Biosorption of carbaryl from aqueous solution onto *Pistia stratiotes* biomass

Soumya Chattoraj · Naba Kumar Mondal · Biswajit Das · Palas Roy · Bikash Sadhukhan

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Abstract In this work, adsorption of carbaryl from aqueous solution on *Pistia stratiotes* biomass was investigated. The effects of operating parameters such as initial concentration, pH, adsorbent dose and contact time on the adsorption of carbaryl were analyzed using response surface methodology. The proposed quadratic model for central composite design fitted very well to the experimental data that it could be used to navigate the design space according to analysis of variance results. Response surface plots were used to determine the interaction effects of main factors and optimum conditions of the process. The optimum adsorption conditions were found to be initial carbaryl concentration = 15.57 mg L\(^{-1}\), pH 2.01, adsorbent dose = 0.72 g and contact time = 30 min. The Langmuir, Freundlich and Temkin isotherm models were applied to the equilibrium data. The maximum biosorption capacity of *P. stratiotes* biomass for carbaryl was found to be 3.1 mg g\(^{-1}\). The pseudo-second-order kinetic model described the carbaryl biosorption process with a good fitting.

Keywords Adsorption · Carbaryl · *Pistia stratiotes* biomass · Central composite design

Introduction

One of the industrial by-products threatening the environment worldwide today is pesticides residues. Reports have shown that the presence of pesticide in the environment and the threat they pose to wild life and mankind have generated great concern in the past 20 years. The excessive and non-judicial use of pesticide and insecticide in crop farms, orchards, fields and forest lands contaminate the surface and groundwater. This contamination arises from surface runoff, leaching, wind erosion, deposition from aerial applications, industrial discharges and various other sources (Salman et al. 2011). It is not surprising, therefore, that small amounts of these chemicals have been isolated from many phases of the environment, including water supplies. The harmful influence of pesticides on human health and environment has resulted in the imposition of stringent legislation on drinking water quality in many countries (Derylo-Marczewska et al. 2010).

Carbaryl (1-naphthyl methyl carbamate) is one of the most widely used insecticides today. The IRED cited a study by the US Geological Survey’s National Water Quality Assessment program that 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.

There are several procedures available for pesticides removal from water which includes photocatalytic degradation (Ugurlu and Karaoglu 2011; Gong et al. 2011), ultrasound combined with photo-Fenton treatment (Katsumata et al. 2011), advanced oxidation processes (Zhou et al. 2011), aerobic degradation (Rajashekara Murthy and Manonmani 2007), electrodialysis membranes (Banasiak et al. 2011), ozonation (Maldonado et al. 2006) and adsorption (Al-Muh-taseb et al. 2011). Among these, adsorption is effective and economical (Ahmad et al. 2009). Various adsorbents are used for the removal of pesticides in water samples including activated carbon (Ohno et al. 2008; Castro et al. 2009), straw (Akhtar et al. 2007), lignocellulosic substrate from agro industry (Bakouri et al. 2009), bagasse fly ash (Traub-
Eberhard et al. 1995), coal fly ash (Singh 2009) and charcoal from agro waste (Sudhakar and Dikshit 1999) and bark (Boudsocque et al. 2008). 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, profound research attention is now focused on cost-effective, eco-friendly and easily available adsorbent, particularly of biological origin (Chatterjee et al. 2010). In recent years, various natural adsorbents such as agricultural wastes including Rhizopus oryzae biomass (Chatterjee et al. 2010), bagasse fly ash (Gupta et al. 2002), thermally treated egg shell (Elwakeel and Yousif 2010) and waste jute fiber carbon (Senthilkumara et al. 2010) have been tried to achieve effective removal of 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.

Pistia stratiotes is a floating macrophyte. It is a genus of aquatic plant in the arum family, Araceae. The single species it comprises, P. stratiotes, is often called water cabbage, water lettuce, Nile cabbage or shellflower. The living aquatic macrophyte P. stratiotes has been extensively used in bioaccumulation processes (Sune et al. 2007), phytoremediation (Skinner et al. 2007) and for removal of Cr(VI) ions (Das et al. 2013), which makes the study using dead biomass very important. So, this biomass can also be utilized to remove carbaryl from aqueous solutions which formed the motivation of this study.

