Response Surface Methodology for Optimizing Adsorption Process Parameters for Methylene Blue Removal by a Hydrogel Composite

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(Received 27 November 2010; accepted 16 January 2011)

ABSTRACT: Response surface methodology was employed to optimize the adsorption parameters of Methylene Blue onto a chitosan-*g*-poly(acrylic acid)/halloysite hydrogel composite with 50% halloysite content. Such optimization was undertaken to ensure a high efficiency over the experimental ranges employed, and to evaluate the interactive effects of the initial concentration of Methylene Blue, the pH and the temperature on the adsorption process in order to improve the conditions employed in the batch process. A total of 17 adsorption experimental runs were carried out employing the detailed conditions designed by response surface methodology based on the Box–Behnken design. The analysis of variance (ANOVA) indicated that a second-order polynomial regression equation was the most appropriate for fitting the experimental data. The experimental confirmation tests showed a correlation between the predicted and experimental responses (R^2 = 0.9904). The optimal point obtained was located in the valid region and the optimum adsorption parameters were predicted as an initial Methylene Blue concentration of 1034 mg/ℓ, a pH value of 6.1 and a temperature of 41 ºC. Under these adsorption conditions, a higher adsorption capacity of 1336.05 mg/g was achieved from a simulated dye solution.

INTRODUCTION

The development of new adsorbents exhibiting superior properties is, at present, attracting a great deal of interest for the removal of dyes from aqueous solution (Kaşgöz and Durmus 2008). Among such adsorbents, the polymer/clay hydrogel composite has received considerable attention because of its relatively low production cost, high mechanical stability and high adsorption capacity towards some dyes (Kaşgöz and Durmus 2008; Wang and Wang 2008). A hydrogel contains a porous three-dimensional polymeric network and this special structure allows the diffusion of solutes into the interior of the network. In addition, hydrogels possess large numbers of ionic or non-ionic functional groups such as carboxyl, hydroxy, sulphonic acid and amine groups, which can adsorb or trap ionic dyes from wastewater (Öztop *et al*. 2004; Paulino *et al*. 2006).

Reports in the literature provide considerable detail regarding the removal of Methylene Blue (MB) or other textile dyes by hydrogel composites (Ekici *et al*. 2003; Jeon *et al*. 2008; Paulino *et al*. 2006; Yi and Zhang 2008), but most of the adsorption studies were conducted using conventional methods, i.e. investigating a process by varying one factor whilst maintaining all other factors involved at constant levels; such methods are time-consuming and of low efficiency

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in optimizing a given process. In addition, the conventional optimization process cannot give an indication of the interactive effects between any two factors in a multi-variable system. To date, there have been no reports regarding the optimization of process parameters for MB onto the hydrogel composite.

Response surface methodology (RSM) can avoid the limitations of conventional methods and is commonly used in many fields. The main purpose of RSM is to check the optimum operational conditions for a given system or to determine a region that satisfies the operational specifications (Montgomery 2001). It might then be possible to obtain a second-order polynomial prediction equation or some other mathematical equations to describe the experimental data obtained at some particular combination of input variables.

Halloysite (HT) is a two-layered tubular aluminosilicate clay with exchangeable cations and active –OH groups on the surface (Hedicke-Höchstötter *et al*. 2009). Based on the relative merits of HT and hydrogel composites, a chitosan-*g*-poly(acrylic acid)/50% halloysite (CTS-*g*-PAA/50% HT) hydrogel composite was synthesized in the present work. This was then used as an adsorbent to optimize the adsorption parameters of MB using RSM, thereby ensuring high removal efficiency and determining the interactive effects of the initial MB concentration, the pH and temperature on the adsorption process. It was anticipated that such data could give guidance for the process optimization of dye removal by adsorption.

