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ORIGINAL ARTICLE

Removal of carbaryl insecticide from aqueous solution using eggshell powder: a modeling study

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Abstract
A batch study was done for exploring the performance of eggshell powder (EGP) for adsorptive removal of carbaryl from aqueous solution. In the experiment, the operating factors were initial carbaryl concentration (5–20 mg L^{-1}), solution pH (2–10), adsorbent dose (0.01–0.1 g/100 ml) and contact time (10–60 min). For optimization, evaluation of the effects and interactions of the operating factors response surface modeling was applied and the influence of the factors was checked through a two-level four factor Box–Behnken design (BBD) model. The predicted data had shown good agreement ($R^2 = 0.9985$) with experimental data. Furthermore, the adsorption data were best fitted with Freundlich isotherm and pseudo-second-order kinetics. Thermodynamic parameters revealed that the adsorption of process was spontaneous and endothermic. Finally it can be concluded that the EGP can be used as an alternative adsorbent for the removal of carbaryl from aqueous medium.

Keywords Carbaryl · EGP · Adsorption · Batch · RSM · Optimization

Introduction

Pollution of water is a major problem in today's world, and extensive application of pesticides in agriculture and domestic practice in daily basis for controlling pest is one of the causes of such problem. Many of the pesticides are carcinogenic and non-biodegradable (Al-Zaben and Mekhamer 2017) that is why they are known as strong pollutants. Indeed, recent researchers reported that pesticide concentrations in waste and surface water and groundwater are higher than pollution threshold limit (Yadamari et al. 2011). Developing countries are suffering mostly due to contamination of pesticides in groundwater as it is used for drinking purpose (Singh et al. 2005). As a result, the frequent detection of pesticides in surface as well as in groundwater has increased interest in finding the proper technique for the removal of pesticides from aqueous medium either completely or by minimizing their concentrations down to the permissible level (US; EPA 2003).

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The adsorption technique has been used successfully for controlling water pollution due to several contaminations like heavy metals (Das et al. 2012; Roy and Mondal 2015, 2017), dyes (Sadhukhan et al. 2014, 2016) and organic pollutants and pesticides (Ouardi et al. 2013; Chattoraj et al. 2014a, 2016). Among the various processes for removal of pesticides from water samples, adsorption processes are easily operated and have shown high removal efficiency, hence low cost.

The adsorption technology also can remove pesticides completely even from very dilute solutions (Salman et al. 2011).

Among all types of conventional and non-conventional adsorbents, renewable and low-cost materials have exerted to a growing exploitation to investigate the suitability of these in the water pollution control. However, a limited number of adsorbents have been used to remove pesticides from aqueous environment (Traub-Eberhard et al. 1995; Sudhakar and Dikshit 1999; Akhtar et al. 2009; Boudesocque et al. 2008; Bakouri et al. 2009; Singh 2009; Chattoraj et al. 2014a, b, 2016).

Among the numerous agrochemicals in use today, the insecticide carbaryl (1-naphthyl methyl carbamate) is one of the most widely used to protect cereals, fruits, vegetables and other crops against insect pests (Chattoraj et al. 2014a).

It is classified as a human carcinogenic by the US Environmental Protection Agency. Carbaryl moderately binds to soil and has the potential to leach into groundwater (Mondal et al. 2013). Carbaryl is reported as the second most frequently found insecticide in groundwater (EPA 2003). Therefore, carbaryl is dangerous to both humans and to other animals (Gunasekara et al. 2008).

However, limited works have been found for removal of carbaryl insecticide by suitable adsorbents. Eggshell is easily available and biodegradable hence it is cost-effective and ecofriendly. That is why in this study eggshell powder (EGP) has been utilized as adsorbent to remove carbaryl insecticide from aqueous medium. In recent years, EGP has drawn much attention to the researchers due to its easy availability.

Previously, the removal of malathion (Elwakeel and Yousif 2010), fluoride (Bhaumik et al. 2012) and dyes (Pramanpol and Nitayapat 2006; Ali Zulfikar and Setiyanto 2013; Chowdhury et al. 2013) from aqueous solution using the eggshell powder (EGP) had been investigated, but no such work has been reported on the removal of carbaryl by EGP.

