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Application of statistical design of experiment with desirability function for the removal of organophosphorus pesticide from aqueous solution by low-cost material

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ABSTRACT

This paper deals with the multiple response optimization for the removal of organophosphorus pesticide quinalphos [QP: *O,O-diethyl O-2-quinoxalinyl phosphorothioate*] from the aqueous solution onto low-cost material and tried to overcome the drawbacks of univariate optimization. Used tea leaves were used as low-cost adsorbent and batch equilibration method was followed for this study. A Box–Behnken design was used to develop response model and desirability function was then used for simultaneous optimization of all affecting parameters in order to achieve the highest removal% of quinalphos. The optimum conditions of factors predicted for quinalphos removal% were found to be: pH 8.83, concentration 7 mg L^{-1} and dose 0.40 g. Under these conditions, maximum removal% of quinalphos was obtained 96.31%. Considering the above optimum conditions, the adsorption isotherms were developed and provided adsorption capacity of 196.07 $\mu g\, g^{-1}$ by using Langmuir equation, indicating that used tea leaves may be applied as a low-cost material for pesticides removal from aqueous matrices.

1. Introduction

The usage of organic pesticides is increasing day by day with increasing world population, especially organophosphorus pesticides (OPPs) due to their relatively low persistence in the environment and by the transfer from highly persistent organochlorine pesticides. The toxicity effects of OPPs were well documented by several workers [1–3]. Therefore, these compounds are potential hazards to human health as well as ecosystems by surface and ground water contamination.

The OPPs are in general categorized into four subgroups according to molecular structures: phosphates, phosphorothioates, phosphorodithioates, and phosphorothiolates [4]. Among them, phosphorothioates group, in which phosphorus atom (P) is bound to three oxygens and one sulfur (the double bond), are used extensively all over the world. Quinalphos (QP; *O,O-diethyl, O-2 quinoxalinyl phosphorothioate*) is a phosphorothioate group based insecticide and acaricide [5]. It is moderately hazardous according to WHO (World Health Organization) hazardous classification [6] and frequently used for control of pests over certain crops like cotton, groundnuts, rice, tea, coffee, soybeans, etc. [5,7,8]. Quinalphos is very vulnerable to hydrolysis and photodegradation [9]. Photolytic degradation of quinalphos in water and soils has been studied by Goncalves et al. [10]. Quinalphos is an acetylcholinesterase (enzyme) inhibition OPP, the enzyme that terminates the action of acetylcholine neurotransmitter, which is released by nerve stimulation, on postsynaptic cholinergic receptors in the nervous system. The exposure to the excess acetylcholine causes stable acetylcholine receptor triggering, resulting in malfunction of the autonomic, somatic and central nervous systems [1]. A study by Srivastava et al. [11] reported that the toxicity of quinalphos on 74 workers during its manufacture, revealed alterations in central nervous system (CNS) function that were manifested as memory, learning, vigilance, and motor deficits, despite having normal acetylcholinesterase activity. Many studies have also been documented about the toxicity of quinalphos and its metabolites (2-hydroxyquinoxaline) on plants and soil microorganisms [12], humans, laboratory animals and several wildlife species including aquatic and terrestrial [13–17]. Therefore, Quinalphos was selected for the present study due to its low solubility, toxicity and its extensive use.

Adsorption is one of the most recognized methods used in the removal of such hazardous substances from polluted water. For this, activated carbon is the most widely used material for the removal of organic pollutants [18,19] that is very costly and involved sophisticated management. So it is an urgent need to search low-cost materials for the removal of pesticides. In recent times, many studies have reported about the application of various low-cost materials

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of diverse origin for the removal of pesticides from aqueous solution. These include watermelon peels [20], rice husk [21], etc. In this study, used tea leaves were used as a low-cost material for the removal of OPP quinalphos. Recently, used tea leaves were successfully used by the different researchers for basic dye removal [22,23]. Malkoc and Nuhoglo [24] also found that the tea factory waste is very effective and environmental friendly biosorbent for the removal of Nikel(II). According to our knowledge, no work has been done for the removal of pesticides from aqueous solutions onto used tea leaves with statistical design of experiments.

