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Carbaryl removal from aqueous solution by *Lemna major* biomass using response surface methodology and artificial neural network

S. Chattoraj, N.K. Mondal *, B. Das, P. Roy, B. Sadhukhan

Department of Environmental Science, The University of Burdwan, Burdwan 713104, West Bengal, India

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ABSTRACT

In this present work, biosorption process of carbaryl from aqueous solution on *Lemna major* biomass was studied in a batch process. Both response surface methodology (RSM) and artificial neural network (ANN) model involving 29 experiments were applied to optimize and stimulate the adsorption process. The effects of operating parameters such as initial concentration, pH, biomass dose and contact time on the adsorption of carbaryl were analyzed through a three level four factor based on Box–Behnken design (BBD) using RSM. The proposed quadratic model showed good fit of the experimental data with coefficient of determination (R^2) value of 0.992 and Fisher F-value of 132.33. Response surface plots were used to determine the interaction effects of main factors and optimum conditions of process. The optimum adsorption conditions were found to be initial concentration 34 ppm, pH 5.22, biomass dose of 0.86 g and contact time 12.52 min. ANN model developed from the same design provided reasonable predictive performance ($R^2 = 0.921$) of carbaryl adsorption. Both the model was compared by the coefficient of determination (R^2) and individual importance order of the operating parameters. Finally both the model fitted well to the experimental data. The rate of the biosorption process followed pseudo-second-order kinetics while equilibrium data well fitted to the Freundlich and Langmuir isotherm model. The maximum biosorption capacity of the biomass for carbaryl was found to be 6.21 mg g^{-1}.

Introduction

Presently on worldwide basis intoxications due to pesticides is very high. Rapid use of pesticides for high yielding of crops causes many environmental problems. Extensive applications of these agrochemicals in crop farms, orchards, fields and forest lands contaminate the surface and ground water. This contamination arises from surface runoff, leaching, wind erosion, deposition from aerial applications, industrial discharges and various other sources [1]. Therefore contamination of groundwater affects the health of human beings as it is being directly used for drinking purpose. This situation needs urgent attention with acceptable solution for the removal of pesticides from aqueous solutions.

Carbaryl(1-naphthyl methyl carbamate) is one of the most widely used insecticide today. U.S. Geological Survey's National Water Quality Assessment (NAWQA) Program reported carbaryl as the second most frequently found insecticide in water. At present, there is increased concern about the environmental fate and toxicity of carbaryl because of its high toxicity to both humans and wildlife.

Biosorption is relatively new and one of the effective alternative methods for the removal of pesticides in contaminated water samples. In addition to scientific preference, economic considerations also play an important role in the selection of appropriate biomass for pollution control. Thus, intense research attention is now focused on cost effective, ecofriendly and easily available adsorbent particularly of biological origin [2]. In recent years, various natural adsorbents such as *Rhizopus oryzae* biomass [2], bagasse fly ash [3], thermally treated egg shell [4], waste jute fibre carbon [5] and *pistia stratiotes* biomass [6] have been tried to achieve effective removal of various pesticides. The search for an appropriate and inexpensive biomass is a continuing process. The most effective and optimized utilization of a biomass demands a detailed understanding of the binding mechanism.

In the present study *Lemna major* biomass is used for removal of carbaryl from aqueous solution. Adsorption isotherms were established to explain the solute and solvent interaction mechanism. Various kinetic models were used to determine the rate and order of the adsorption process. To optimize the process parameters for the adsorption process a Box–Behnken design in response surface methodology (RSM) by Design Expert Version 7.0.3 [7] and artificial neural network model (ANN) by SPSS-17 statistical software used jointly. When compared to other

* Corresponding author. Tel.: +91 9434545694; fax: +91 03422634200.
E-mail address: nkmenvbu@gmail.com (N.K. Mondal).

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similar adsorption studies, the novelty of using RSM in this work is to reduce the number of experiments, to study the effect of factor interactions and to develop the statistical mathematical model equation, to identify optimum conditions where the high uptake capacity was obtained for the removal of carbaryl using *Lemna major* biomass to ensure the high uptake capacity at low adsorbent dosage and high carbaryl concentration to reduce the time consumption. Finally optimal solutions offered by RSM and ANN were statistically compared by the coefficient of determination (R^2) and individual importance order of the operating parameters.

Materials and methods

Chemicals

A fresh 0.03% (wv^{-1}) methanolic solution of 4-nitrobenzene diazonium fluoborate (Sigma–Aldrich) A.R. (99.9% purity) was used as the main reagent. An Analytical standard pure sample of carbaryl was obtained by the recrystalisation of a technical grade sample supplied by Bayer. The solvent used for the extraction was optima grade methanol. Stock solutions were made in A.R. grade $CaCl_2$, A.R. grade NaOH and subsequent dilutions were made in methanol. All standard solutions were kept at room temperature for further use.