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 biosorption process, a central composite design (CCD) in response surface methodology (RSM) by Design Expert Version 7.0.3 [Stat-Ease, Inc. (2009), USA] is used. When compared with other similar adsorption studies, the novelty of using RSM in this work is in reducing the number of experiments, studying the effect of factor interactions and developing a statistical mathematical model equation, to identify optimum conditions where high uptake capacity is obtained for the removal of carbaryl using P. stratiotes biomass, to ensure high uptake capacity at low adsorbent dosage and to reduce time consumption with high carbaryl concentration.

**Materials and methods**

**Chemicals**

A fresh 0.03 % (w v⁻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 recrystallisation of a technical-grade sample supplied by Bayer. The solvent used for the extraction was Optimagrade methanol. Stock solutions were made in A.R. grade CaCl₂ and 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**

P. stratiotes, 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 a 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 any adhering dust that might be present in the material, then dried and stored in sterile, closed glass bottles and used as an adsorbent. The physicochemical properties of the adsorbent are summarized in Table 1. Characterization of the adsorbent has been previously reported (Das et al. 2013).

**Batch adsorption procedure**

The spectrophotometric determination of carbaryl was done by the method of Stansbury and Miskus (1964). 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 % (w v⁻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 color of the resulting solution was measured at 590 nm using UV–VIS spectrophotometer (Sytronics, Vis double beem Spectro 1203).

**Table 1 Physicochemical characteristics of adsorbent**

| Analysis                    | Value |
|-----------------------------|-------|
| pH slurry                   | 6.5   |
| pH zpc                      | 5.07  |
| Specific gravity            | 0.253 |
| Moisture content (%)        | 0.115 |
| Bulk density (g cm⁻³)       | 0.217 |
| Particle density (g cm⁻³)   | 0.385 |
| Conductivity (µS cm⁻¹)      | 43.63 |
| Surface area (m² g⁻¹)       | 27.95 |
| Na+ (mg L⁻¹)                | 108   |
| K+ (mg L⁻¹)                 | 570   |
The influence of pH (2.0–8.0), initial carbaryl concentration (5, 10, 15, 20 mg L⁻¹), contact time (1, 5, 10, 20, 30, 60 min) and adsorbent dose (0.05, 0.1, 0.5, 0.8 g per 100 ml) 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:

\[
q_e = \frac{(C_i - C_e)V}{m}
\]

where \(C_i\) and \(C_e\) are carbaryl concentrations (mg L⁻¹) before and after biosorption, respectively, \(V\) is the volume of adsorbate in liter and \(m\) is the weight of the adsorbent in grams. The percentage of removal of carbaryl ions was calculated from the following equation:

Removal (%) = \(\frac{(C_i - C_e)}{C_i}\) \(\times 100\).

The biosorption 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 biosorption of carbaryl on the walls of flasks were negligible.

**Results and discussion**

Central composite design analysis

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 to obtain the appropriate regression equations. To determine the adequacy of the models depicting the removal of carbaryl by \(P.\ stratiotes\) biomass, two different tests, i.e., the sequential model sum of squares and the model summary statistics, were conducted. The corresponding results are tabulated in Tables 3 and 4. The fitness of the model was determined by \(R^2\) and its statistical significance was evaluated by an \(F\) test (Peng et al. 2002).

### Table 2 Variables and levels considered for the adsorption of carbaryl onto \(P.\ stratiotes\) biomass

| Name (factor) | Units | Low | High |
|---------------|-------|-----|------|
| Initial concentration \((X_1)\) | ppm | 5 | 20 |
| pH \((X_2)\) | | 2 | 8 |
| Adsorbent dose \((X_3)\) | g | 0.5 | 4 |
| Time \((X_4)\) | min | 1 | 60 |

(3) predicting the response and checking the adequacy of the model (Sahu et al. 2009; Kumar et al. 2009). An empirical model was developed to correlate the response to the biosorption process and is based on second-order quadratic model for removal of carbaryl using \(P.\ stratiotes\) biomass as given by Eq. 4 to analyze the effect of parameter interactions

\[
Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \epsilon \quad (4)
\]

where \(Y\) is the response variable; \(\beta_0 \) is the intercept; \(\beta_i\), \(\beta_{ij}\) and \(\beta_{ii}\) are coefficients of the linear effect, double interactions; \(x_i, x_j\) are the independent variables or factors and \(\epsilon\) is the error (Table 2).

