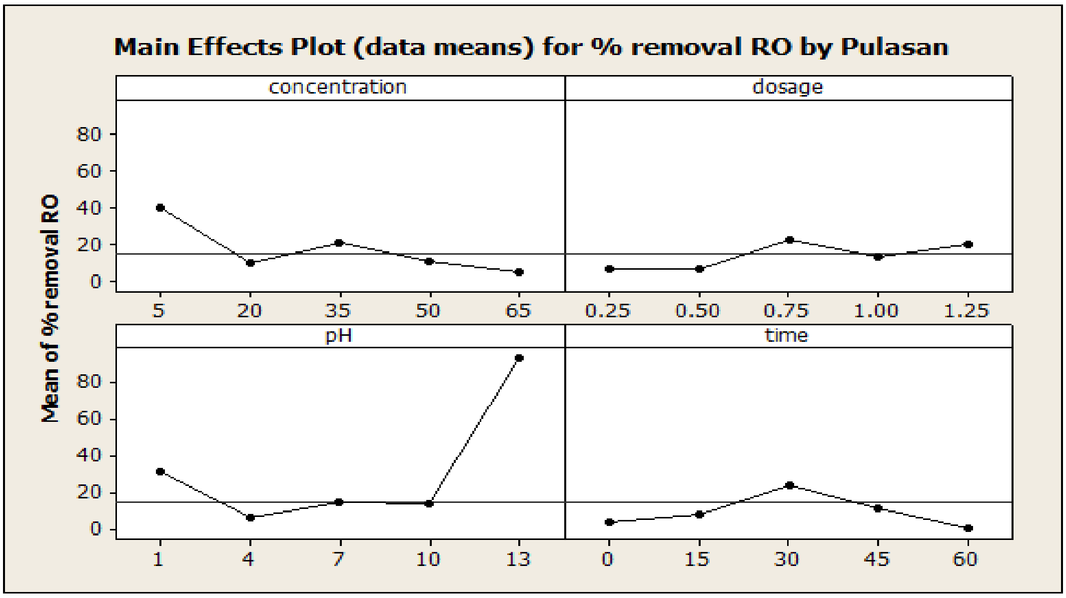

Figure 3: Main effects plot for RO16 removal using Pulasan

Table 3: ANOVA for removal of RO16 by Pulasan

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	14	3764.15	3764.15	268.87	3.01	0.019
Linear	4	1218.65	1218.65	304.66	3.41	0.034
Square	4	2509.6	2509.6	627.4	7.03	0.002
Interaction	6	35.9	35.9	5.98	0.07	0.998
Residual Error	16	1427.67	1427.67	89.23		
Lack-of-Fit	10	1427.57	1427.57	142.76	8869.53	0
Pure Error	6	0.1	0.1	0.02		
Total	30	5191.82				

Table 3 shows the analysis of variance, ANOVA for the removal of RO16 by Pulasan. According to ANOVA, the F value for square effect of the parameters was much lower than that of linear effect but both were highly significant since the corresponding P values are less than 0.05. The large value of F indicates more variation in the response as explained by the regression equation. It is also observed that the model F value of 3.01 and P of 0.019 implied that model was significant. The linear and square effects are statistically significant and the interaction effect is not significant. The regression equation for the removal of RO16 (Y, %) can be derived as:

$$Y = 0.01964X_c + 69.0107X_d - 7.8458X_p + 1.3009X_t - 0.0025x_c^2 - 43.8671X_d^2 + 0.7055X_p^2 - 0.0247X_t^2 + 0.1420X_cX_d - 0.0128X_cX_p - 0.0011X_cX_t - 0.3400X_dX_p + 0.2450X_dX_t + 0.0180X_pX_t + 12.0040$$

(Equation .1)

The regression coefficient, T and P values for all the linear, quadratic and interaction effect of the parameters for RO16 removal using Pulasan as adsorbent are given in Table 4. It was observed that all the parameters were not significant except the quadratic effect of pH and time. The coefficient of determination,

R^2 value is found to be 0.725 which means 72.5% of the sample variation for the RO16 is explained by independent variables.