In view of these above facts, the present study deals with a series of adsorption experiments in order to investigate the possibility for application of EGP for removal of carbaryl from aqueous environment. For optimization abilities, the adsorption experiments have been statistically modeled using Box–Behnken design (BBD). The models were also applied to study the individuals as well as the dual effect of different variables. Finally, an overall study for the easily available and ecofriendly solution of carbaryl pesticide pollution has been done that can be implemented in future.

Materials and methods

Adsorbent collection and preparation

Eggshells were collected from local market of Burdwan, West Bengal, India. Then it was washed several times with double-distilled water and then dried in a hot air oven over 80 °C for a day. The dried eggshells were grinded and sieved well in fraction of 200 µm mesh size particles that were preserved in different sterilized containers for further use as an adsorbent.

Characterization of adsorbent

The physicochemical properties of eggshell powder (ash content, bulk density, particle density, moisture, pH, pH_{zpc}, porosity, surface area, moisture content and carbon, hydrogen and nitrogen) were checked. In this study, surface area analyzer (Model: Nova-2200e, Quantachrome corporation, Boynton Beach, USA) was operated to analyze the specific surface area of the EGP.

Batch adsorption procedure

The Stansbury and Miskus method was followed for the spectrophotometric determination of carbaryl samples. The collected samples from the flasks were used for analyzing the residual carbaryl concentration in the solution at different time periods. The equilibrium concentration (q_e) of the adsorbent was calculated by the given equation.

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

Where C_i and C_e are carbaryl concentrations (mg L^{-1}) before and after adsorption, respectively, V is the volume of adsorbate in liter and m is the weight of the adsorbent in grams. The efficiency of the adsorption process was represented as percentage of removal of carbaryl using the following relation.

$$\text{Percentage removal} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

Experimental design

The optimization of carbaryl adsorption onto EGP using response surface methodology (RSM) via Box–Behnken design (BBD) in Design Expert software version 7.1.6 (Stat-Ease Inc 2009) was carried out by four independent factors (initial carbaryl concentration, pH of the solution, adsorbent dose and contact time) that influenced carbaryl adsorption process onto various natural adsorbents (Chattoraj et al. 2014b, 2016). The percentage removal of carbaryl was the output (response). The detailed BBD process was described in our previously published papers (Chattoraj et al. 2013, 2014b). The effect of interaction between different operating parameters was explained by perturbation and response surface 3D plots. The optimum values of the selected variables were found from the ramp desirability plots (Bhaumik et al. 2013).

Desorption study

Desorption of carbaryl-loaded EGP by following our previously established and published method (Chattoraj et al. 2014a). Moreover, the desorption percentage of carbaryl was calculated by the following equation.

$$\text{Desorption}\,(\%) = \frac{(C_a - C_d)}{C_a} \times 100 \quad (3)$$

Table 1 The physicochemical characteristics of EGP

Parameters	Value
Surface area ($m^2\ g^{-1}$)	98.3
pH_{ZPC}	6.51
Conductivity ($\mu S\ cm^{-1}$)	1.21
Specific gravity	0.798
Moisture content (%)	2.1
Bulk density ($g\ cm^{-3}$)	0.83
Particle density ($g\ cm^{-3}$)	1.3
Porosity (%)	36.15

Table 2 Variables and levels considered for the adsorption of carbaryl onto EGP

Name (factor)	Units	Low	High
Initial concentration (A)	$mg\ L^{-1}$	5	20
pH (B)		2	10
Adsorbent dose (C)	g	0.01	0.1
Contact time (D)	min	10	60

where C_a is adsorbed carbaryl concentration and C_d is concentration of carbaryl after desorption.

Results and discussion

Characterization of adsorbent

The physicochemical properties of the adsorbent are determined and presented in Table 1.