EXPERIMENTAL

Materials

Acrylic acid (AA) monomer (chemically pure, distilled before use), ammonium persulphate (APS) initiator (A.R. grade, recrystallized from distilled water before use) and *N,N′*-methylenebiacrylamide (MBA) cross-linker (chemically pure, used as received) were provided by the Shanghai Reagent Corporation, Shanghai, P. R. China. Chitosan (CTS) with a viscosity average molecular weight of 3.0×10^5 and a de-acetylation degree of 0.9 was purchased from the Zhejiang Yuhuan Ocean Biology Co., Zhejiang, P. R. China. Halloysite (HT), as supplied by the Zhengzhou Golden Sunshine Ceramics Co., Ltd., Henan Province, P. R. China, was milled through a 200-mesh screen before use. Methylene Blue (MB) was acquired from Alfa Aesar, Ward Hill, MA, U.S.A. and used without further purification. All other reagents used were of A.R. grade and all solutions were prepared employing distilled water.

Preparation of CTS-*g*-PAA/50% HT

The process employed for the preparation of the hydrogel composite, CTS-*g*-PAA/50% HT, was similar to that used previously (Zheng and Wang 2010). The resulting product was milled and sieved through a 200-mesh screen. The processes used for characterizing the as-prepared hydrogel composite were similar to those reported previously (Zheng and Wang 2010).

Adsorption experiments

For each run, 50 mℓ of an MB solution of known initial concentration and pH was placed in a 100 mℓ conical flask with a stopper together with 0.025 g adsorbent and then shaken on a thermostatic shaker (THZ-98A) at a constant speed of 120 rpm for 60 min. The pH of the MB

solution was adjusted by the addition of 0.1 M HCl or NaOH solution. The contact time and other conditions were chosen according to results obtained from preliminary experiments, since a prior knowledge and understanding of the process and process variables under investigation are essential for obtaining a more realistic model. After their withdrawal from the flasks, all samples were centrifuged at 5000 rpm for 10 min. The residual MB solution was analyzed via a Specord 200 UV–vis spectrophotometer by monitoring the absorbance changes at the wavelength of maximum absorbance (670 nm).

The adsorption capacity was calculated according to the following equation:

$$q = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where q represents the adsorption capacity of the adsorbent at equilibrium (mg/g), C_0 and C_e denote the initial and equilibrium concentration of MB (mg/ℓ), respectively, V is the volume of MB solution used (ℓ) and W is the weight of the adsorbent employed in the study (g).

Experimental design

The process parameters affecting the removal of MB by CTS-*g*-PAA/50% HT were studied using RSM combined with the three-level, three-factorial Box–Behnken experimental design as established using Design Expert software (7.0 trial version). The variable input parameters were an initial MB concentration of 900–1100 mg/ℓ, pH values in the range 4.0–7.0 and temperatures in the range 30–50 ºC, the factor levels being coded as –1 (low), 0 (medium) and 1 (high), respectively (Evans 2003). The three independent variables were designated as A (initial MB concentration, mg/ℓ), B (pH) and C (temperature, ºC), respectively, for statistical computations. The range and levels used in the experiments are listed in Table 1.

A total of 17 runs were performed to optimize the process parameters and experiments were carried out according to the actual experimental design matrix. The results were analyzed applying the coefficient of determination (R^2), analysis of variance (ANOVA) and response plots. Employing RSM, the most widely used second-order polynomial equation developed to fit the experimental data and identify the relevant model terms may be written as:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_{ii}^2 + \sum \beta_{ij} x_i x_j + \varepsilon \tag{2}$$

where Y is the predicted response, i.e. the adsorption capacity for MB by the hydrogel composite, β_0 is the constant coefficient, β_i is the ith linear coefficient of the input factor x_i, β_{ii} is the ith