Adsorbent collection and preparation

Lemna major, a floating macrophyte was collected from the surrounding area of University of Burdwan, West Bengal, India. The macrophyte was washed several times with distilled water and then it was initially sun-dried for 7 days followed by drying in hot air oven at 343 ± 1 K for 2 days. The dried material was crushed and sieved to give a fraction of 250 mesh screen. The material was washed thoroughly with deionised water to remove all impurities that might be present in the material and then stored in sterile, closed glass bottles and used as an adsorbent.

Characterization of adsorbent

Adsorbent characterization was performed by means of spectroscopic and quantitative analysis. According to the classical BET method, the specific surface area of the adsorbent is usually measured by adsorption of nitrogen at 77 K using molecular area am of nitrogen as 0.162 nm^2 and the measurement of BET surface area of the adsorbent in the study was conducted using a surface area analyzer (Model: Nova-2200e, Quantachrome corporation, Boynton Beach, USA). The pH of aqueous slurry was determined by soaking 1 g of biomass in 50 mL distilled water, stirred for 24 h and filtered and the final pH was measured. The physico-chemical characteristics of the adsorbent were determined using standard procedures. The concentrations of sodium and potassium were determined by Flame Photometer (Model No. Systronics 126). For stirring purpose magnetic stirrer (TARSONS, Spinot digital model $MC0_2$, CAT No. 6040, S. No. 173) was used. The Fourier transform infrared (FTIR) spectra of the adsorbent was recorded with Fourier transform infrared spectrophotometer (PERKINELMER, FTIR, Model-RX1 Spectrometer, USA) in the range of 400–4000 cm^{-1}. In addition, scanning electron microscopy (SEM) analysis was carried out using a scanning electron microscope (HITACHI, S-530, Scanning Electron Microscope and ELKO Engineering, B.U. Burdwan) at 15 kV to study the surface morphology of the adsorbent.

Batch adsorption procedure

The spectrophotometric determination of carbaryl was done by using the following method of Stansbury and Miskus [8]. 5 mL of 0.5 (N) NaOH solution was added to 5 mL of aliquot taken in a 20 mL volumetric flask followed by the addition of 5 mL of 0.03% (wv^{-1}) methanolic solution of *p*-nitrobenzene diazonium fluoborate .The mixture was then diluted to 20 mL with methanol. After 20 min the absorbance of the greenish-blue colour of the resulting solution was measured at 590 nm using UV–vis spectrophotometer (Systronics, Vis double beem Spectro 1203). The influence of pH (2.0–10.0), initial carbaryl concentration (20–50 $mg\,L^{-1}$), biomass (0.1–2.50 g/50 mL) and contact time (10–60 min) were evaluated during the present study. Samples were collected from the flasks at predetermined time intervals for analyzing the residual carbaryl concentration in the solution. The amount of carbaryl ions adsorbed in milligram per gram was determined by using the following mass balance equation:

$$q_e = \frac{(C_i - C_e)V}{m} \tag{1}$$

where C_i and C_e are carbaryl concentrations ($mg\,L^{-1}$) before and after adsorption, respectively, V is the volume of adsorbate in litre and m is the weight of the adsorbent in grams. The percentage of removal of carbaryl ions was calculated from the following equation:

$$\text{Removal}\,(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \tag{2}$$

The adsorption experiments were performed in triplicate, and mean values were used in the data analysis. The control experiments were performed without the addition of adsorbent which confirmed that the adsorption of carbaryl on the walls of flasks were negligible.

Optimization of adsorption process by response surface methodology

The optimization of carbaryl biosorption was carried out by four chosen independent process variables including initial carbaryl concentration, pH of the solution, biomass and contact time. For the three level four factor design the four independent variables are coded as *A*, *B*, *C* and *D*. The levels are designated as −1(low), 0(middle) and +1(high) of variables investigated in the research are given in Table 2. Montgomery [9] has defined the statistical terms and their definitions. The percent removal of carbaryl was taken as response of the system. The quadratic equation model for predicting the optimal point was expressed according to Eq. (3).

$$Y = \beta_o \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \sum_{j=1}^{k} \beta_{ij} x_{ii}^2 + \varepsilon \tag{3}$$

where Y is the response variable; β_0 is the intercept; β_i, β_{ij} and β_{ii} are coefficients of the linear effect, double interactions; x_i, x_j are the independent variables or factors and ε is error. Percentage removal of carbaryl was studied with a standard RSM design Box–Behnken Design (BBD). Twenty nine experiments were performed in duplicate according to the scheme mentioned in Table 2. Design Expert Version 7.1.6 [7] was used for regression and graphical analysis of the data obtained. The optimum values of the selected variables were obtained by solving the regression equation and by analyzing the response surface contour plots. The variability in dependent variables was explained by the multiple coefficient of determination, R^2 and the model equation was used to predict the optimum value and subsequently to elucidate the interaction between the factors within the specified range.

ANN modelling

ANN based model was also developed during the present study for describing the carbaryl removal process. It is now used as a very