Statistical analysis

Box–Behnken design analysis

The scheme of experiments carried out in this study is presented in Table 2. Regression analysis was performed to fit the response functions, i.e., percentage removal of carbaryl. The functions of the model were initial concentration (A), pH (B), adsorbent dose (C) and contact time (D).

The ANOVA analysis for the response is shown in Table 3. The model *F* value of 120.9 indicates that the model terms are statistically significant. The nonsignificant values of lack of fit showed that developed model is fitted well (Roy et al. 2015). The coefficient of variation was 1.45 and standard deviation was 1.13 (Table 3). Adequacy of precision value of 37.74 indicates an adequate signal (Roy et al. 2015). The value of the standard error design was 0.6422. So, the present model can be applied to plot a pathway to the design space (Fig. 1). Again the comparison between experimental (actual) and predicted values of percentage carbaryl adsorption capacity is plotted in Fig. 2. The values of R^2 and adjusted R^2 have showed a high correlation between actual and predicted values.

Effect of factors and response surface estimation

Response surface methodology (RSM) was used to estimate the effect of four process variables on the removal of carbaryl by adsorption. Perturbation and 3D surface plots were drawn by using RSM to investigate the effect of all the factors on the responses. The inferences so obtained are discussed below.

Effect of main factors

The individual effect of numerical factors such as the initial concentration (A), pH (B), adsorbent dose (C) and contact time (D) was found by perturbation plots (Fig. 3). Perturbation plot helps to compare the effect of all the

Table 3 Analysis of variance (ANOVA) for adsorption of carbaryl onto EGP

Source	Sum of squares	*DF*	Mean square	*F* value	*p* value	Prob > *F*
Model	2175.2	14	155.4	120.9	< 0.0001	Significant
A-Initial concentration	48.5	1	48.5	37.7	< 0.0001	
B-pH	528.1	1	528.1	410.9	< 0.0001	
C-Adsorbent dose	6.4	1	6.4	5.0	0.0428	
D-Contact time	1.0	1	1.0	0.7	0.4016	
Lack of fit	15.0	10	1.5	2.0	0.2633	Not significant
SD	1.133783		*R*-squared		0.991794	
Mean	78.11485		Adj *R*-squared		0.983589	
C.V. (%)	1.451431		Pred *R*-squared		0.971895	
PRESS	61.63882		Adeq precision		37.74712	