### Table 3 Model summary statistics for carbaryl adsorption onto \(P.\ stratiotes\) biomass

| Source | SD \(R^2\) | Adjusted \(R^2\) | Predicted PRESS | \(R^2\) |
|--------|-------------|-----------------|-----------------|---------|
| Linear | 13.65 0.7541 | 0.7148 0.6297 | 0.6304 7,013.88 | 7,003.88 |
| 2FI    | 11.72 0.8623 | 0.7898 0.6304 | 0.6304 7,000.06 | 7,000.06 |
| Quadratic | 2.94 0.9932 | 0.9868 0.9707 | 0.9707 554.85 | 554.85 |
| Cubic  | 2.33 0.9983 | 0.9917 0.9917 | 0.9917 137.65 | 137.65 |

(3)
Table 4 Adequacy of the model tested

| Source          | Sum of squares | df  | Mean square | F value | P value | Prob > F |
|-----------------|----------------|-----|-------------|---------|---------|----------|
| Mean vs total   | 82,603.52      | 1   | 82,603.52   |         |         |          |
| Linear vs mean  | 14,284.49      | 4   | 3,571.12    | 19.17   | < 0.0001|          |
| 2FI vs linear   | 2,049.20       | 6   | 341.53      | 2.49    | 0.0601  |          |
| Quadratic vs 2FI| 2,478.45       | 4   | 619.61      | 71.64   | < 0.0001|          |
| Cubic vs quadratic | 97.15      | 9   | 10.79       | 1.99    | 0.2080  |          |
| Residual        | 32.59          | 6   | 5.43        |         |         |          |
| Total           | 1.015E + 005   | 30  | 3,384.85    |         |         |          |

The higher the value of $R^2$, the better is the model. The results from the sequential model indicated that the 2FI model did not provide a good description of the experimental data. $R^2$ is a measure of the reduction amount in the variability of the response obtained by the independent factor variables in the model. Furthermore, the quadratic model had maximum “predicted $R^2$” and “adjusted $R^2$” values indicating 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 and a ratio $>4$ is desirable. 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.

The optimization of biosorption conditions

In the first step of the study, the effects of operating variables such as initial carbaryl concentration, pH, adsorbent dose and contact time on carbaryl capacity of *P. stratiotes* biomass were investigated using RSM according to CCD. In the second step, the main objective was to select the initial pH and time to achieve the optimal carbaryl biosorption capacity of the biosorbent. The batch runs were conducted in CCD-designed experiments to visualize the effects of independent factors on responses and the results along with the experimental conditions. Figure 3 shows the response surface plots described by the regression model and drawn to illustrate relationships between factors on carbaryl biosorption capacity on *P. stratiotes* biomass under the sets of conditions and treatment levels tested (Table 3). The experimental results were evaluated and the approximating function of carbaryl biosorption capacity of biosorbent was obtained in Eq. (5) by utilizing Design Expert software. Equation (5) could be used in predicting the response for the given values of initial carbaryl concentration, pH, adsorbent dose and time. Approximating equation of the fitted response surface was also checked for the model adequacy using analysis of variance (ANOVA) results and the diagnostic plots of Figs. 1, 2, 3 and 4. The experimental and predicted values of removal of carbaryl are given in Table 4.

\[
Y = + 65.15 - 1.57 \times X_1 - 23.73 \times X_2 + 13.95 \times X_3 \\
- 2.26 \times X_4 + 2.45 \times X_1 \times X_2 + 2.55 \times X_1 \times X_3 - 1.40 \\
\times X_1 \times X_4 - 9.20 \times X_2 \times X_3 + 3.10 \times X_2 \times X_4 \\
+ 4.40 \times X_3 \times X_4 - 3.76 \times X_1^2 - 1.43 \times X_2^2 - 10.52 \\
\times X_3^2 - 2.08 \times X_4^2. 
\]  