It is factual that only the use of low-cost materials cannot ensure the desired output of removal efficiency if the processes or input parameters are not well optimized, organized and efficient. The conventional one factor at a time approach to optimization is time-consuming, non-feasible and inept of getting the true optimum condition due to the lack of interactions among the factors. For this reason, Response Surface Methodology (RSM) is now days a widely used statistical tool for process optimization through a relatively smaller number of systematic experiments that can reduce time, cost and resources. In the present study, RSM with Box–Behnken design was successfully employed to verify the various interactions of responsible factors for the removal of quinalphos. Besides, the desirability function for optimization of adsorption process was employed in order to develop an efficient method for achieving maximum removal% of quinalphos from the aqueous solutions by combination of all optimized input factors and, an optimized response model was proposed. Finally, removal capacity of used tea leaves was determined by considering all optimized factors.

2. Materials and methods

2.1. Preparation and characterization of used tea leaves

The manufactured used tea leaves (tea bags) were collected from local cafeteria. Leaves were washed thoroughly by normal water and afterwards with double distilled water for the removal of pigments and impurities. After drying 3 days in room temperature, leaves were placed in the oven at 80 °C for removing of extra moisture and before stored for further use, tea leaves were sieved in order to find particle size in the range of 0.710–1.00 mm according to US standard testing sieves. No other physical and chemical treatments were performed before experiments. Precautions were taken to avoid contamination during drying and storage.

In order to determine the existence of active functional groups on used tea leaves, FTIR (Fourier transform infrared spectroscopy) spectrometer (Shimadzu-8400, Japan) was used at room temperature with pellet (pressed-disk) technique. The spectral range was used from 4000 to 400 cm^{-1}. Scanning electron microscopy (SEM) pictures of used tea leaves were performed on a Jeol JSM 5600 at 20 kV. The zeta potential was measured seven times for a single pH to obtain an average reading by Zeta Meter System 3.0 (Zeta-Meter. Inc., USA). Between the samples, the cell was flushed with deionized water.

2.2. Chemical

The pesticide quinalphos (QP, 98.9% purity) was residue analysis grade, purchased from Riedel-de Haen (Germany). The solubility of QP in water is 17.8 mg L^{-1} and its octanol–water coefficient ($\log K_{ow}$) is 4.4 [6]. However, due to its non-ionizable functional group, removal% of QP may not vary depending on solution pH. All other chemicals, solvents and salts were of the highest purity level supplied by Merck pro-analysis or Lab Scan, Pestiscan.

Table 1
Design matrix and results for quinalphos removal% onto used tea leaves.

Run	pH	Initial concentration (mg L^{-1})	Adsorbent dose (g)	Removal%
1	0	0	0	72.52
2	+1	0	+1	89.83
3	0	0	0	72.30
4	0	−1	+1	74.09
5	+1	−1	0	64.49
6	0	+1	−1	48.00
7	+1	+1	0	80.81
8	−1	−1	0	69.55
9	+1	0	−1	42.11
10	−1	+1	0	69.00
11	0	−1	−1	41.00
12	0	+1	+1	86.67
13	−1	0	+1	81.17
14	−1	0	−1	47.12
15	0	0	0	71.03

	Range and level		
	Low (−1)	Middle (0)	High (+1)
pH	5	7	9
Initial concentration	1	4	7
Adsorbent dose	0.2	0.3	0.4

2.3. Experimental procedures

Batch equilibration method was followed for the optimization process according to the Box–Behnken design matrix shown in Table 1. For this, 10 mL of pesticides aqueous solution with different pH, initial concentration and adsorbent dose were placed in 15 mL polypropylene centrifuge tube. The mixture was shaken at fixed contact time (300 min) that obtained from kinetic study. At the end of the shaking, the samples were centrifuged at 4200 rpm for 5 min and the supernatant was collected with a pipette for the determination of QP concentration.