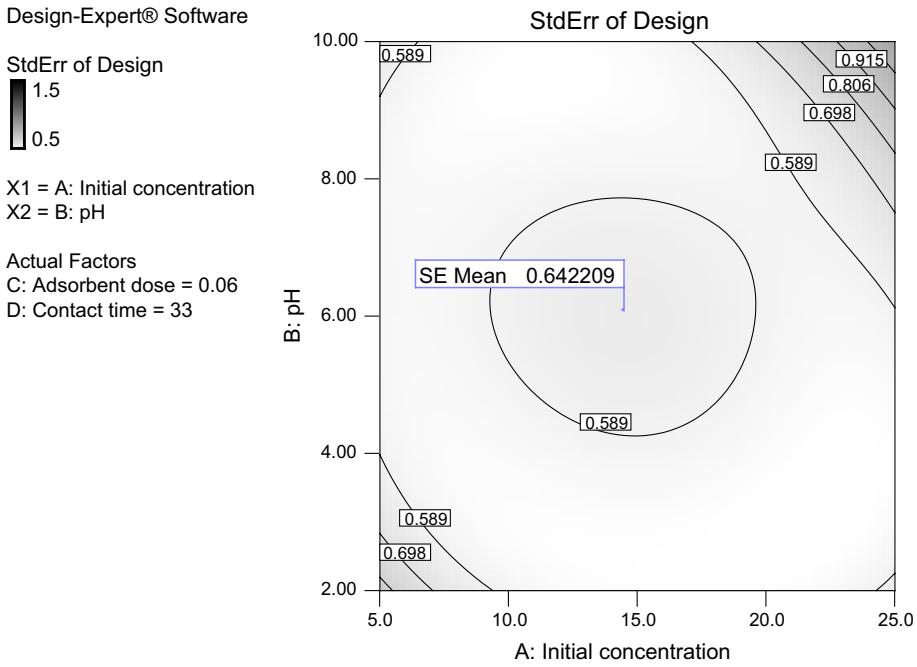

Fig. 1 Standard error of design of carbaryl adsorption onto EGP

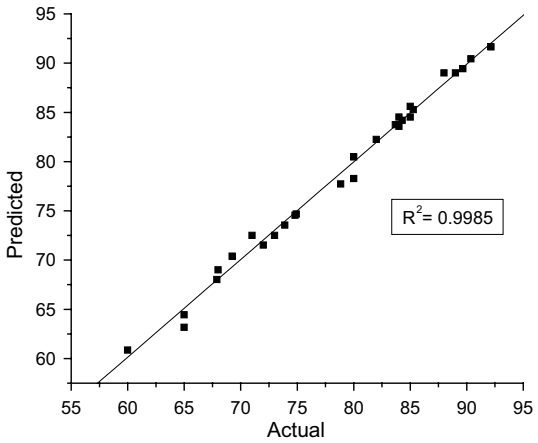

Fig. 2 Comparison of the experimental data (line) with those predicted data (symbols) of carbaryl adsorption onto EGP

fact at a particular point in the design space. In this plot, the response (percentage removal) is plotted by altering only one factor and the other factors were constant (Gottipati and Mishra 2012). The steep curvature of a factor explains that the response is sensitive to the factor and a relatively flat line shows insensitivity to change in that particular factor (Anderson and Whitcomb 2005). It is clearly stated from Fig. 3 that the increasing order of influence on removal of carbaryl is contact time < adsorbent dose < initial concentration < pH.

Effect of interactions

The interactions of the operating factors also have a significant effect on the removal percentage of carbaryl. The 3D plots are presented in Fig. 4. The 3D plot is three-dimensional representation of responses at different conditions. The most significant information about individual effect of various parameters as well as their interaction is explained by the Pareto chart (Fig. 5). The length of the Pareto chart is relative to the value of regression coefficient. From the chart, it is clear that the quadratic term of contact time (D*D) indicates that this variable is exceptional during the process and its behavior illustrates the maximum effect that changes the slope for its quadratic behavior.

Optimization by response surface modeling

Keeping in mind about the economically viable condition, to calculate maximum percentage removal, the conditions of the operating factors were selected as 'maximum' for the initial concentration 'in range' for pH, 'minimum' for adsorbent dose and 'in range' for contact time, respectively. The percentage removal of carbaryl by EGP at optimum conditions (initial concentration—24.40 mg L^{-1}, pH—2, adsorbent dose—0.01 g and contact time—5 min) is 92.2%. The response surface plots at optimum conditions are shown in Fig. 4, considering the key factors (observed from perturbation plots, Fig. 3). A well-known multiple response method, i.e., desirability (D) function, was used to find the optimum conditions for the removal