Table 4: T and P value from ANOVA for the removal of RO16 by Pulasan

Term	T	P
Constant	-0.200	0.844
Concentration	0.156	0.878
Dosage	1.093	0.290
pH	-1.926	0.072
Time	1.237	0.234
concentration*concentration	-0.464	0.649
dosage*dosage	-1.398	0.181
pH*pH	3.838	0.001
time*time	-2.601	0.019
concentration*dosage	0.171	0.866
concentration*pH	-0.185	0.855
concentration*time	-0.078	0.939
dosage*pH	-0.081	0.936
dosage*time	0.294	0.772
pH*time	0.260	0.798

The interaction effects of the process parameters are explained by the Figures 4 through 9. Figure 4 shows the interaction between pH and time for the removal of RO16 on Pulasan. In the surface plot it is clear that the increase in pH leads to fall and rise of the dye removal whereas increase in time leads to rise and fall of the dye removal symmetrically. The same is observed in the contour plot as saddle curves which indicate that there is a tendency to have minimum. Figure 5 shows the interaction between dosage and time for the removal of RO16 on Pulasan. In the surface plot it is clear that the increase in adsorbent dosage leads to rise and fall of removal percentage and so does the time also. Hence, the contour plot is observed in the form of circles which indicates that there is a tendency to have maximum. Figure 6 shows the interaction between pH and dosage for the removal of RO16 on Pulasan. In the surface plot it is clear that the increase in dosage leads to rise and fall of the dye removal whereas increase in pH leads to fall and rise of the dye removal symmetrically. The same is observed in the contour plot as saddle curves which indicate that there is a tendency to have minimum.

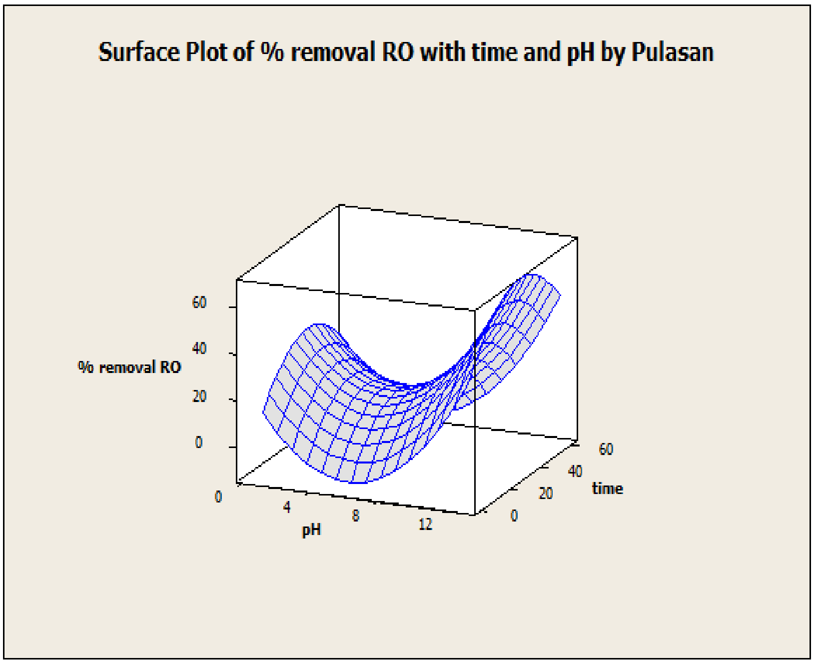

Figure 4 (a): Response surface plot for the removal of RO16 on Pulasan: Interaction effect of pH and contact time

