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Research Note

Box–Behnken Design of Experiments in the Adsorption of Anionic Dyes on the Bio Polymer Chitosan

N. Sivakumar*, R. Basker[1] and R. Sridhar[2]

Department of Chemical Engineering
Kongu Engineering College
Perundurai, Erode–638 052, Tamil Nadu, India
✉ sukisivakumar@yahoo.com
[1]✉ naturebaskar@yahoo.com
[2]✉ sridhar36k@yahoo.co.in

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Abstract: The adsorption of anionic dye acid Orange 10 and acid Orange 51 on chitosan, a food processing industrial bio polymeric waste was studied. Box-Behnken model and analysis of variance (ANOVA) have been applied to the experimental adsorption studies. Response surface method with three levels of variances namely pH (6.7, 7.4, 9.2), particle size (0.100, 0.175 and 0.250 mm) and temperature (30, 45 and 60°C) were used in the identification of significant effects and interaction in the batch adsorption studies. A second order polynomial regression model has been developed using experimental data. From the results it was found that the selected variables as a strong effect on adsorption and also the experimental values were in good agreement with predicted values with the correlation coefficient value in the range of ≈ 0.99.

Key words : Adsorption, anionic dyes, chitosan.

Introduction

Colour removal from textile effluents has become the target of great attention in the last few years because of its toxicity and negative impact to nature (Weeter & Hodgson, 1977). In dying and finishing industries, a considerable amount of wastewater is generated which is notoriously known to contain strong colour, a large amount of suspended solids with a highly fluctuating pH and temperature.

Although some existing technologies may have certain efficiency in the removal of reactive dyes, their initial and operational cost is so great, that they constitute an inhibition to dyeing and finishing industry. On the other hand, low cost technologies not allowing a wishful colour removal have certain advantages; their integration into more complex and complete treatment plan being, consequently, necessary is, however, more onerous such as combination of biological, chemical and physical procedures (Weber and Chakravarthi, 1974). Hence research has been directed to other non-conventional materials for colour removal with effectiveness at low cost (Deo & Ali, 1993).

Adsorption is one of the most effective physical procedures for the removal of colour and treatment of textile effluents due to its low cost, simple design, sledge free operation and superior colour removal (Allen et al., 1989).

Polysaccharides isolated from marine organisms are a new class of potentially inexpensive and environmentally benign solid adsorbents that exhibit a high specificity towards metal ions and dye molecules. Of particular interest is the amine biopolymer chitosan, which selectively binds to virtually all types of dyes. Chitosan is a linear glucosamine biopolymer possessing

* Corresponding Author

an average molecular weight of 1,20,000. Chitosan is derived from the de-acctylation of chitin, a linear N–acetyl glucosamine biopolymer. Chitin is the principal component of the shells of crustacean organisms and the second-most abundant biopolymers in nature next to cellulose, which is being wasted.

In this paper, the effects of several factors including the dye adsorption such as temperature, pH and particle size have been studied.

The adsorption equilibrium is well correlated by Box–Behnken design of experiments (Box & Behnken, 1960). The determination of optimal conditions for the above mentioned parameters would require experiments with all possible combinations of parameter values. However, it is possible to undertake a rational study by using experimental statistical designs, which reduces the number of experiments and broadens the range of information about the system (Box & Hunter, 1957). Temperature, pH and particle size have been considered as the critical variables. Statistical design was used to determine optimal levels of adsorption studies.

Mathematical Model

Design of experiments is a technique for conducting experiments that compromises nothing in thoroughness, but delivers results in a fraction of time. Design of experiments is a methodology for systematic application of statistics to experimentation. Generally, this is less time consuming than classical methods. Design of experiments works in both laboratory research and manufacturing processes. Using statistics based on experiment data mathematical models that predict low changes in input (or) control, variables (e.g., temperature, particle size and pH) interact to produce changes in output variable (or) response (adsorption) in a system have been developed. Experiments produce a model which show that low variables and responses are related by performing a planned reference of experiments. The sequence is called a design.