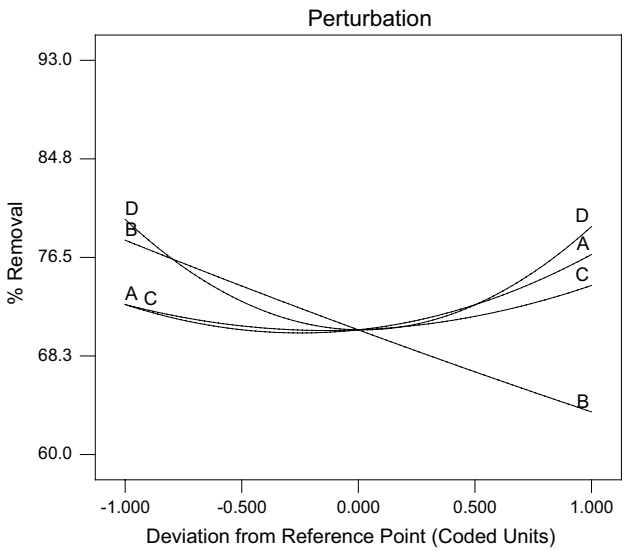

Fig. 3 Perturbation plot of carbaryl adsorption onto EGP

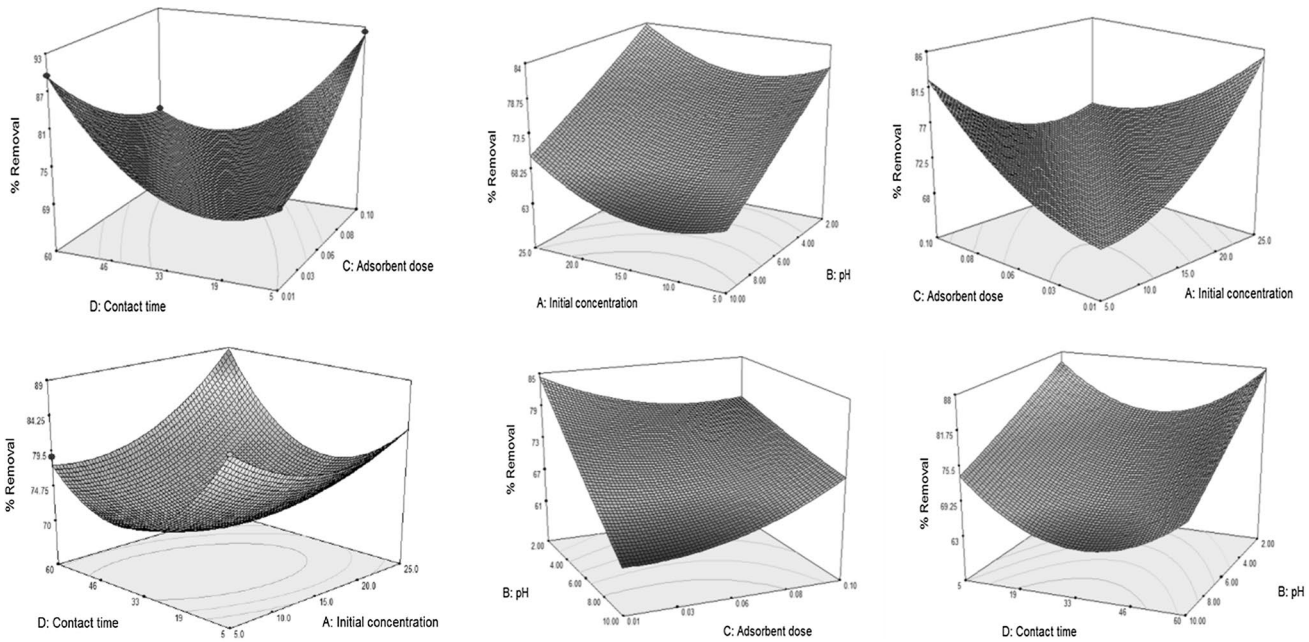

Fig. 4 Response surface 3D plots showing the effect of independent variables on carbaryl adsorption onto EGP

of carbaryl using EGP by targeting the process parameters within the various ranges (Table 2).

Experiments for validation of models

The results obtained after optimization were checked experimentally which resulted 88% carbaryl removal by EGP. Using these values, the maximum adsorption capacity was calculated (using Eq. 1) and found to be 105.6 mg g^{-1}.

Adsorption isotherms

Freundlich and Langmuir isotherm equations were used to describe the equilibrium characteristics of adsorption of carbaryl onto EGP. The isotherms constants calculated are provided in Table 4. Freundlich model exhibited a slightly better fit to the adsorption data than the Langmuir model (Table 4).