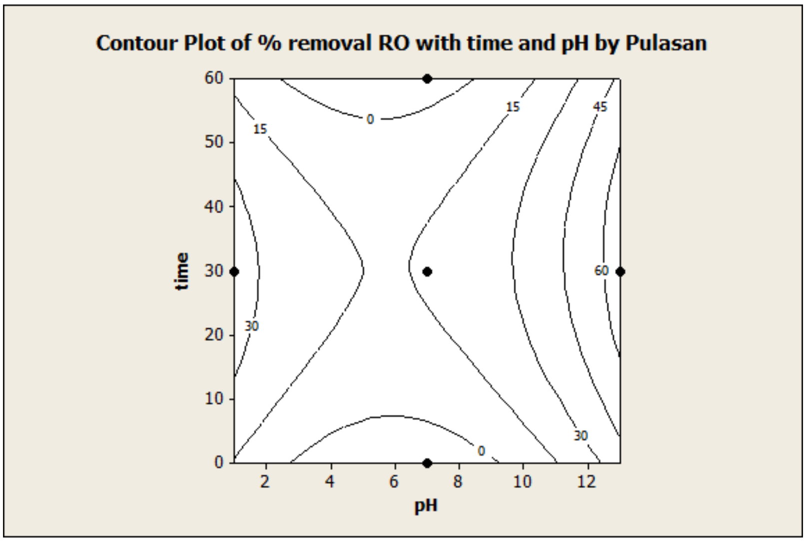

Figure 4(b): Contour plot for the removal of RO16 on Pulasan: Interaction effect of pH and contact time

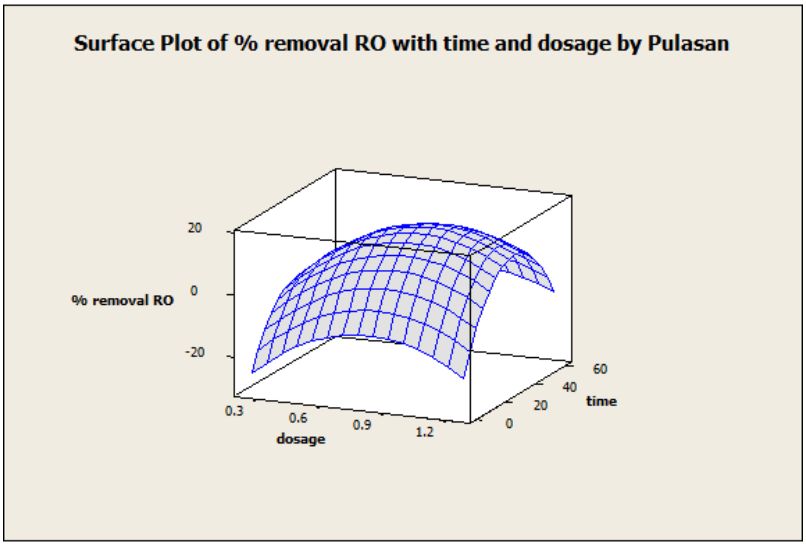

Figure 5 (a): Response surface plot for the removal of RO16 on Pulasan: Interaction effect of dosage and contact time

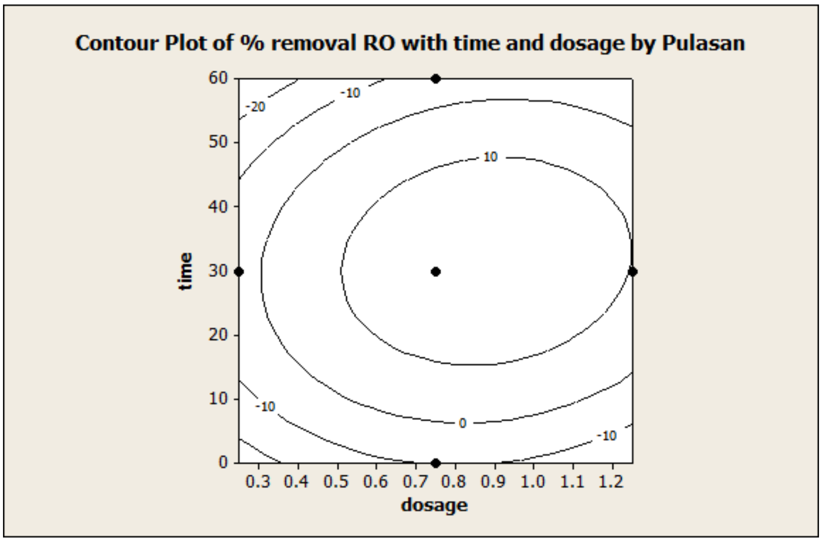

Figure 5 (b): Contour plot for the removal of RO16 on Pulasan: Interaction effect of dosage and contact time