Five milliliters of each aqueous phase were extracted twice with 2.5 mL *n*-hexane using a vortex for 1 min. In the combined extracts a small amount of anhydrous Na_2SO_4 was added to remove moisture content. To evaluate interference due to used tea leaves, an adsorption test without pesticide was carried out as described above. Besides, blank samples (no adsorbent added) indicated that losses due to adsorption onto polypropylene centrifuge tubes were negligible.

The removal% was calculated as

$$\text{Removal}\,\% = 100 \times \frac{(C_0 - C_e)}{C_0} \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of pesticide in the solutions in mg L^{-1} respectively.

2.4. Analysis of pesticides

The samples were analyzed on a Shimadzu 14B gas chromatograph equipped with ^{63}Ni electron capture detector (ECD) at 300 °C. A DB-1 column (J & W Scientific, Folsom, CA, USA), 30 m of length, 0.32 mm i.d., coated with dimethylpolysiloxane of a film thickness of 0.25 μm, was used. The temperature program was: from 80 °C (2 min) to 290° (10 min) at 21 °C min^{-1}. Injector temperature was set to 250 °C. Helium was used as the carrier (1.5 mL min^{-1}) and nitrogen as the make-up (35 mL min^{-1}) gases respectively. The injector mode was splitless and the injection volume was of 1.0 μL. Under this condition, the retention time for QP was 11.40 min and recovery was more than 90%.

2.5. Box–Behnken experimental design

RSM is a collection of statistical and mathematical techniques useful for developing, improving and optimizing process [25]. Box–Behnken design is one of the most powerful and efficient experimental design among other response surface designs (central composite, Doehlert matrix, and three-level full factorial designs), because its ability to estimate the parameters of the quadratic model, building of sequential designs, detection of lack of fit of the model, use of blocks [26]. Moreover, it needs fewer runs and has specific positioning of the design points. In recent years, Box–Behnken design is used in different fields of chemistry that are highlighted by many researchers [27–29] for its feasibility and efficiency.

In the present study, the three factors Box–Behnken with three levels experimental design model was used. Actual values of the factors were selected at three levels, coded as −1, 0 and +1 for low, middle and high value respectively (Table 1). The pH (X_1), initial concentration (X_2) and adsorbent dose (X_3) were the input factors in order to get the removal efficiency of pesticide onto used tea leaves.

Design-expert 7.1.3 [30] statistical software (trial version) was used for the design of experiment. The sequential model fitting test was carried out in order to choose a suitable model. A second-order polynomial model has been used to identify all possible interactions of selected factors obtained from the Box–Behnken model:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \quad (2)$$

where Y is the percentage of pesticide adsorbed, β_0 is the intercept parameter and β_i, β_{ii} and β_{ij} are parameters for linear, squared and interaction factor effects, respectively.

2.6. Desirability function

Presently, desirability function is a popular and established technique for the simultaneous determination of optimum settings of input variables that can determine optimum performance levels for one or more responses. Recently, several articles are reported in the application of desirability function in various fields of chemistry. Amini et al. [31] successfully employed the desirability function for the removal of lead from aqueous solution by *Aspergillus niger*. Another work, dealing with iron determination in finished water, desirability function was applied in order to find optimal experimental conditions [32]. A desirability function was also proposed for simultaneous optimization of the chloroanisoles and chlorophenols in oak barrel sawdust by microwave-assisted extraction [33].

Harrington [34] first developed the desirability function, and it was later modified by Derringer and Suich [35] for specifying the relationship between predicted responses on a dependent variable and the desirability of the responses. The desirability procedure involves two steps: (1) finding the levels of the independent variables that simultaneously produce the most desirable predicted responses on the dependent variables and (2) maximize the overall desirability with respect to the controllable factors. Therefore, the desirability functions are used in order to obtain qualitative and quantitative responses by the simple and quick transformation of different responses to one measurement.