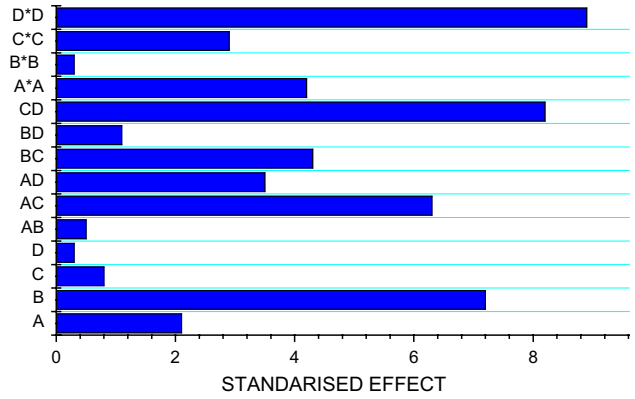

Fig. 5 Pareto chart

Adsorption kinetics

The kinetic study for adsorption of carbaryl onto EGP was performed. Different kinetic models and their constants at different temperatures are presented in Table 5. The pseudo-second-order kinetic model showed excellent linearity with high correlation coefficient ($R^2 > 0.99$).

Thermodynamics study

Different thermodynamic parameters such as change in free energy (ΔG°), change in enthalpy (ΔH°) and change in entropy (ΔS°) were calculated by considering the equilibrium constants at different temperatures. The change in free

Table 4 Summary of parameters for various isotherm models for adsorption of carbaryl onto EGP

Isotherm model	Equation		Constants at different temperature		
			293 K	303 K	313 K
Langmuir isotherm	$\frac{C_f}{q_s} = \frac{C_f}{q_m} + \frac{1}{k_L q_m}$	K_L (L mg^{-1})	0.036	0.09	0.102
		R^2	0.807	0.849	0.871
Freundlich isotherm	$\log q_s = \log k_f + \left(\frac{1}{n}\right) \log c_f$	$1/n$	0.816	0.867	0.967
		K_F (mg g^{-1}) L mg^{-1})$^{1/n}$	1.09	1.07	0.962
		R^2	0.993	0.991	0.987

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})$^{1/n}$ are the adsorption equilibrium constant. n is the heterogeneity factor

Table 5 Summary of parameters for various kinetic models for adsorption of carbaryl onto EGP

Kinetic model	Equation		Constants at different temperature		
			293 K	303 K	313 K
Pseudo-first order	$\log(q_s - q_t) = \log q_s - \frac{k_1}{2.303} t$	R^2	0.978	0.971	0.947
		K_1 (min^{-1})	0.011	0.024	0.011
		R^2	0.993	0.994	0.990
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_s^2} + \frac{t}{q_s}$	K_2 (mg^{-1} min^{-1})	0.0015	0.0019	0.012
		q_s (mg g^{-1})	111.11	100	83.3

q_t and q_s are the amount of carbaryl adsorbed (mg g^{-1}) at time t and at equilibrium and K_1 (min^{-1}) is the Lagergren rate constant of first-order adsorption and K_2 (mg^{-1} min^{-1}) is the second-order adsorption rate constant

Table 6 Thermodynamic parameters for adsorption of carbaryl onto EGP

Equation	ΔG° (KJ mol^{-1})			ΔH° (KJ mol^{-1})	ΔS° (KJ mol^{-1} K^{-1})
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$	293 K	303 K	313 K	20.83	0.097
	−4.22	−5.54	−7.27		

energy ($\Delta G°$) for adsorption process was calculated by using the equations that are presented in Table 6.

The value of heat of adsorption ($\Delta H°$) and entropy change ($\Delta S°$) was calculated from the slope and intercept of the plot $\Delta G°$ versus T. The free energy change ($\Delta G°$) ensured that the adsorption process is spontaneous and thermodynamically favorable under the experimental conditions. The decrease in $\Delta G°$ value with increasing temperature strongly suggests of significant adsorption. Positive value of $\Delta H°$ means the adsorption process was endothermic (Mondal et al. 2017; Wang et al. 2018) and positive value $\Delta S°$ displayed the affinity of carbaryl and increased randomness at the solid–solution interfaces toward adsorption onto eggshell in aqueous solution (Salman et al. 2011). Moreover, the desirability plot clearly indiacate the optimized parameters such as initial concentration, pH, adsorbent dose and contact time are 24.4 mg L^{-1}, 2.0, 0.01 g/50 mL, and 5.0 min, respectively for 92.2% removal (Fig. 6).