TABLE 1. Independence Factors and their Coded Levels Used for Optimization

Variable	Real values of coded levels		
	–1	0	+1
Initial concentration, A (mg/ℓ)	900	1000	1100
pH, B	4.0	5.5	7.0
Temperature, C (ºC)	30	40	50

quadratic coefficient of the input factor x_i, β_{ij} is the different interaction coefficients between the input factors x_i and x_j, and ε is the error of the model (Benyounis *et al*. 2005). For this study, the independent variables were coded as A, B and C, and thus the equation could be described as:

$$Y = \beta_0 + \beta_i A + \beta_i B + \beta_i C + \beta_{ii} A^2 + \beta_{ii} B^2 + \beta_{ii} C^2 + \beta_{ij} AB + \beta_{ij} AC + \beta_{ij} BC \quad (3)$$

RESULTS AND DISCUSSION

Box–Behnken analysis

The initial concentration (A), the pH (B) and the temperature (C) are three important factors affecting an adsorption process for a given adsorbent. Consequently, A, B and C were chosen as the independent variables while the removal of MB at equilibrium (Y) was selected as the response (dependent variable) in the present study. According to the Box–Behnken design, a series of experiments was conducted for exploring different combined parameters and for evaluating the combined effects of these factors. The Box–Behnken model does not contain combinations of all the factors at their highest or lowest values at the same time and, in particular, it can avoid extreme treatment combinations (Ferreira *et al*. 2007).

Generally, a system or process with several variables is likely to be driven primarily by some principal factors and low-order interactions. In the present work, only two-way interactions were investigated. Linear, two-factor interaction (2FI), quadratic and cubic models were used to analyze the experimental data in order to obtain the appropriate regression equations. To determine the adequacy of the models depicting the removal of MB by CTS-*g*-PAA/50% HT, two different tests, i.e. the sequential model sum of squares and the model summary statistics, were conducted. The corresponding results are tabulated in Table 2. The fitness of the model was determined by R^2 and its statistical significance was evaluated by an F-test (Peng *et al*. 2002). The higher the value of R^2, the better the model. The results from the sequential model indicated that the 2FI model did not provide a good description of the experimental data. From the model summary statistics, it can be seen that the "Predicted R^2" of 0.8463 was in reasonable agreement with the "Adjusted R^2" of 0.9780 for the quadratic model. Furthermore, the quadratic model had maximum "Predicted R^2" and "Adjusted R^2" values. The afore-mentioned results indicate that the quadratic model provided an excellent explanation for the relationship between the independent variables and the corresponding response. "Adequate Precision" measures the signal-to-noise ratio. It is clear that only the "Adequate Precision" value of the quadratic model indicated an adequate signal, validating the viewpoint mentioned above. Consequently, the quadratic model could be used to navigate the design space and for this reason it was selected as the most appropriate model for further analysis.

Statistical analysis

The quadratic equation for predicting the optimal point was achieved according to the Box–Behnken experimental design and input variables, and the empirical relationship between the response and the independent variables in the coded units based on the experimental results was given by:

$$Y = 1315.47 + 83.72A + 28.77B + 9.51C - 0.56AB - 0.99AC - 1.17BC - 120.55A^2 - 37.52B^2 - 31.50C^2 \quad (4)$$

TABLE 2. Adequacy of the Model Tested

Source	Sum of squares	df[a]	Mean square	F value	Probability > F	Remarks
Sequential model sum of squares						
Linear	63418.34	3	21139.45	3.54	0.0451	Significant
2FI	63428.90	6	10571.48	1.36	0.3166	Not significant
Quadratic	1.396×10^5	9	15513.30	80.18	< 0.0001	Significant
Cubic	1.410×10^5	12	11747.83	6.366×10^7	< 0.0001	Significant

Source	Std. Dev.	Predicted R^2	Adjusted R^2	R^2	Adeq. precision	
Model summary statistics						
Linear	77.24	0.1206	0.3229	0.4499	6.005	Inadequate signal
2FI	88.06	–0.6945	0.1199	0.4499	3.982	Inadequate signal
Quadratic	13.91	0.8463	0.9780	0.9904	25.415	Adequate signal
Cubic	0.000	N/A[b]	1.0000	1.0000	0.000	Inadequate signal

[a]Degrees of freedom. [b]Case with leverage of 1.0000, Pred. R^2 statistic is not defined.