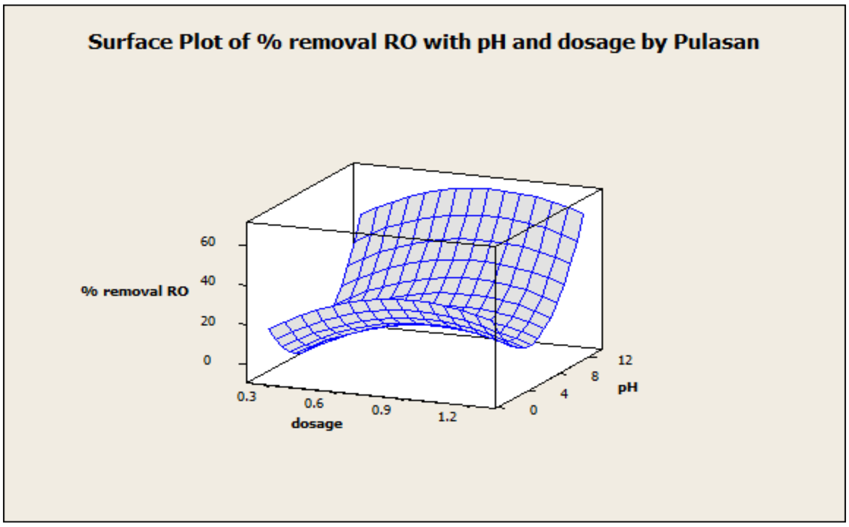

Figure 6 (a): Response surface plot for the removal of RO16 on Pulasan: Interaction effect of pH and dosage

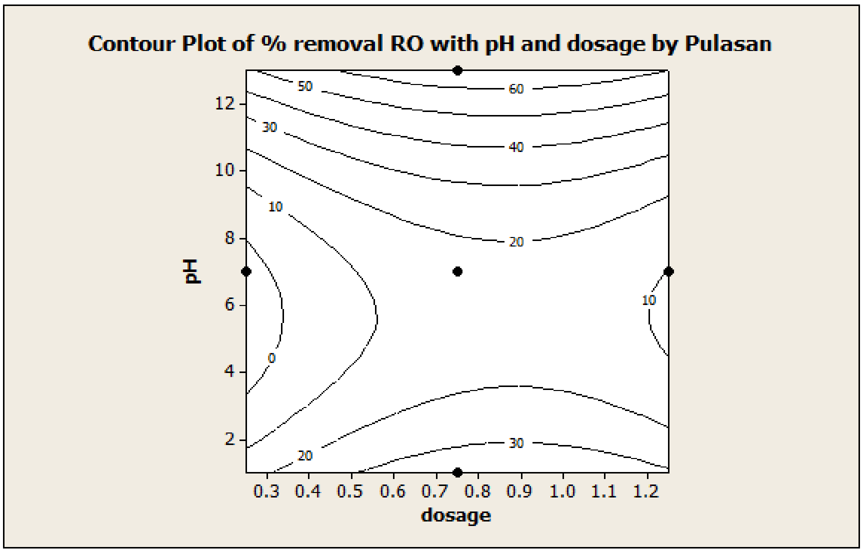

Figure 6 (b): Contour plot for the removal of RO16 on Pulasan: Interaction effect of pH and dosage

