반응성 염료 제거 공정의 공정 최적화

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Process Optimization of the Removal of Reactive Red Dye by bioaccumulation

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서론

The current popularity of cotton fabrics and bright colors has lead to greater usage of reactive and azo dyes in the textiles industry and more often, these dyes are recalcitrant organic molecules that cause strong color in the effluents and contribute to their organic load and toxicity (Banat et al., 1996). Color is the first contaminant to be recognized, and environmental regulation in most European countries (EU directive 91/271) has made it mandatory to decolorize the dye wastewater prior to discharge. Removal of dyes using physical or chemical treatment processes including flocculation, floatation and membrane filtration are not favored due to their high initial investment and operational costs, and hence economically unfeasible (Banat et al., 1996). Among the many microorganisms explored for the above purpose, the potential use of white-rot fungus *Trametes versicolor*for the removal of textile dyes such as Gris Lanaset G, Remazol Brilliant Blue R, Congo Red, etc. have attracted the attention of a few researchers (Binupriya et al., 2007).

The effectiveness of potential bioadsorbent depends on the levels of the variables (pH, temperature, stirring rate, contact time, etc) used in the adsorption process (Mussatto and Roberto, 2004). As each of these operational variables interacts with the others and influences the adsorption of the dye material, it is essential to optimize the treatment conditions through a method taking these interactions into account and to determine a set of optimal experimental conditions. The optimization of the variables through factorial design and response surface methodology (RSM) fulfils this requirement.

In the present study, we have evaluated the bioaccumulation of Reactive Red-198 dye (RR-198) using *Trametes versicolor* and their process optimization using RSM and multistage Monte-Carlo statistical methods.

실험

Reactive Red-198 (RR-198) dye was obtained from S.D. Fine Chem. Ltd., India. All other chemicals and solvents used in this study were AR grade purchased from Glaxo Ltd., India.

Fungal isolation and cultivation

Trametes versicolor (white-rot fungus) was obtained from the Institute of Microbial Technology(IMTECH), Chandigarh, Indiafor color removal study. These strains were grown aerobically in potato dextrose broth medium in a temperature-controlled shaker maintained at the temperature between 20 to 30 ^{o}C at 180 rpm. After 72 h, the cultures were transferred into the azo dye solution.

Accumulation experiment

The growth and dye uptake by *T. versicolor* was carried out in 250 ml Erlenmeyer flask containing 100 ml of RR-198 dye solution. For the pH studies, 30 mg/L of RR-198dye solution was prepared and the pH of the dye solution was adjusted to 1, 2, 3, 4, 5 and 6 using tartaric acid. Dye solutions of different concentration were prepared and the solution pH was optimised with the help of the initial dye concentration studies. All the solutions were sterilized. 15% (v/v) of the fungal pure culture was inoculated into the dye solutions and the experiment was repeated (same as that used for the growth of the fungus). Samples were withdrawn at every 12 h intervalduring the growth phase.

Factorial experimental design and optimization of parameters

The central composite design (CCD) is the standard response surface methodology (RSM), which was selected for the optimization of parameters used in this study(Montgomery, 1991). For statistical calculations, the variables X_i were coded as x_i according to the following equation (1):

$$x_i = (X_i - X_o)/X \tag{1}$$

where X_i is the uncoded value of the *i*th independent variable, X_o is the value of X_i at the centre point of the investigated area and X is the step change. Temperature, pH and initial dye concentration were chosen as independent variables and the efficiency of colour removal as dependent output response variable.

The behavior of the system was explained by the following quadratic equation (2):

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

where Y is a dependent variable and x_i and x_j are independent variables. The results of the experimental design were studied and interpreted by MINITAB 14 (PA, U.S.A) statistical software to estimate the response of the dependent variable.