The general approach of desirability function is to first convert the response into an individual desirability function (d_i) that varies from 0 to 1 (lowest desirability to highest desirability). The individual desirability scores for the predicted values for each dependent variable are then combined into overall desirability function, D, by computing their geometric mean of different d_i values.

$$D = (d_1 \times d_2 \times d_3 \times \cdots \times d_n)^{1/n} = \left(\prod_{i=1}^{n} d_i\right)^{1/n} \quad (3)$$

where d_i indicate the desirability of the response and n is the number of responses in the measure. If any of the responses beyond the desirability, then overall function turned into zero.

It can be extended to

$$D = [d_1^{v1} \times d_2^{v2} \times \cdots \times d_n^{1/n}]^{1/n},$$

$$0 \le v_i \le 1\,(i = 1, 2, \ldots, n),\ \sum_{i=1}^{n} v_i = 1 \quad (4)$$

where d_i indicate the desirability of the response y_i (i = 1, 2, 3,. . .,n) and v_i represents the importance of responses. So, maximum overall desirability function D, depends on the v_i (importance) value.

For simultaneous optimization each response must have a low and high value assigned to each goal. The meanings of the goal parameters are:

Maximum:

$d_i = 0$ if response < low value.
$0 \le d_i \le 1$ as response varies from low to high.
$d_i = 1$ if response > high value.

Minimum:

$d_i = 1$ if response < low value.
$1 \le d_i \le 0$ as response varies from low to high.
$d_i = 0$ if response > high value.

Target:

$d_i = 0$ if response < low value.
$0 \le d_i \le 1$ as response varies from low to target.
$1 \ge d_i \ge 0$ as response varies from target to high.
$d_i = 0$ if response > high value.

Range:

$d_i = 0$ if response < low value.
$d_i = 1$ as response varies from low to high.
$d_i = 0$ if response > high value.

The d_i for "in range" are included in the product of the desirability function "D", but are not counted in determining "n": $D = \left(\prod d_i\right)^{1/n}$.

If the goal is none, the response will not be used for the optimization.

3. Results and discussion

3.1. FTIR and SEM analysis

The FTIR analysis showed various functional groups observed on the surface of used tea leaves (data not shown). Among these, a strong sharp peak in the region of 1660–1730 cm^{-1} indicates the presence of C=O (carboxylic acids) group and the peak at 1300–1400 cm^{-1} related to N=O (nitro compounds). The peak at 2850–3000 cm^{-1} corresponds to C–H (alkanes) groups. The broad peak at 3100–3600 cm^{-1} indicates the presence of alcohol and phenol compound that represent the H-bonded O–H Stretch.

From the SEM analysis, several minute openings or pores observed (Fig. 1) on the surface of the adsorbents which were mainly responsible for QP adsorption.