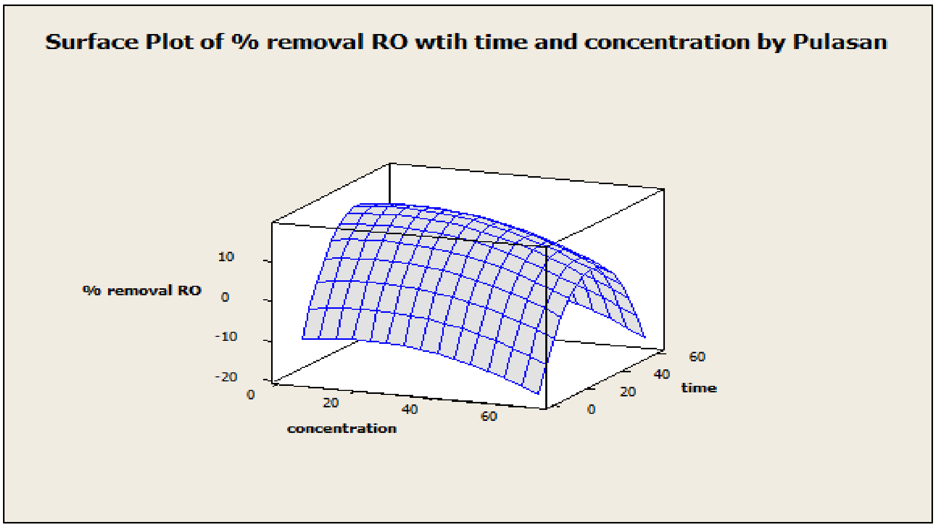

Figure 7 (a): Response surface plot for the removal of RO16 on Pulasan: Interaction effect of concentration and contact time

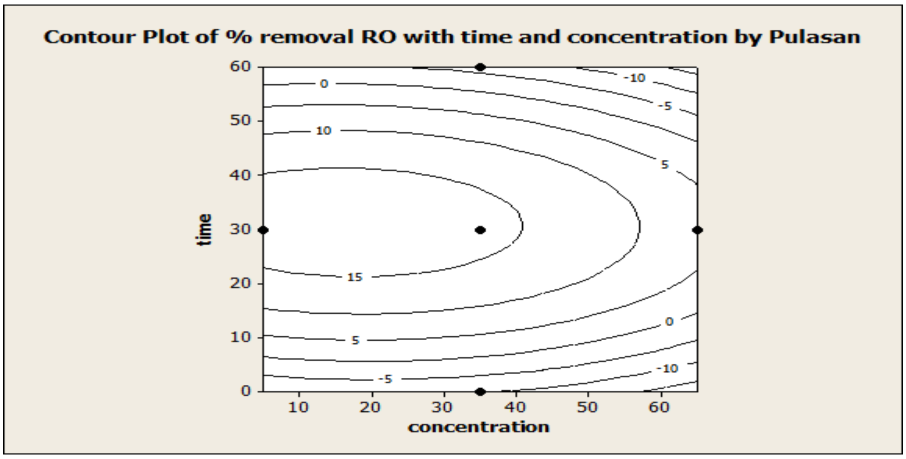

Figure 7 (b): Contour plot for the removal of RO16 on Pulasan: Interaction effect of concentration and contact time

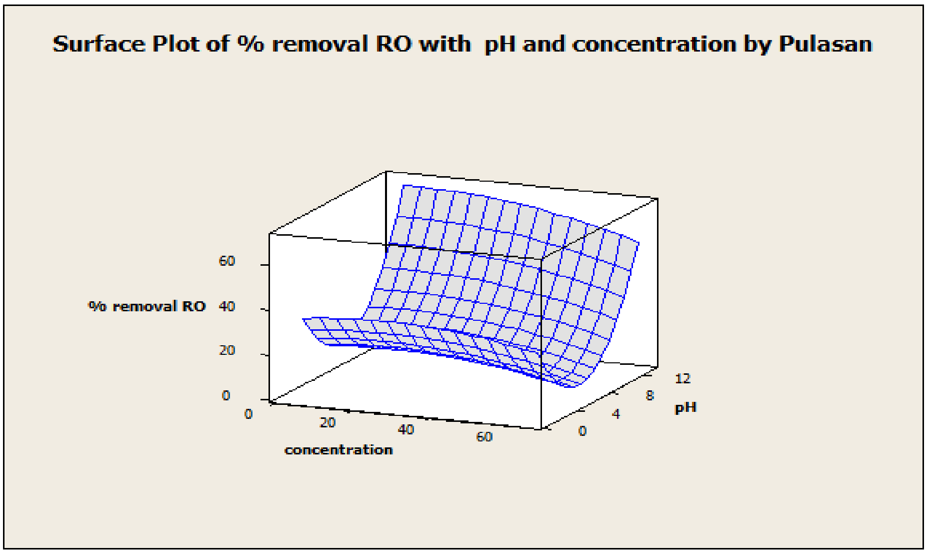

Figure 8 (a): Response surface plot for the removal of RO16 on Pulasan: Interaction effect of pH and concentration

