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Optimized Response Surface Methodology for Adsorption of Dyestuff from Aqueous Solution

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ABSTRACT

The aim of the present study was to discover the effect of various experimental parameters such as dye concentration, pH and temperature on removing dye Bromophenol blue (Bb) from aqueous solution using orange peel nano-porous adsorbent and the optimal experimental conditions were ascertained. The effect of various experimental parameters and optimal experimental conditions were ascertained by response surface methodology using Box-Behnken model. The optimum values of the parameters were dye concentration 60 mg L^{-1}, pH 6.8-6.95 and temperature 45°C for maximum removal of dye. The results showed that a second-order polynomial regression model could properly interpret the experimental data with an R^2-value of 0.9996. The Model F-value of <0.0500 implied that the model is significant. Based on the results of the present study indicated that nano porous adsorbent was an attractive candidate for removing Bb dye from the wastewater.

Key words: Orange peel waste, nano-porous adsorbent, bromophenol blue, response surface method, box-behnken model, wastewater treatment

INTRODUCTION

Wastewater from textile industries constitutes a threat to the environment in large parts of the world. The degradation products of textile dyes are often carcinogenic (Das *et al*., 1995; Banat *et al*., 1996). Furthermore, the absorption of light due to textile dyes creates problems to photosynthetic aquatic plants and algae. Earlier studies have shown that many reactive dyes are not degraded in ordinary aerobic sewage treatment processes and that they can be discharged from the treatment plant unaffected (Carliell *et al*., 1996; Panswad and Luangdilok, 2000). The reactive dyes are highly water-soluble polyaromatic molecules, which mean that their adsorption to solids is relatively poor (Ganesh *et al*., 1994). Some dyes are decolorized under anaerobic conditions. The effluent might, however, be toxic (Brown and De Vito, 1993) furthermore, there might be a risk for reverse colorization when anaerobic degradation products are exposed to oxygen (Knapp and Newby, 1995). Actually, some methods are used in the removal of pollutants. Among them, the liquid-phase adsorption has been shown to be an effective technique for removing dyes, odors and oil from aqueous streams (Juang *et al*., 1997). The commercial activated carbon is the most widely used adsorbent, but recently some non-carbonized low cost adsorbents such as: avocado kernel (Elizalde-Gonzalez *et al*., 2007), banana peel (Annadurai *et al*., 2002), coconut shell (Namasivayam *et al*., 2001), orange peel (Sivaraj *et al*., 2001), peanut hulls (Gong *et al*., 2005),

shells of bittim (Aydin and Baysal, 2006), sugar cane bagasse and wastes of maize (Ho and Mckay, 1999) and (Davila-Jimenez *et al.*, 2005) are being studied for the adsorption of acid dyes. The agricultural wastes (Juang *et al.*, 2002) corn cob (Wu *et al.*, 2001) and plum kernels (Wu *et al.*, 1999) have been used as precursors of carbon for the removal of acid blue 25. The adsorption of acid violet 1, acid blue 264 and acid yellow 36 has been studied on carbon from cassava shell (Rajeshwarisivaraj *et al.*, 2001), pine wood (Tseng *et al.*, 2003) and rice husk (Malik, 2003), respectively. The use of waste materials from agricultural origin is an interesting alternative for the preparation of carbonaceous adsorbents. In the world, Mexico is an important producer of mango (*Mangifera indica* L.), whose seeds are abundant but their use as adsorbent has been only reported for methylene blue (Kumar and Kumaran, 2005). Thereby, the present investigation was made on orange peel nano-porous adsorption of bromophenol blue (Bb) dye is optimized by Box-Behnken design method and was finally correlated with process variables such as dye concentration, pH and temperature.

MATERIALS AND METHODS

Adsorbents and dye: *Citrus reticulata* (orange) peels were obtained from a local fruit stall at Tirunelveli, India on November, 2009. The peels were cut into small pieces, crushed and washed thoroughly with deionized water to remove the adhering dirt. They were air dried in an oven at 40-50°C for 48 h. The BET surface areas of orange peels were in the range 0.0263-0.6719 $m^2 g^{-1}$ obtained from N_2 adsorption isotherms by sorptiometer (Quantochrome NOVA 1000). Bromophenol blue was obtained from Merck Co. The solution pH was adjusted by adding a small amount of 0.1 M HCl or NaOH.

Box-Behnken design experiments: To optimize the range of experimentation the Box-Behnken design was utilized during the investigation. The following were measured dye concentration, X_1 (40, 60, 80 mg L^{-1}); pH, X_2 (5.7, 6.95, 8.2); Temperature X_3 (30, 45, 60°C). These served as the critical variables for the actual experiments as shown in Table 1. For each experimental batch a known weight of nano porous sorbent (1 g L^{-1}) was transferred to a 250 mL flask, then it was incubated on an orbital shaker (150 rpm) at 30°C for 24 h in Lab-line environ shaker. The dye solution was filtered before it was subjected to spectrophotometer analysis. After incubation period, the amount of sorbed dye was calculated by taking samples. All experiments were carried out in triplicate and average values are reported.