In the present system, the Box-Behnken design experiments use chitosan as adsorbent. The Box-Behnken design experiments are an alternative and more efficient approach, which is increasingly used in adsorption. Basically this optimization process involves three major steps viz., performing the statistically designed experiments, estimating the coefficients in a mathematical model, and predicting the response and checking the adequacy of the model. The response surface methodology uses the Box-Behnken design of experiments to develop a mathematical correlation between temperature, particle size and pH which are chosen as the critical variables and designated as X_1, X_2 and X_3 respectively. The statistical design was used to determine the optimal levels of adsorption studies and also was subjected to analysis of variance (ANOVA), appropriate to the design of experiment. The low, middle and high levels of each variable—temperature (30, 45 and 60°C), particle size (0.100, 0.175 and 0.250 mm) and pH (6.7, 7.9 and 9.2)—were designated as -1, 0 and +1(Table 1).

Table 1: The Levels of Variables Chosen for Box–Behnken Trails

Box–Behnken levels	*Variables*		
	pH X_1	*Adsorbent particle size X_2 (mm)*	*Temperature X_3 (°C)*
–1	6.4	0.100	30
0	7.8	0.225	45
+1	9.2	0.350	60

For the three significant independent variables X_1, X_2 and X_3, the mathematical relationship of the response M on these variables can be approximated by the quadratic model equation:

$$M = A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_{11}X_1^2 + A_{22}X_2^2 + A_{33}X_3^2 + A_{12}X_1X_2 + A_{13}X_1X_3 + A_{23}X_2X_3 \quad (1)$$

where M is predicted response, A_0 is constant, X_1 is temperature, X_2 isparticle size and X_3 is pH, A_1, A_2, A_3 are linear coefficients, A_{12}, A_{13}, and A_{23} are cross product coefficients. The degree of experiments chosen for this study was Box-Behnken (Box & Hunter, 1957), a fractional design for three independent variables. It is applicable once the critical variables have been identified (Kpat et al., 1996). In the model given in equation (1), interactions higher than the first order have been neglected. The design is preferred because relatively few experimental combinations of the variables are adequate to estimate potentially complex response functions. A total of 17 experiments were necessary to estimate 15 coefficients of the model (Table 2).

Material and Methods

Chitosan used in this investigation was supplied by a local manufacturing company (moisture 3%, nitrogen 7.84%, deacetylation degree 70%, ash content at 900° C < 1.0%). It was sieved into discrete particle size ranges (0.100 mm, 0.225 mm and 0.350 mm). An analar grade acid dye (acid orange 10) was used as adsorbate material.

Table 2: The Box–Behnken Design for Three Independent Variables

Trial No	*pH*	*Particle size (mm)*	*Temperature (°C)*
1.	–1	–1	0
2.	1	–1	0
3.	–1	1	0
4.	1	1	0
5.	–1	0	–1
6.	1	0	–1
7.	0	0	1
8.	0	0	1
9.	0	–1	–1
10.	0	1	–1
11.	0	–1	1
12.	0	1	1
13.	0	0	0
14.	0	0	0
15.	0	0	0
16.	0	0	0
17.	0	0	0

Design of Experiments

Standard solution of 1000 mg/lit was prepared and subsequently diluted when necessary. Experiments were carried out using 100 ml of 50 mg/lit dye solution in an open erlenmeyer flask of 250 ml capacity using a temperature controlled orbital shaker. Three variables like temperature (30, 45 and 60°C), particle size (0.100, 0.175 and 0.250 mm) and pH (6.7, 7.9 and 9.2) served as the critical variables X_1, X_2 and X_3, as chosen in Table 1. Design of experiments was carried out with different variables in accordance with Table 2. After the equilibrium time (two hours) the flasks were removed from the shaker and centrifuged at 5000 rpm and the supernatant liquid was used for the analysis of amount of dye adsorbed by the adsorbent. The concentration of the dye solution was determined using spectronic 21D model spectro-photometer. All the experiments were carried out in duplicate.