The results from the ANOVA for the quadratic equation are presented in Table 3. The ANOVA suggests that the equation and the actual relationship between the response and the significant variables represented by the equation were adequate. The larger the value of F and the smaller the value of p, the more significant is the corresponding coefficient term (Amini *et al*. 2008; Kalavathy *et al*. 2009). The value of p was lower than 0.05, indicating that the model may be considered to be statistically significant (Kim *et al*. 2003). For the removal of MB by CTS-*g*-PAA/50% HT, the ANOVA results (Table 3) indicated that the F-value for the model was 80.18, implying that most of the variation in the response could be explained by the regression equation and that the model was significant. Furthermore, the probability $p < 0.0001$ also suggested that the model was significant. In this study, A and A^2 were highly significant factors, while B, B^2 and C^2 were significant parameters. The other model terms whose p-values are listed as being greater than 0.1000 in Table 3 were not significant factors. Analysis of equation (4) showed that the variables A, B and C had a positive relationship in the adsorption of MB by the hydrogel composite (Kumar *et al*. 2009). On checking the R^2 values, it was clearly seen that only ca. 2% of the total variation could not be explained by the model. Furthermore, the adequacy of the as-developed model was demonstrated by a high "Adequacy precision" value of 25.415 (Table 2) (Muthukumar *et al*. 2003).

TABLE 3. ANOVA for Response Surface Quadratic Model for MB Removed by CTS-*g*-PAA/50% HT

Source	Sum of squares	df	Mean square	F value	p value Prob. > F
Model	1.396×10^5	9	15513.30	80.18	< 0.0001
A	56070.63	1	56070.63	289.82	< 0.0001
B	6623.43	1	6623.43	34.23	0.0006
C	724.28	1	724.28	3.74	0.0942
AB	1.24	1	1.24	6.426×10^{-3}	0.9384
AC	3.88	1	3.88	0.020	0.8914
BC	5.43	1	5.43	0.028	0.8717
A^2	61192.45	1	61192.45	316.29	< 0.0001
B^2	5828.56	1	5928.56	30.64	0.0009
C^2	4178.23	1	4178.23	21.60	0.0023
Residual	1354.29	7	193.47		
Lack-of-fit	1354.29	3	451.43		
Pure error	0.000	4	0.000		
Cor. total	1.410×10^5	16			

The data were also analyzed to check the correlation between the experimental and predicted adsorption capacities (Y, mg/g), as shown in Figure 1. The experimental values were the measured response data for the runs designed by the Box-Behnken model, while the predicted values were obtained by calculation from the quadratic equation. It can be seen from Figure 1 that the data points on the plot were reasonably distributed near to the straight line ($R^2 = 0.9904$), indicating a good relationship between the experimental and predicted values of the response, and that the underlying assumptions of the above analysis were appropriate. The result also suggests that the selected quadratic model was adequate in predicting the response variables for the experimental data.

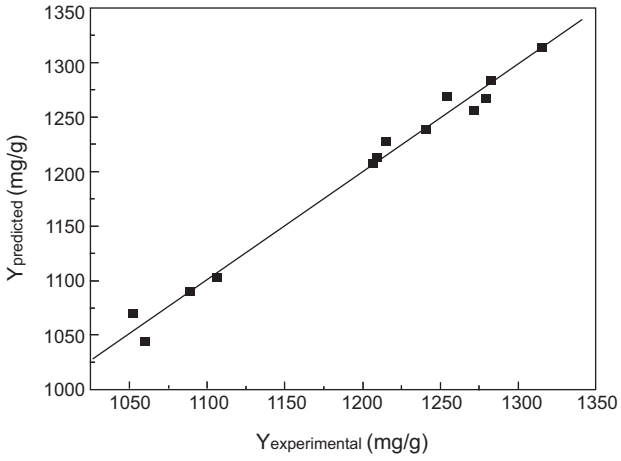

Figure 1. Plot of the experimental and predicted uptake values.