Design of experiments: Response surface methodology is an empirical modelization technique derived to the evaluation of the relationship of a set of controlled experimental factors and observed results (Cochran and Cox, 1964; Box and Behnken, 1960; Box and Hunter, 1957). It requires a prior knowledge of the process to achieve statistical model. Basically this optimization process involves three major steps, performing the statistically designed experiments, estimating the coefficients in a mathematical model, predicting the response and checking the adequacy of the model.

$$Y = f(X_1, X_2, X_3 \ldots\ldots\ldots X_k) \quad (1)$$

The true relationship between Y and X_k may be complicated and, in most cases, it is unknown; however, a second-degree quadratic polynomial can be used to represent the function in the range of interest;

Table 1: Adsorption of dyes calculated from the three variables at each experimental point along experimental with theoretical values

Run No.	Dye concentration (mg L^{-1}) X_1	pH X_2	Temperature (°C) X_3	Experimental value (mg g^{-1})	Predicted value (mg g^{-1})
1	40	5.7	45	20.33	20.33
2	80	5.7	45	17.25	17.75
3	40	8.2	45	16.05	15.55
4	80	8.2	45	16.68	16.68
5	40	6.95	30	18.24	18.49
6	80	6.95	30	17.41	17.16
7	40	6.95	60	20.59	20.84
8	80	6.95	60	20.96	20.71
9	60	5.7	30	29.04	28.79
10	60	8.2	30	23.01	23.26
11	60	5.7	60	29.39	29.14
12	60	8.2	60	28.56	28.81
13	60	6.95	45	32.40	32.40
14	60	6.95	45	32.40	32.40
15	60	6.95	45	32.40	32.40
16	60	6.95	45	32.40	32.40
17	60	6.95	45	32.40	32.40

$$Y = R_o + \sum_{i=1}^{k} R_i X_i + \sum_{i=1}^{k} R_{ii} X_i^2 + \sum_{i=1,i<j}^{k-1} \sum_{j=2}^{k} R_{ij} X_i X_j + \varepsilon \quad (2)$$

where, $X_1, X_2, X_3, \ldots, X_k$ are the input variables which affect the response Y, R_0, R_i, R_{ii} and R_{ij} (i = 1-k, j = 1-k) are the known parameters, ε is the random error. A second-order model is designed such that variance of Y is constant for all points equidistant from the center of the design. The parameters and their values (in brackets) were four levels like dye concentration (40, 60, 80 mg L^{-1}), pH (5.7, 6.95, 8.2), temperature (°C) (30, 45, 60). This also enabled the identification of significant effects of interactions for the batch studies. In system involving four significant independent variables X_1, X_2 and X_3, the mathematical relationship of the response of these variables can be approximated by quadratic (second degree) polynomial equation:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^{32} + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (3)$$

Y = Predicted value, b_o = Constant, b_1X_1 = dye concentration (mg L^{-1}), b_2X_2 = pH, b_3X_3 = Temperature (°C), b_1X_1, b_2X_2 and b_3X_3 = linear coefficients, $b_{12}X_1X_2$, $b_{13}X_1X_3$, b23X2X3 = cross product coefficients and X_1^2, X_2^2 and X_3^3 = quadratic coefficients. These parameters were chosen as the critical variables and designed X_1, X_2 and X_3, respectively. The low middle and high levels of each variable were designated as -1, 0 and +1, respectively, as given in Table 2. A total of 17 treatments were necessary to estimate the coefficients of the model using multiple linear regressions. The design of experiments was carried out for analysis using the design expert by Stat Ease Inc., Statistics Made Easy, Minneapolis, MN Version 5.7.1. A total of 17 experiments were necessary to estimate the 10 coefficients of the model. 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. At this

Table 2: The box–behnken design for the three independent variables adsorption dye in actual and predicted values

Source	Coefficient value	Mean square	F-value	Prob>F value
X_0	32.4	77.06812	539.4768	< 0.0001*
X_1	-0.3625	1.05125	7.35875	<0.0301*
X_2	-1.4625	17.11125	119.7788	< 0.0001*
X_3	1.475	17.405	121.835	< 0.0001*
X_1^2	-11.5125	3.4225	23.9575	<0.0018*
X_2^2	-3.3125	0.36	2.52	0.1564
X_3^2	-1.5875	6.76	47.32	<0.0002*
X_1X_2	0.925	558.0533	3906.373	< 0.0001*
X_1X_3	0.3	46.20066	323.4046	< 0.0001*
X_2X_3	1.3	10.61118	74.27829	< 0.0001*
Residual	1	0.142857	R-Squared = 0.9998	
Lack of fit	1	0.333333	Adj R-Squared=0.9996	
Pure error	0	0		
Correlation total	694.6131			

*Values of "Prob>F" less than 0.0500 indicate model terms are significant

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 isotherms.