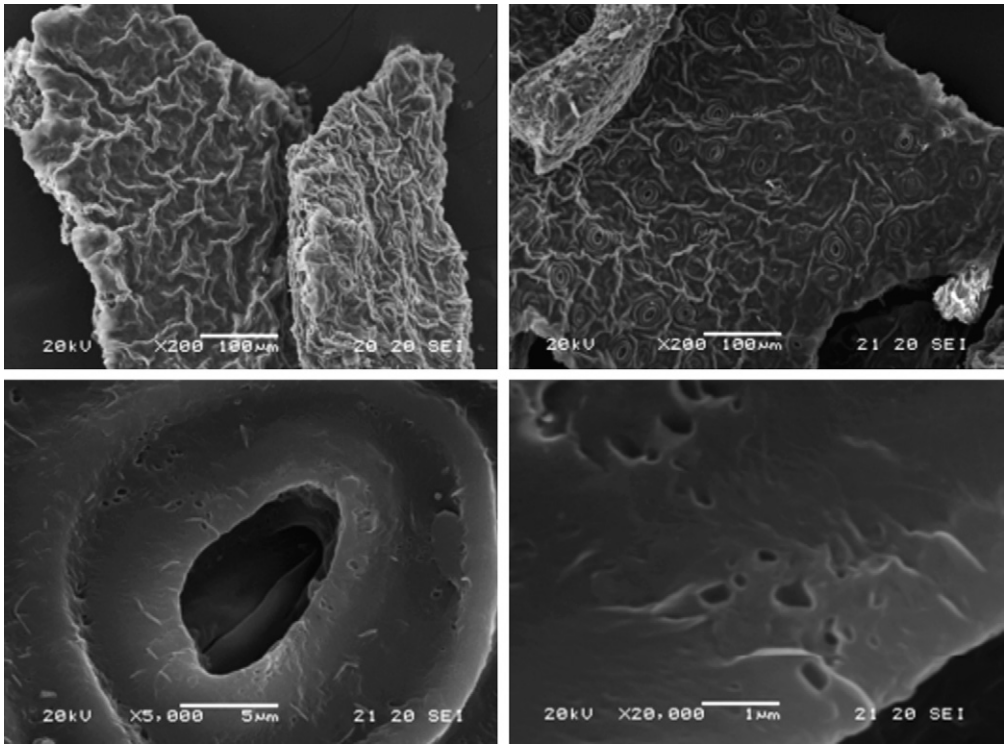

Fig. 1. SEM pictures of used tea leaves.

3.2. Kinetic study

The kinetic experiments were carried out for different contact times (30, 60, 120, 180, 240 and 300 min) with constant adsorbent dose (0.3 g), concentration (5 mg L^{-1}) and pH (7). This kinetic study showed that a contact time of 300 min was sufficient to achieve equilibrium of QP onto used tea leaves (Fig. 2) and this time was fixed for further study. Two commonly used kinetic models were applied in order to analyze adsorption data.

The Lagergren pseudo-first-order model that can be represented by following the equation (Eq. (5))

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1 t}{2.303} \quad (5)$$

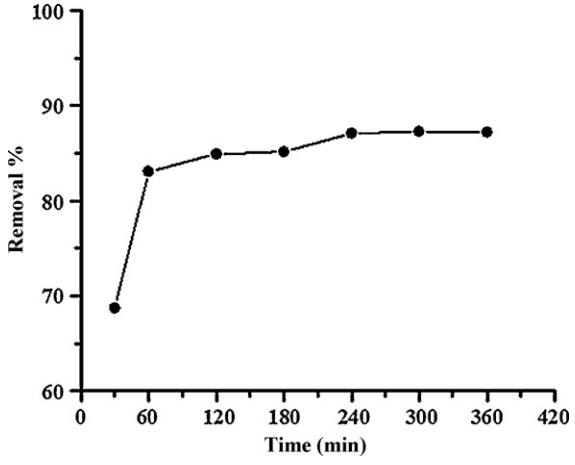

Fig. 2. Effect on contact time for the removal of QP (adsorbent dose: 0.30 g, concentration: 5 mg/L).

The pseudo-second-order can be expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where q_e is the amount of pesticides adsorbed onto used tea leaves at equilibrium (mg g^{-1}) and q_t is the amount (mg g^{-1}) of pesticide adsorbed at any time t (min) and K_1 and K_2 are the rate constants of pseudo-first-order and second-order model, respectively.

The pertinence of the two models was developed by constructing linear plot of $\log(q_e - q_t)$ vs. t for pseudo-first-order model and t/q_t vs. t for pseudo-second-order model. The rate constants K_1 and K_2 were obtained from the slopes of corresponding linear plots. According to the high regression coefficient, the adsorption of QP on used tea leaves are best described by the pseudo-second-order kinetic model ($R^2 = 0.996$) compare to pseudo-first-order kinetic model ($R^2 = 0.674$). Besides, the calculated q_e values (0.134) for pseudo-second-order kinetic model is similar to experimental q_e value (0.130), indicating the efficiency of the fitted model (Fig. 3).

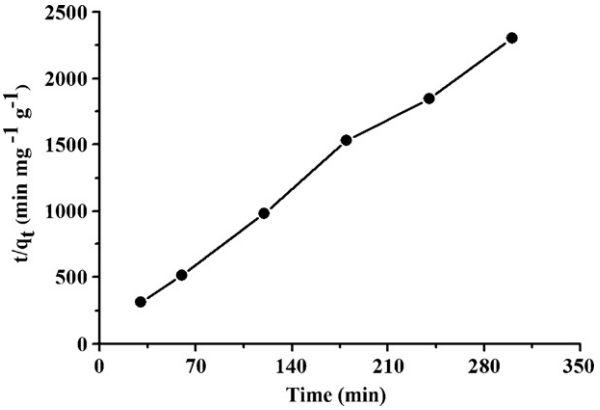

Fig. 3. Pseudo-second-order plot for quinalphos onto used tea leaves.