Three-dimensional response surface plot

The three-dimensional response surface plots, obtained as a function of two factors maintaining all other factors constant, are helpful in understanding both the main effects and the interaction effects of these two factors (Adinarayana and Ellaiah 2002). The corresponding contour plots, represented by the projection of the response surfaces in the x–y plane, provide a straightforward determination of the effects of the independent variables on the dependent variable (Wu *et al*. 2009). The three-dimensional response surface plots and related contour plots obtained are depicted in Figures 2 and 3, respectively. The response surface plots in Figures 2 and 3 were both part of a parabolic cylinder, exhibiting a minimum and maximum ridge, respectively, in the investigated domain. In each response surface, the optimum values of both variable factors, such as the initial MB concentration (C_0) and the temperature (T), could be analyzed by the saddle point or by determining the maxima formed by the x- and y-coordinates.

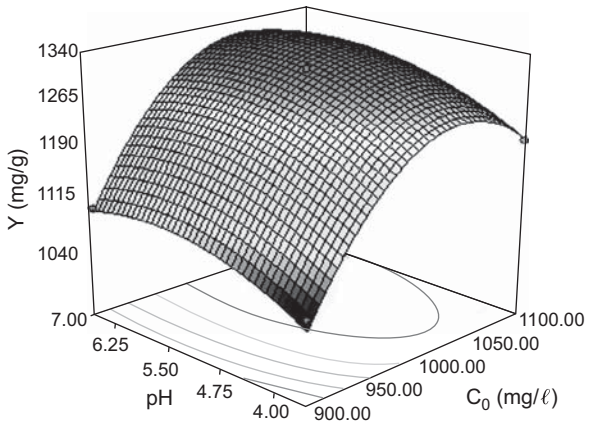

Figure 2. Response surface plot for the effects of pH and initial MB concentration.

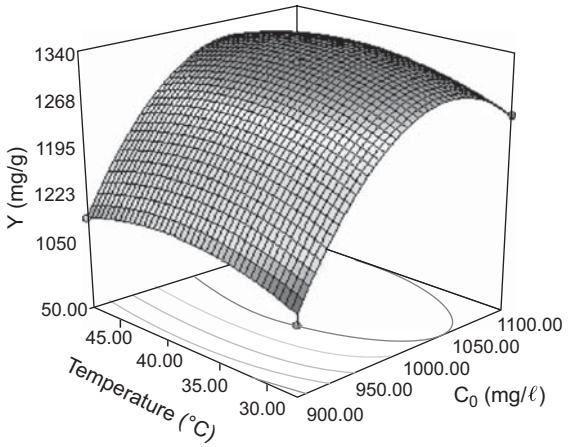

Figure 3. Response surface plot for the effects of temperature and initial MB concentration.

Figure 2 depicts the three-dimensional response surface relationship between pH and the initial MB concentration on the removal of MB by the hydrogel composite at a constant temperature of 40 ºC. It will be seen that, at a given constant pH, the MB uptake increased with increasing initial concentration up to a certain point, beyond which it decreased. An increase in the initial MB concentration resulted in an increase in the removal extent of MB; this could possibly be attributed to a continuous increase in the concentration driving force. The higher the initial concentration, the large is this driving force (Al-Qodah 2000). In addition, the resistance to MB uptake decreased as the mass-transfer driving force increased. However, the adsorption capacity decreased on further increasing the initial concentration of MB as a result of the aggregation of MB molecules. Such aggregation would lead to hindrance of the diffusion of MB molecules into the hydrogel composite networks, thereby leaving some adsorption sites unoccupied (Coates 1969; Mall *et al*. 2005, 2006). At any particular initial concentration, the MB uptake initially increased with increasing pH but the adsorption capacity remained constant under the same circumstance.