(5)

In Eq. (5), $Y$ is the response of carbaryl biosorption capacity of biosorbent at the end of biosorption time. $X_1$, $X_2$, $X_3$, and $X_4$ correspond to independent variables of initial carbaryl concentration, pH, adsorbent dose and contact time, respectively. ANOVA results of this quadratic model presented in Table 5 indicate that it could be used to navigate the design space. It is probably the most useful technique in the field of statistical inference. As can be seen in Table 5, the model $F$ value for carbaryl biosorption capacity of biosorbent was evaluated as 155.36. This value indicated that the quadratic model was significant. The values of $R^2$ pred. (0.9707) and $R^2$ adj. (0.9868) for carbaryl biosorption capacity of *P. stratiotes* biomass well satisfied the model. “Adequate precision” ratio of 40.483 indicates an adequate signal for the model to be used to navigate the design space. The $P$ values $>$0.0500 indicate that the model terms are significant, whereas the values $>$0.1000 are not significant.

By constructing a normal probability plot of the residuals, a check was made for the normality assumption, as given in Fig. 1. The residuals show how well the model satisfies the assumptions of the ANOVA where the studentized residuals measure the number of standard deviations separating the actual and predicted values (Montgomery 1996; Myers 2002; Korbahi and Rauf 2008). The normality assumption was satisfied as the residual plot approximated along a straight line (Table 6).

The actual and the predicted carbaryl biosorption capacity of *P. stratiotes* biomass is shown in Fig. 2.
actual values are the measured response data for a particular run, and the predicted values are evaluated using the approximating functions generated for the models (Montgomery 1996; Myers 2002; Korbahti and Rauf 2008).

Figure 3 shows Cook’s distance plot; according to this plot there were no points that were potentially powerful due to their location in the factor. So we conclude that the empirical model is adequate to describe the carbaryl biosorption capacity on *P. stratiotes* biomass.

Optimal conditions for the carbaryl biosorption process

Figure 5 shows the pH and biomass dose interaction that had the most significant effect on carbaryl removal. At pH 2.01 and biomass dose of 0.72 g, the model-predicted carbaryl removal efficiency by biomass is close to 100%. At these predicted optimal conditions, *P. stratiotes* biomass

- **Fig. 1** Normal plots of residuals vs internally studentized residuals
- **Fig. 2** Comparison between the actual values and the predicted values of RSM model for adsorption of carbaryl
- **Fig. 3** Plot of Cook’s distance vs run number
- **Fig. 4** Plot of leverage vs run
- **Fig. 5** pH and biomass dose interaction for carbaryl removal
achieved a carbaryl biosorption capacity of 3.1 mg g\(^{-1}\) (initial concentration 15.57 mg L\(^{-1}\) and contact time 30 min). Figure 5 shows the removal of carbaryl as a function of biomass dose. Increase in biomass dose increased the percentage removal of carbaryl. The optimal biomass dose is 0.72 g. Nevertheless, carbaryl removal decrease at biomass dose higher than the optimal value may be due to biomass agglomeration. A similar effect was reported on carbaryl adsorption by soils (Chattoraj et al. 2013) and lead biosorption on Aspergillus terreus biomass (Cerino-Cordova et al. 2011).

**Adsorption isotherms**

Various isotherm equations like Freundlich, Langmuir and Temkin were used to describe the equilibrium characteristics of biosorption of carbaryl onto P. stratiotes biomass. The linearized form of isotherms (Babu and Gupta 2008) and their constants are given in Table 7. The experimental data obtained at equilibrium was fitted satisfactorily with Freundlich isotherm and is shown in Fig. 6. The value of the Freundlich constant, \(K_F\) represents the degree of adsorption. The magnitude of \(n\) gives a measure of favorability of biosorption. Values of \(n\) between 1 and 10 represent a favorable biosorption process. For the present study, the value of \(n\) also presents the same trend (Table 7) representing a beneficial biosorption process. The Freundlich isotherm reveals the multilayer adsorption.