Table 2
Sequential model fitting for the quinalphos adsorption on used tea leaves.

	Sequential model sum of squares					
Source	Sum of squares	df	Mean square	*F*-value	Prob > *F*	Comment
Mean vs. total	67964.93	1	67964.93			
Linear vs. mean	3116.16	3	1038.72	30.42	<0.0001	
2FI vs. linear	125.65	3	41.88	1.34	0.3280	
Quadratic vs. 2FI	233.11	3	77.70	23.08	0.0023	Suggested
Cubic vs. quadratic	15.54	3	5.18	8.01	0.1130	Aliased
Residual	1.29	2	0.65	–	–	
Total	71456.68	15	4763.78	–	–	

	Lack of fit tests					
Source	Sum of squares	df	Mean square	*F*-value	Prob > *F*	Remark
Linear	374.31	9	41.59	64.29	0.0154	
2FI	248.66	6	41.44	64.06	0.0154	
Quadratic	15.54	3	5.18	8.01	0.1130	Suggested
Cubic	0.000	0		–	–	Aliased
Pure error	1.29	2	0.65	–	–	

	Model summary statistics					
Source	Std. dev.	R^2	Adjusted R^2	Predicted R^2	Press	Remark
Linear	5.84	0.8924	0.8631	0.7884	738.99	
2FI	5.59	0.9284	0.8747	0.6975	1056.18	
Quadratic	1.83	0.9952	0.9865	0.9280	251.56	Suggested
Cubic	0.80	0.9996	0.9974	–	–	Aliased

Similar results were also reported for the removal of basic dye onto spent tea leaves [22].

3.3. Box–Behnken statistical analysis

Box–Behnken is an efficient three-level design for fitting second-order response surfaces. The most important advantage of Box–Behnken design is that it does not contain combinations for which all factors are at the same time at their highest or lowest levels and in particular it avoids treatment combinations that are extreme [26]. The pH, initial concentration and adsorbent dose are the vital parameters which effect adsorption process. Table 1 represents the experimental parameters and levels used by Box–Behnken design model for QP. The corresponding design matrix consisted of 15 experiments including three center points.

In order to evaluate the combined effects of these factors, experiments were executed with the combinations of different parameters using Box–Behnken design. From Table 2, one can see that quadratic model is the most suitable for the removal of QP by used tea leaves. The adequacy of the model was further justified through analysis of variance (ANOVA). The ANOVA for the quadratic model for QP adsorption onto used tea leaves is depicted in Table 3. The Model *F*-value of 114.68 implies that the model is significant. In this case initial concentration (X_2), adsorbent dose (X_3) and interactions X_1X_2, X_1X_3, X_3^2 are significant model terms. The values ≥0.050 indicate the model terms that are not significant. The Lack of Fit (LOF) is the variation of the data around the fitted model. LOF is a special investigative test for adequacy of a model fit, because the effects of the additional higher-order terms are removed from the error. If the model does not fit the data well, this will be significant. In our present study with regards to QP removal% onto used tea leaves, the LOF is not significant relative to the pure error, indicating good response to the model. The "Predicted R^2" of 0.928 is in reasonable agreement with the "Adjusted R^2" of 0.986 and it may be also said that the model regression coefficient (R^2) of 0.995 is reasonable

Table 3
ANOVA for response surface quadratic model for quinalphos.