The chemical structure of the adsorbent is helpful in understanding the effect of pH on the removal of MB. Thus, only a small amount of CTS was used in the preparation of the hydrogel composite and most of the active amino groups of CTS took part in the copolymerization process. Hence, the carboxyl groups within the polymeric network played a most important role in controlling the nature and adsorption properties of the hydrogel composite. The value of pK_a for poly(acrylic acid) is ca. 4.7 (Lee *et al*. 1999) and hence the carboxyl group is readily ionized at pH values above 4.7. This means that a portion of the carboxyl groups existed as –COOH groups at pH < 4.7, which would not be conducive towards the removal of MB molecules. Nevertheless, even at such pH values, some ionized –COOH groups are still present, thereby allowing electrostatic interaction between the MB molecules and the electron-donor sites on the surface of the hydrogel composite. Accordingly, even at pH < 4.7, a considerable adsorption capacity was observed. In addition, over the wide pH range examined, the adsorption capacity towards MB of the hydrogel composite with a high content of HT was high, which would favour its practical application. The maximum adsorption capacity was found to be 1315.47 mg/g at a pH value of 5.5 and an initial MB concentration of 1000 mg/ℓ.

The combined effect of temperature and initial concentration on the uptake of MB by the hydrogel composite at pH 5.5 is depicted in Figure 3. From this figure, it will be noted that the relationship between the extent of MB adsorption and the initial concentration was similar to that depicted in Figure 2. As the temperature was increased from 30 ºC to 40 ºC, an increase occurred in the adsorption capacity towards MB, following which the adsorption capacity decreased as the temperature was increased further. Similar phenomena have been reported by other workers (Kumar *et al*. 2009). The maximum removal of MB of 1315.47 mg/g occurred at an initial MB concentration of 1000 mg/ℓ and a temperature of 40 ºC.

The interactive influence of temperature and pH on the extent of adsorption at a constant initial MB concentration of 1000 mg/ℓ could also be plotted as a response surface figure (not shown here). The effect of temperature on the adsorption process was in line with the earlier discussion (Figure 3) and the trend in the plot of the adsorption capacity versus pH was similar to that depicted in Figure 2 over the experimental range examined.

Numerical optimization

One of the primary objectives of the present study was to find the optimum process parameters for maximizing the adsorption of MB from aqueous solution. The model capable of predicting the maximum adsorption capacity showed that the optimum values of the process variables were an initial MB concentration of 1034 mg/ℓ, a pH value of 6.1 and a temperature of 41 ºC. Under these conditions, the predicted adsorption capacity was 1336.05 mg/g which was in good agreement with the experimental value of 1315.47 mg/g.

CONCLUSIONS

A CTS-*g*-PAA/50% HT hydrogel composite was prepared and used to trap MB from aqueous solution. The response surface modelling was successfully combined with the three-level three-factorial Box–Behnken design to determine the effects of several important process parameters, such as the initial MB concentration, the pH and the temperature, on the adsorption process and then to enable the optimization of MB removal by the hydrogel composite over the experimental range examined. The results showed that a second-order polynomial regression model was capable of accurately interpreting the experimental data. Through ANOVA by the second-order polynomial regression equation, it was shown that the initial MB concentration and the pH had significant effects on MB adsorption. Process optimization was conducted and a maximum predicted adsorption capacity of 1336.05 mg/g was obtained at an initial MB concentration of 1034 mg/ℓ, a pH value of 6.1 and a temperature of 41 ºC. The present study has shown that RSM combined with a Box–Behnken design provides a very reliable and accurate methodology for optimizing experiments for the removal of dye from aqueous solution by adsorption processes.

ACKNOWLEDGEMENTS

The authors thank the National Natural Science Foundation of China (Grant No. 20877077) and the Project of Jiangsu Provincial Science and Technology Office (Grant No. BE2008087) for their joint support of this study.

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