**Adsorption kinetics**

The pseudo-first-order and pseudo-second-order kinetic models were tested to investigate the rate of biosorption of carbaryl on P. stratiotes biomass. The linearized form of biosorption kinetics (Guo et al. 2002) and their constants are presented in Table 8. The plot of \(t/q\) versus \(t\) shows a linear relationship which confirmed that the biosorption of carbaryl on P. stratiotes biomass followed the pseudo-second-order reaction and is shown in Fig. 7. The values of
and $k_2$ can be determined from the slope and intercept of the plot. It is clear that the pseudo-second-order kinetic model showed excellent linearity with high correlation coefficient ($R^2 > 0.99$) at all the studied concentrations in comparison to the first-order kinetic model (Table 8). In addition, the calculated $q_s$ values also agree with the experimental data in the case of pseudo-second-order kinetic model.

**Table 7** Summary of parameters for various isotherm models

| Isotherm model     | Equation                                                                 | Constants                        |
|--------------------|--------------------------------------------------------------------------|----------------------------------|
| Langmuir isotherm  | $\frac{C_f}{q_s} = \frac{C_f}{q_m} + \frac{1}{K_L q_m}$                | $K_L = 11.379 \text{ L mg}^{-1}$, $R^2 = 0.993$ |
| Freundlich isotherm| $\log q_s = \log k_f + \left(\frac{n}{2}\right) \log c_f$               | $n = 2.1$, $K = 1.63 \text{ mg g}^{-1}$, $R^2 = 0.999$ |
| Temkin isotherm    | $q_s = B\ln A + B\ln c_f$                                               | $B = 0.227$, $A = 3.74$, $R^2 = 0.949$ |

$q_s$ (mg g$^{-1}$) and $c_f$ (mg L$^{-1}$) are the solid phase concentration and the liquid phase concentration of adsorbate at equilibrium, respectively. $q_m$ (mg g$^{-1}$) is the maximum adsorption capacity and $K_L$ (L mg$^{-1}$) and $K_F$ (mg g$^{-1}$)(L mg$^{-1}$) are the adsorption equilibrium constant. $n$ is the heterogeneity factor. $RT/bT = B$ where $T$ is the temperature (K) and $R$ is the ideal gas constant (8.314 J mol$^{-1}$ K$^{-1}$) and $A$ and $bT$ are constants.
To assess the reusability of carbaryl-loaded *P. stratiotes* biomass, desorption experiments were carried out. The effect of the strength of the desorbing solution (NaOH) on the recovery of carbaryl is shown in Fig. 8. It is evident from the above figure that when the strength of the desorbing solution increased from 0.2 to 2.5 M, carbaryl desorption percentage increased from 19 to 91%. Thus a significant amount of carbaryl is being desorbed, which shows that the *P. stratiotes* biomass can be effectively reused after desorption.

Comparison of the present study with other adsorbents

Comparison of adsorption capacity (3.1 mg g\(^{-1}\)) observed in this study with other adsorption capacities in the literature is given in Table 9.

Desorption studies

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Conclusions

Carbaryl removal from aqueous solutions by *P. stratiotes* biomass was studied with a CCD. According to the
ANOVA analysis, carbaryl removal is highly affected by biomass dose, pH and the interactions between pH with the other factors (biomass dose, initial concentration and time). The hierarchical quadratic model represents adequately the response surface space based on the adjusted determination coefficient ($R^2$ adj = 0.9868) and the adequate precision ratio (40.483). By using this model, at the optimal conditions (pH 2.1, 0.72 g of biomass, 30 min contact time and 15.57 mg L$^{-1}$ of carbaryl concentration), the predicted removal efficiency achieved near 100% of carbaryl from aqueous solutions when using P. stratiotes biomass. Finally, the reported results in this research demonstrate the feasibility of employing P. stratiotes biomass as a low-cost biosorbent for carbaryl removal.

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