Results and Discussions

Adsorption in a solid–liquid system results in the removal of solutes from solution and their concentration at the surface of the solid, to such a time as the concentration of the solute remaining in solution are in dynamic equilibrium with that at the surface (Mckay, 1982). At this position of equilibrium there is a defined distribution of solute between the liquid and solid phases which is generally expressed by one or more of a series of isotherm. Response surface methodology is an empirical modelization technique devoted to the evaluation of the relationship of a set of controlled experimental factors and observed results. It requires prior knowledge of the process to achieve a statistical model (Jose, 1987). The regression equation obtained after analysis of variance gives the level of adsorption of dyes as a function of the different temperature, pH and particle size. All terms regardless of their significance are included in the following equation (Kpat et al., 1996):

$$M = 27.59 + 1.07X_1 - 2.54X_2 - 10.12X_3 + 0.14X_1^2 + 0.20X_2^2 + 1.12X_3^2 - 0.023X_1X_2 + 0.23\,X_1X_3 - 0.21X_2X_3 \quad (2)$$

where M (36.3194) is the predicted response. Quadratic square regression was significant at the confidence level of 97% (Table 5) indicating the combined effect of the selected variance of isotherm to the variation on the adsorption of acid dye. The adsorptions of dye from the model at each experimental point are summarized in Tables 3 and 4, along with experimental and theoretical observed values. The coefficients of equation (2) are calculated using design and their values are listed in Table 4. The summary of the analysis of variance (ANOVA) is shown in Table 5.

Table 3: Coefficient of the Box–Behnken Model

Coefficient	*Value*
A_0	+27.59
A_1	+1.07
A_2	–2.54
A_3	–10.12
A_{11}	+0.14
A_{22}	+0.20
A_{33}	+1.12
A_{12}	–0.023
A_{13}	+0.23
A_{23}	–0.21

Optimization of Temperature, pH and Particle Size

From Figure 1, it was found that the maximum amount of dye adsorbed increases with increase in temperature and decreases with increase in pH. Optimum level of adsorption with temperature and pH are 39.69 mg/gm at 58.13 ºC and pH 6.45. The increase in temperature would increase the mobility of the large dye ion and also produces a swelling effect within the internal structure of chitosan, thus enabling the large dye molecule to penetrate further (Mckay, 1982).

Table 4: Experimental and Theoretically Predicted Values for Adsorption of Dyes

Experiment no.	*Actual experimental value (Amount adsorbed mg/gm)*	*Box-Behnken predicted response (Amount adsorbed mg/gm)*
1.	29.56	29.38
2.	32.22	31.56
3.	23.68	24.34
4.	26.25	26.43
5.	38.48	38.13
6.	39.68	39.80
7.	17.55	17.43
8.	19.67	20.03
9.	40.82	41.36
10.	37.00	36.70
11.	21.24	21.54
12.	16.57	16.03
13.	27.59	27.59

Table 5: Regression Analysis for the Adsorption of Dyes, Quadratic Response Surface Model Fitting

Source	*Sum of squares*	*Degree of freedom*	*Mean square*	*F*
Model	886.09	9	98.45	348.89
Error	1.98	5	1.0831	($P < 0.0001$ Significant)
Total	886.08	14		
		R = 0.9949	$R^2 = 0.9978$	

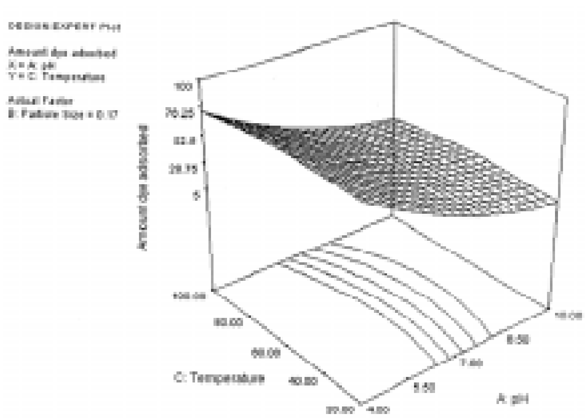

Figure 1: Response surface plot representing amount of dye adsorption pH vs temperature.