RESULTS AND DISCUSSION

Adsorption of dyes from the synthetic solution was carried out by the batch equilibrium studies. In the present investigation adsorption of dyes is optimized by Box-Behnken design method. The influence of three factors such as dye concentration (mg L^{-1}), temperature and pH three level investigated. The regression equation obtained after analysis of variance gives the level of adsorption of dye as a function of different dye concentration (mg L^{-1}), temperature and pH. All terms regardless of their significance are included in the following equation:

$$Y = 32.4 - 0.36X_1 - 1.46X_2 + 1.48X_3 - 11.35X_1^2 - 3.31X_2^2 - 1.58X_3^3 + 0.925X_1X_2 + 0.30X_1X_3 + 1.3X_2X_3 \quad (4)$$

The adsorption of dyes from the model at each experimental point is summarized in Table 1 along with experimental and theoretical observed values. The coefficients of Eq. 3 are calculated using design expert and their values and Analysis of Variance (ANOVA) are listed in Table 2. The results of Analysis of Variance (ANOVA) are shown in Table 2 which indicates that the predictability of the model is at 99% confidence interval. The model was found to be adequate for prediction within the range of variable chosen Fig. 1A-C, observed adsorption Bb versus those from the statistical model (Eq. 3). The figure confirmed that the predicted data of the response from the empirical model is in good agreement with the experimentally obtained data.

Adsorption of dye from the synthetic solution was carried out by the batch equilibrium studies. In the present investigation adsorption of dyes is optimized by Box-Behnken design method. The influence of three factors such as dye concentration (mg L^{-1}), temperature and pH three level investigated. The predicted response fit well with those of the experimentally obtained response. The Pred R-Squared of 0.99985 is in reasonable agreement with the Adj R-Squared of 0.9996 which showed that the equation is highly reliable. Values of Prob>F less than 0.0500 indicate model terms are significant (Table 2). The model was found to be adequate for prediction within the range of variable chosen. Figure 1 shows observed adsorption Bb versus those from the statistical model