Source	Sum of squares	df	Mean square	*F*-value	Prob > *F*
Model	3474.92	9	386.10	114.68	<0.0001
X_1 (pH)	13.52	1	13.52	4.02	0.1014
X_2 (initial concentration)	156.20	1	156.20	46.39	0.0010
X_3 (adsorbent dose)	2946.43	1	2946.43	875.11	<0.0001
X_1X_2	71.15	1	71.15	21.13	0.0059
X_1X_3	46.72	1	46.72	13.88	0.0136
X_2X_3	7.78	1	7.78	2.31	0.1889
X_1^2	2.45	1	2.45	0.73	0.4324
X_2^2	12.00	1	12.00	3.56	0.1177
X_3^2	219.34	1	219.34	65.15	0.0005
Residual	16.83	5	3.37		
Lack of fit	15.54	3	5.18	8.01	0.1130
Pure error	1.29	2	0.65		
Cor total	3491.75	14			

R^2 = 0.995, predicted R^2 = 0.928, adjusted R^2 = 0.986.

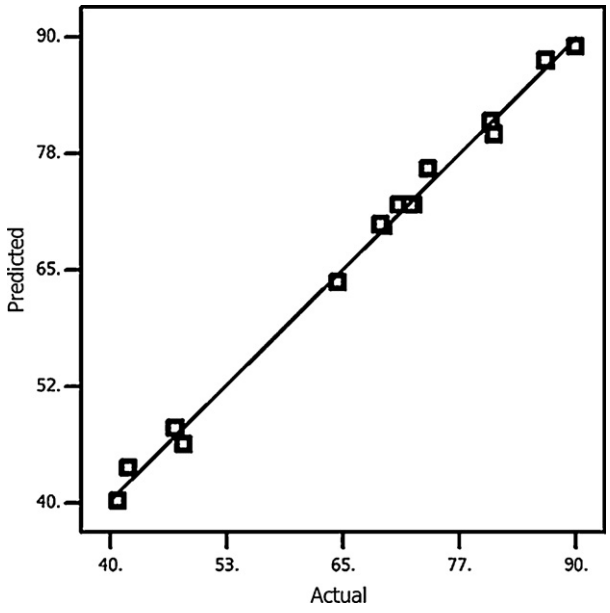

Fig. 4. Actual vs. predicted plot.

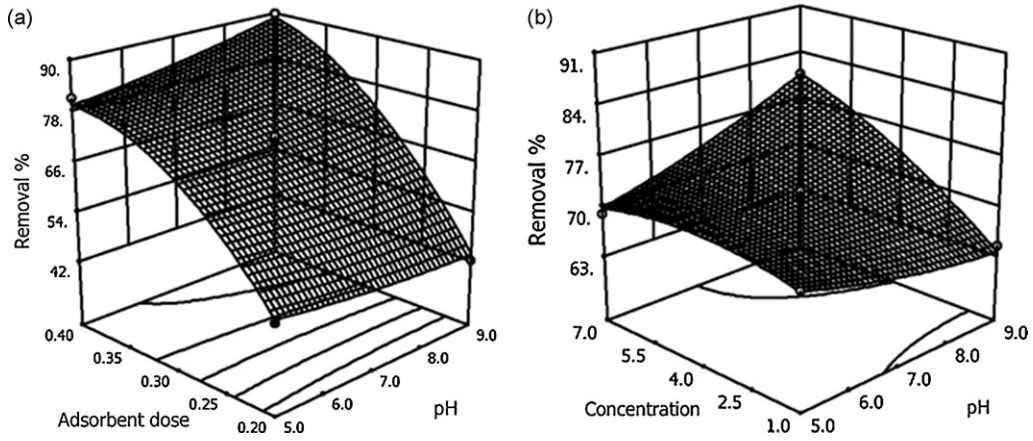

Fig. 5. (a) 3D response surface graph for quinalphos removal% by used tea leaves: dose vs. pH, concentration was kept constant at center point. (b) 3D response surface graph for quinalphos removal% by used tea leaves: concentration vs. pH, dose was kept constant at center point.

agreement with the experimental results, indicating 99.5% of the variability can be revealed by the model and is left with 0.5% residual variability. The value of the adequate precision is a mesure of the signal (response) to noise (deviation) ratio. A ratio >4 is desirable. In the present study, ratio was 32.533, which indicates the adequate signal, therefore, the model is significant for the removal process.