From Figure 2, it can be clearly seen that the dye adsorption decreases with increase in pH. The data indicates that the adsorption capacity of dyes by chitosan is dependent on pH. This can be explained as below. The biopolymer has functional groups OH and NH_2. According to Annadurai and Krishnan (1996), the hydroxyl groups of the polymer are strongly hydrated and are virtually incapable of forming hydrogen bonds with dyes; nevertheless they can adsorb, by the formation of a hydrogen bond, by VanderWaals interactions and also by ion exchange with other groups. Depending on the pH in the water, the polymers containing the amino groups are neutral ($-NH_2$) or cationic ($-NH_3^+$). At a pH of higher acidity, these groups are protonated and to maintain neutrality in an aqueous environment, negative counter-ions are adsorbed. These ions are movable and are exchanged by ions from the dyes at appropriate pH. In this case we have a process of ionic exchange in which electrostatic interactions are involved. The results show a tendency towards greater adsorption for anionic dyes in acidic pH range and decrease in adsorption observed in alkaline pH since the amino groups of the polymer are de-protonated. Considering the effect of pH with particle size from Figure 2, it was found that the adsorption of dye decreases with increase in the magnitude of both variables. It can be explained that with increase in particle size there is a decrease in effective surface area for adsorption, which reduces the adsorption. Similarly Figure 3 explains the effect of temperature and

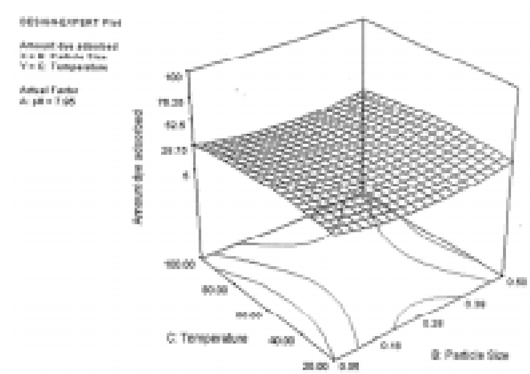

Figure 2: Response surface plot representing amount of dye adsorption temperature vs particle size.

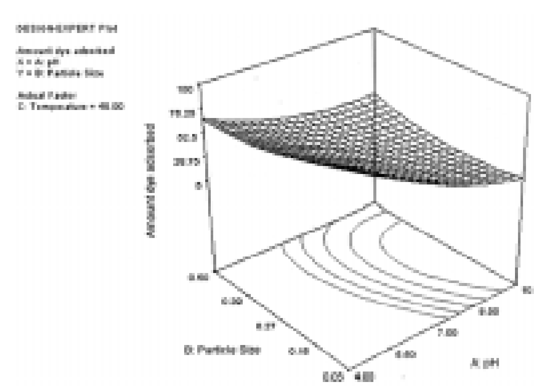

Figure 3: Response surface plot representing amount of dye adsorption pH vs particle size.

particle size on adsorption. From the figure, it is evident that increase in temperature and decrease in particle size affect in higher adsorption. Optimum level of adsorption with temperature and particle size is 38.77 mg/gm at 58.13 ºC and pH 6.45.

The effect of function of a certain factor is a function that describes how the response moves as the level of those factors changes, when the other factors are fixed at their optimum levels. From the study it can be observed that each of the three variables used in the present study has its individual effect on adsorption. Gradual increase in acid dye adsorption by chitosan from low level of temperature 30°C (coded value –1) to higher level at 60°C (coded value +1), decreases from low level of particle size 0.100 mm (coded value –1) to higher level at 0.250 mm (coded value +1) and also decreases from low level of pH 6.7 (coded value –1) to higher level at 9.2 (coded value +1).

Conclusion

Chitosan was found to be a suitable adsorbent for the adsorption of dye from aqueous solution having different concentrations of dye. From the initial studies, the adsorption data approximated a Langmuir and Freundlich isotherm model for both particle size variation, pH and temperature changes. The previous study of analysis of Kinetic data also indicated that intra particle diffusion has a role in determining the adsorption rate for this adsorption system. An optimization of the process of adsorption with addition of varying levels of temperature, particle size and pH was done using Box-Behnken design experiment, which works on regression analysis of experimental data collected. The model predicted the dye adsorption values within confidence level of 99% and indicating the combined effect of the selected variance key role in determining the rate constant of the process of the adsorption of acid dye by chitosan.

Since chitosan is an industrial waste, which is readily available, and also inexpensive, using it as adsorbent provides an effective solution for solid waste management of that industry. Hence the use of this waste as an adsorbent for colour removal is of practical importance and expected to be economical.

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