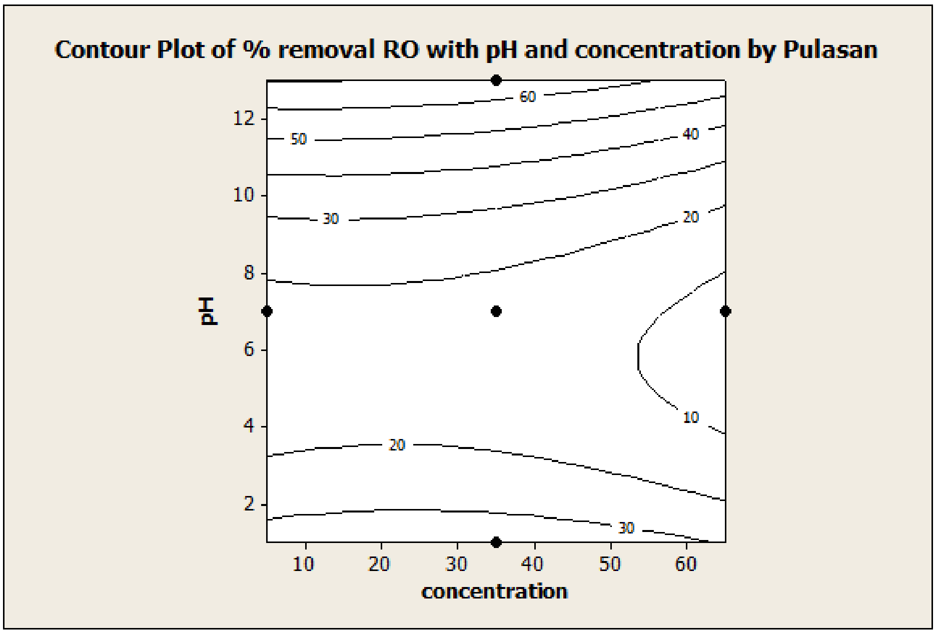

Figure 8 (b): Contour plot for the removal of RO16 on Pulasan: Interaction effect of pH and concentration

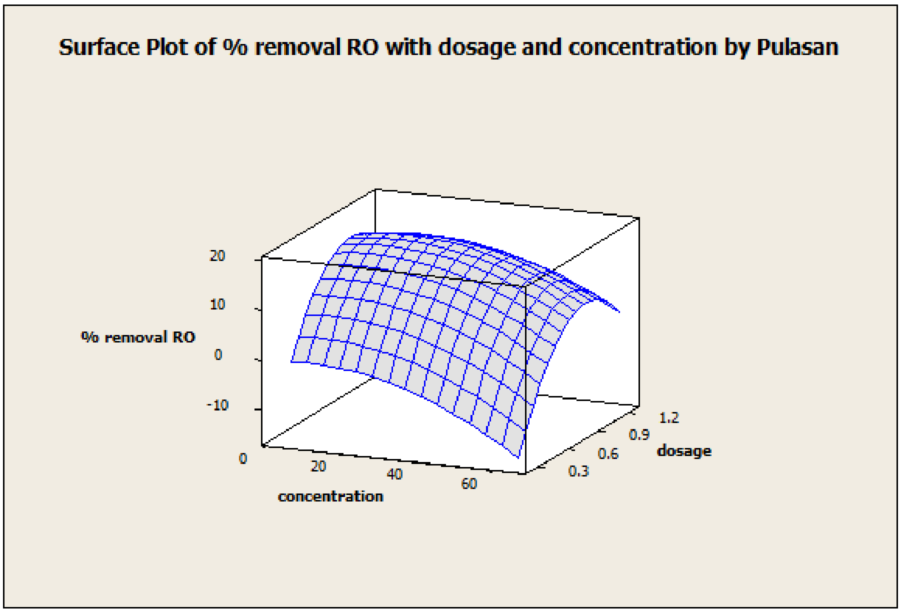

Figure 9 (a): Response surface plot for the removal of RO16 on Pulasan: Interaction effect of pH and contact time