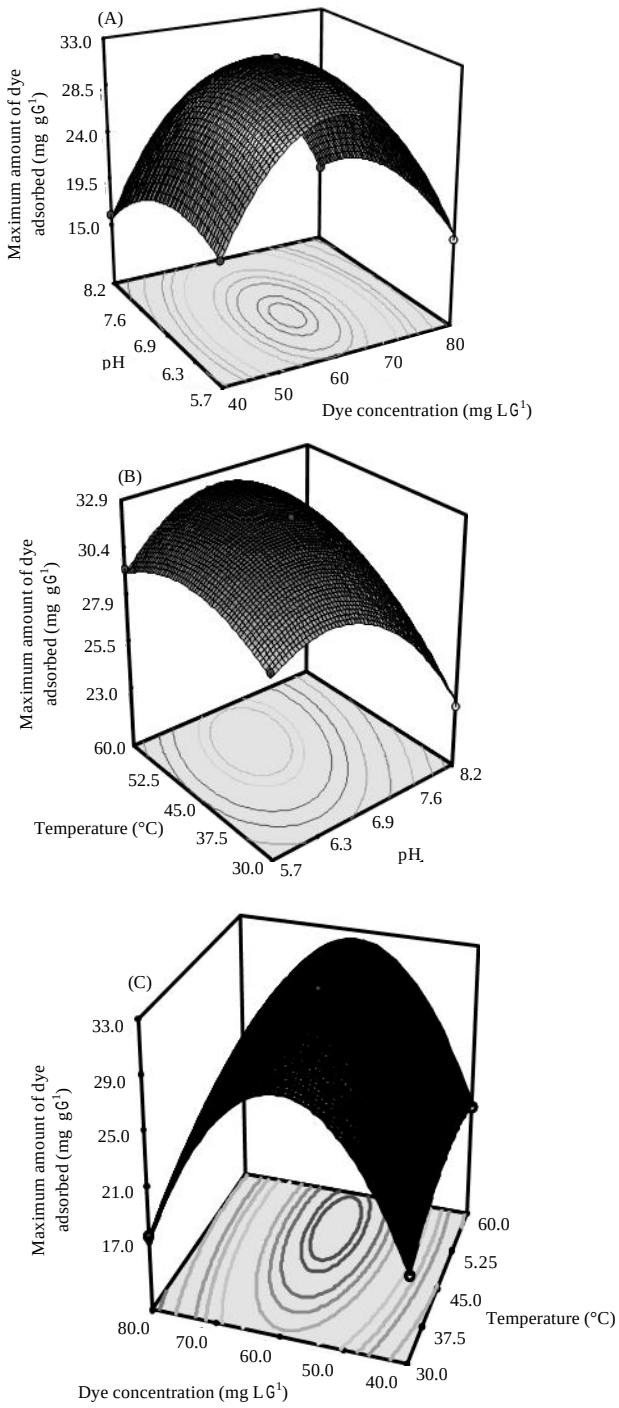

Fig. 1: Adsorption of dye on 3-D graphics (A) for response surface optimization versus dye concentration (mg g^{-1}) vs pH; (B) for response surface optimization versus pH vs temperature (°C) and (C) for response surface optimization versus temperature (°C) vs dye concentration (mg L^{-1})

(Eq. 3). The figure confirmed that the predicted data of the response from the empirical model is in good agreement with the experimentally obtained data.

The contour plot represents maximum percentage of dye adsorption against dye concentration (mg L^{-1}) vs pH. The maximum percentage of dye adsorption is 32.4 mg g^{-1} a particular of dye concentration (mg L^{-1}) (50 to 70 mg L^{-1}) and pH (6.8, 6.95 to 7.6) which is also clearly shown in Fig. 1A. The dye concentration was increased the adsorption also decreased. The optimum level of dye adsorption occurs with 32.4 mg g^{-1} at dye concentration (60.0 mg L^{-1}) and pH (6.95) calculated by derivation of the Eq. 4 and by solving the inverse matrix. The alkaline pH of the present study suggests that the strong chemical reaction occurred between the adsorbate and the adsorbent for more removal of dye (Tripathi *et al.*, 2009).

Figure 1B shows the maximum percentage of dye adsorption was found with pH (6.3 to 7.6) and Temperature (37.5 to 52.5°C) level of adsorption of dye 15 mg g^{-1}. Optimum level of pH (6.8) and Temperature (45°C) showed the maximum percentage of dye adsorption. The result of pH (alkaline) is fit with result of Islam *et al.* (2009) where it's contradict with finding of Tripathi *et al.* (2009). For obtaining maximum adsorption of dye the particle size must be decreased (Chitra and Gowri, 1996; Panday *et al.*, 1986). At lower pH, the lone-pair of electrons of the oxygen atom coordinates with the highly positively charged groups in surface. An increase in the rate with decreasing pH may be caused by an alteration in the adsorbent surface; particularly variation in its electrokinetic's character. That the three variables selected in this study have their individual effect on dye adsorption. The amount of dye adsorption gradually increases with decreasing dye concentration and pH but increasing temperature. Increase of concentration in the solutions decreases the removal percentage of dye. At low concentration, surface activity of used nano-porous adsorbent is higher and resulted more removal of % but at high concentration, the active sites of adsorbent gradually covered by the molecules and show lower removal percent.

Figure 1C shows the maximum percentage of dye adsorption was found to occur with Temperature (37.5 to 52.5°C) and dye concentration (mg L^{-1}) (50 to 70) level of adsorption of dye 32.4 mg g^{-1}. Optimum level temperature (45°C) and dye concentration (60 mg L^{-1}) showed the maximum percentage of dye adsorption. The optimum values of process parameters were dye concentration 60 mg L^{-1}, pH 6.8-6.95 and temperature 45°C for maximum removal efficiency. We are reporting first about orange peel adsorbent for removal of Bb using Box-Behnken model. Tripathi *et al.* (2009) optimized the values like dye concentration 15.7 g L^{-1}, pH 2 and temperature 40°C for maximum removal of Methyl orange dye using coconut based activated carbon-commercial grade adsorbent. In this results the dye concentration and temperature comparable to the present study where the pH in contradiction. The adsorption of dye increases with increasing temperature. An increased adsorption at higher temperature is difficult to explain, although many authors have also reported (Chitra and Gowri, 1996; Panday *et al.*, 1986). The higher removal due to increasing temperature may be due to chemical reaction occurring between the functional groups of the adsorbent and dye (Panday *et al.*, 1989; Chitra *et al.*, 1996).

CONCLUSION

Results from this study suggest that the orange cellulose-based waste peels are suitable adsorbents for Bb. Dyestuff removal by adsorbents of environmental nanomaterial is strongly influenced by physicochemical parameters such as pH, temperature and the concentration of Bb. The model employed provided good quality of predictions for the above variables in terms of effective adsorption of Bromophenol blue and good correlation coefficient (0.99967 was obtained).

The data reported here should be useful for the design and fabrication of an economically viable treatment process using the response for the above variables at any time and also it's revealed that the waste orange peels were the potential materials for dyes removal from aqueous solutions.

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