Desorption study

Finally adsorption study was also performed for the purpose of reuse of the eggshell powder (EGP) and to minimize further pollution. The desorption percentage of carbaryl from EGP is presented in Fig. 7, which implies desorption percentage was high, so the adsorbent can be again after desorption.

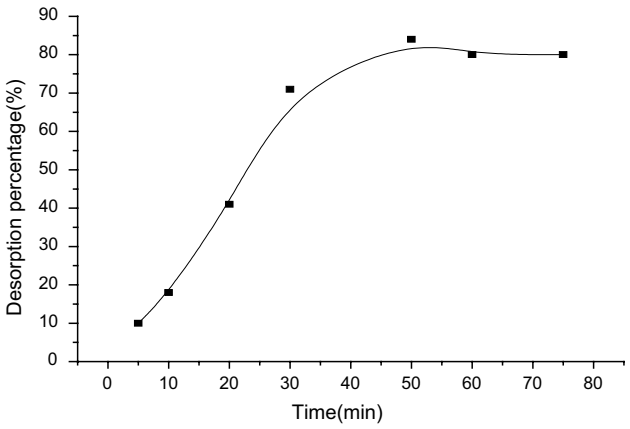

Fig. 7 Effect of time on carbaryl desorption

Conclusion

The objective of the study was to find the effectiveness and optimum conditions to remove carbaryl from aqueous solutions using EGP by adsorption technology. Response surface methodology (RSM) based on four variables Box–Behnken design was used to estimate the effect of different factors on the removal of carbaryl. The model was developed to correlate different variables to the responses by using Design Expert software. After optimization, the major findings are initial concentration—24.40 mg L^{-1}, pH—2, adsorbent dose—0.1 g, contact time—5 min and percentage removal is 92.2. The equilibrium data were best matched with Freundlich and pseudo-second-order kinetics. Thermodynamic data conclude that the adsorption process was spontaneous and endothermic. Subsequently a validation experiment was conducted at optimum conditions, which suggests that developed models well fitted with the experimental results. Finally, it is concluded that EGP can be used as an inexpensive, ecofriendly and effective bioadsorbent as there is no requirement of any

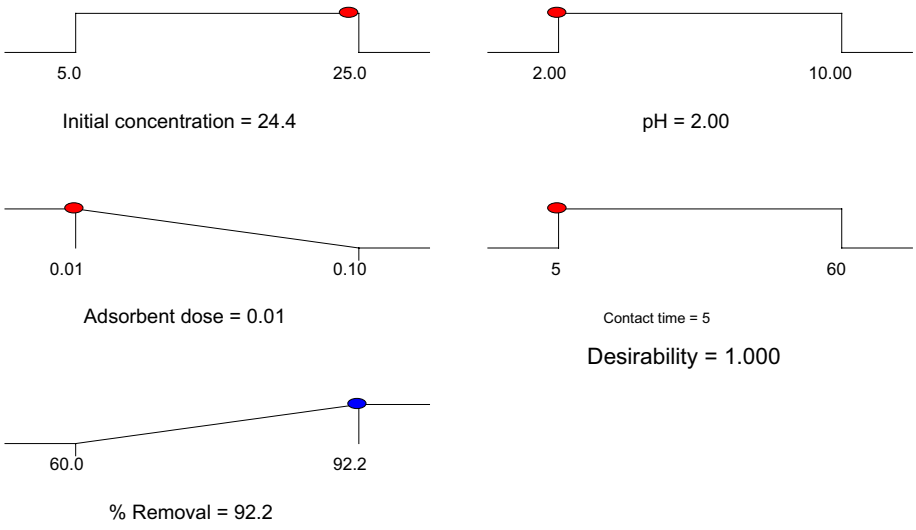

Fig. 6 Desirability (RAMP plot) for numerical optimization of four selected goals

treatment or modification for removal of carbaryl from aqueous solutions.

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