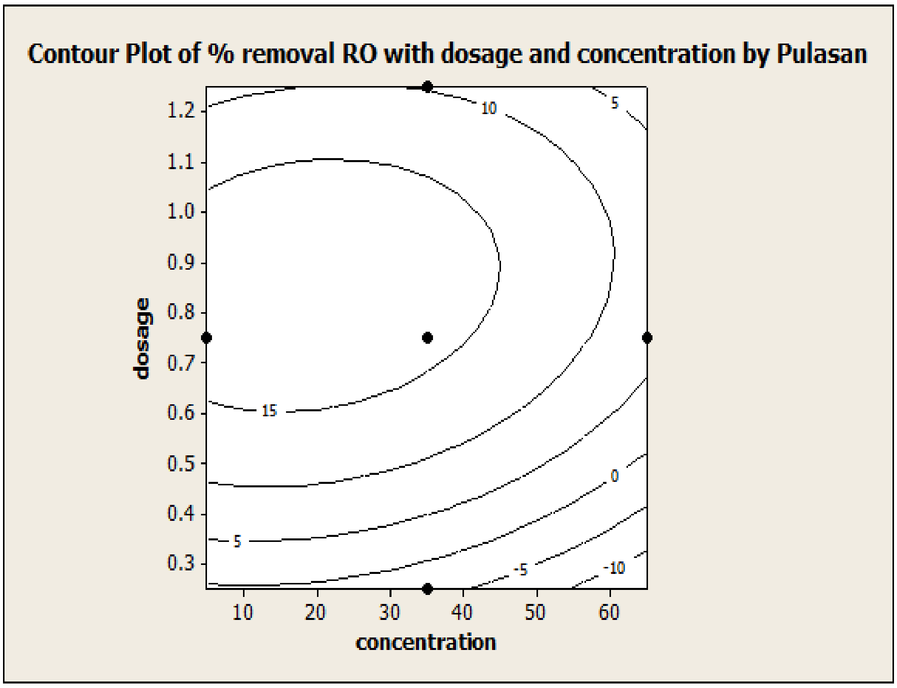

Figure 9 (b): Contour plot for the removal of RO16 on Pulasan: Interaction effect of pH and contact time

Figure.7 shows the interaction between concentration and time for the removal of RO16 on Pulasan. In the surface plot it is clear that the increase in concentration leads to slight rise and fall of removal percentage and increase in time leads to rise and fall of removal percentage. Hence, the contour plot is observed in the form of circles which indicates that there is a tendency to have maximum. Figure 8 shows the interaction between pH and concentration for the removal of RO16 on Pulasan. In the surface plot it is clear that the increase in concentration leads to slightly rise and fall of the dye removal whereas increase in pH leads to fall and rise of the dye removal symmetrically. The same is observed in the contour plot as saddle curves which indicate that there is a tendency to have minimum.

Figure 9 shows the interaction between concentration and dosage for the removal of RO16 on Pulasan. In the surface plot it is clear that the increase in concentration leads to rise and fall of removal percentage and increase in dosage leads to rise and fall removal percentage. Hence, the contour plot is observed in the form of circles which indicates that there is a tendency to have maximum. The developed model equation (1) is solved for the optimal conditions for maximum removal of the dye applying a standard mathematical programming. The optimum set of condition obtained was RO16 concentration: 44.8 ppm; Adsorbent dosage: 0.89 gm; pH: 5.5; contact time: 29.2 minutes. Optimum percentage removal as explained by model was 57.73% and it was then experimentally verified and found to be 57.45%. The percentage error was only 0.48%. It clearly shows that the model developed is in close agreement with the experimental results.

4 CONCLUSION

This experimental study supports that the Pulasan fruit wastes can be effectively used as an adsorbent for the removal of dyes. The results showed the main and interaction effects of parameters in terms of surface and contour plots and also yielded a quadratic model to estimate the optimum conditions for the maximum removal of dyes. For the removal of Reactive Orange 16 on Pulasan, with different combinations of the process parameters up to 68.13% removal was observed. The removal of dye decreased with increase in concentration and increased with increase in adsorbent dosage. At pH > 10 and time at 30 min showed maximum removal efficiency. ANOVA yielded a quadratic model which was solved for optimum values. These optimum values were also experimentally verified and the error between experimental and model values was found to be 0.48%.

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