Results and discussion

Effect of variable parameters on color removal

Experiments were performed at different combinations of pH range (1 to 6), temperature range (25 to 30 ^{o}C) and initial RR-198 dye concentration (20 and 100 mg/L) of the solution using statistical experiments. From experimental result, it was observed that the maximum color removal was found to be at pH = 3, temperature = 27.5 ^{o}C and initial dye concentration = 20 mg/L. The removal efficiency obtained at a lower pH may be due to the electrostatic attraction between the positively charged fungal surfaces and the negatively charged acid dyes as reported earlier. Maximum bioaccumulation of RR-198 dye occurred at pH = 3 due to the fact that, when the dyes are in ionized form, adjacent molecules of the dyes on the bioaccumulating adsorbent surface are presumed to repel each other to a significant degree due to their equal electrical charge resulting in higher accumulation. McKay et al. has earlier reported a similar trend for dye removal on chitin (McKay et al., 1983). Accumulation efficiency was also found to be increased with increasing temperature which may have produced a swelling effect onthe internal structure of the hybrid bioaccumulating adsorbent enabling the dye to penetrate further. Similar temperature effects on the adsorption of reactive dye on chitosan beads have been reported earlier (Shen and Ya, 2002).

Statistical optimization studies

In our study, the predicted values (using the model equations) were compared with experimental results. The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested using analysis of variance (ANOVA). The dye removal efficiency (%) was found to be more at 20 mg/L. From the results, it is observed that the adsorption yield decreases with increase in initial dye concentration. This may be due to the saturation of the sorption sites on the biomass as the dye concentration increased. Using experimental results, the regression equation of second-order polynomial which relates to the removal efficiency and process parameters were developed using Eq. (2).

The ANOVA values for removal efficiency and biomass concentration respectively also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct. The response surface contour plots to estimate the removal efficiency surface over the variables, pH and initial dye concentration (temperature variable kept constant) is shown in Fig. 1. The coordinates of the central point within the highest contour levels in each of these figures will correspond to the optimum value. The maximum predicted yield is indicated by the surface confined in the smallest curve in contour diagram (Gopal et al., 2002).

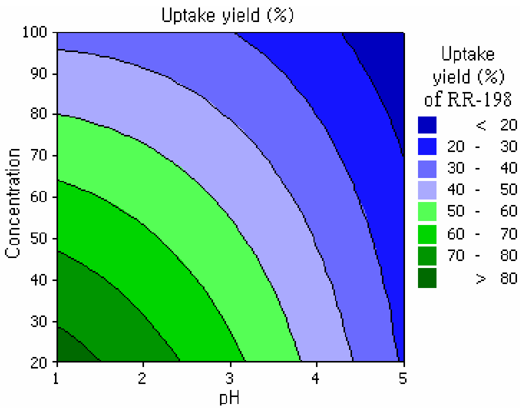

Fig. 1. Response surface contour plot for influence of pH and initial dye concentration on Reactive Red dye removal (holding temperature: 27.5 ^{o}C).

On the other hand, the two model equations used in this study were also optimized using multistage Monte-Carlo optimization technique (Conley, 1984). The optimum values of the process variables for the maximum removal efficiency and maximum biomass concentration are shown in Table 1. These results closely agree with those obtained from the response surface analysis, confirming that the RSM could be effectively used to optimize the process parameters. The optimal operating conditions are pH (X_1) = 2.0, temperature (X_2) = 30 °C, and initial dye concentration (X_3) = 30 mg/L, where the color removal is 99.99% at this optimal conditions.

Table 1. Optimum value of the process parameters for maximum color removal by multistage Monte-Carlo optimization technique

Parameter	Optimum value
Color removal	99.99 mg/L
pH (X_1)	2.0
Temperature(X_2, °C)	30
Initial dye concentration(X_3, mg/L)	30

결론

This study demonstrated the applicability of RSM and statistical optimization of *Trametes versicolor* biomass for effective dye removal. Under optimal values of process parameters, complete removal (100%) was found for Reactive Red-198 dye using *T. versicolor*. It clearly showed that response surface methodology was one of the suitable methods to optimize the best operating conditions which can simultaneously maximize the dye removal and biomass concentration. Graphical response surface and contour plot were used to locate the optimum point. Finally, the experimental results clearly improved the removal capability of dye treatment by the proposed method.

감사

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