Raw residuals are the deviations of the actual values from the predicted values and represent the difference that is not explained by the model. The better the fit of the model, the smaller the values of residuals is, more to the point, residuals should be normally distributed. For these, *Shapiro–Wilk W* normality *test* was carried out and normality tests gave non-significant value of *W* statistics ($W = 0.948$, $p = 0.476$), indicating model may predict very well for QP removal% onto used tea leaves. The points of all predicted and actual responses (Fig. 4) fell in 45° line indicating also good response to the model.

From the above statistical results, it may be inferred that the Box–Behnken design was adequate to predict the adsorption efficiency of QP onto used tea leaves within the range of variables studied. The final predicted model in terms of significant actual factors for QP removal% by used tea leaves that are determined by Design-expert software is given below:

$$\begin{aligned}\text{QP removal \% by used tea leaves} = {} & +2.49 - 10.14 \times X_1 - 3.24 \times X_2 \\ & +516.15 \times X_3 + 0.70 \times X_1X_2 \\ & +17.09 \times X_1X_3 - 0.20 \times X_2^2 \\ & -770.75 \times X_3^2 \end{aligned} \quad (7)$$

From Eq. (7), it has been observed that the main effects of pH (X_1) and concentration (X_2) had significant negative effect on removal, if pH or concentration increased then removal percent may be decreased. The surface charge (zeta potential) of the bio-adsorbents plays a vital role in electrostatic adsorption on the biomaterial. The zeta potentials of the used tea leaves (data not shown) under different pH were negatively charged, indicating the affinity of used tea leaves for cations. The maximum negative charge of the used tea leaves was found at pH 6 and afterwards its values are slightly positive. Therefore, at high pH value, negatively charged surface of used tea leaves dissociate the anions and resulted into lower removal percent. On the other hand, although, QP is nonionic compound, without strong acidic or basic functionalities. But an increase of concentration in the solutions decreases the removal percentage of QP. At low concentration, surface activity of used tea leaves is higher and resulted more removal% but at high concentration, the active sites of adsorbent gradually covered by the molecules and showed lower removal percent. From Eq. (7), it has been also observed that the main effect of adsorbent dose (X_3) had the highest positive significant impact on removal of QP from aqueous solution, indicating increases of adsorbent dose increases the removal percent due to more available active surface site.

The interactions effect of pH and adsorbent dose (X_1X_3) had positive significant impact on removal% of QP as it is observed from the model and this interaction is depicted in Fig. 5a. For instance, at constant initial concentration (4 mg L^{-1}), for pH 5 and adsorbent dose 0.2 g gave 47.12% of removal but increasing dose at 0.4 g with the same pH 5, produced 81.17% of removal. Afterwards, when pH increases (pH 9) and dose decreases at 0.3 g, the removal% also decresed. Finally, at pH 7 with 0.2 g adsorbent dose resulted the lowest removal% (41%). From above observations, it can be established that for interactions of pH and adsorbent dose, adsorbent dose mainly governed the removal% of QP and there has no marked influence of pH for this. QP has phosphorus atom (P) in its aromatic ring and P has affinity to nitro, cyano, halogen, ketone, and carboxylic ester that are the active functional group on adsorbent obtained from FTIR analysis. The increses of adsorbent dose, increses the amount of surface area of adsorbents as well as the activity of functional groups and finally produced higher removal%. On the other hand, when dose kept constant (0.3 g), the interaction effect of pH and concentration showed the same influence of pH (Fig. 5b). For example, at pH 5 and concentration 7 mg L^{-1}, 69% of removal was obtained and further increment of pH 9 with the same concentration guided more removal% (80.81%). The highest removal% (86.67%) was obtained at the combination of medium pH and high concentration. It was also noticed that at pH 7

Table 4
Optimization of the individual responses (d_i) in order to obtain the overall desirability response(D).

Name	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
pH	Is in range	5	9	1	1	1
Concentration	Maximize	1	7	1	1	5
Dose	Maximize	0.2	0.4	1	1	3
Removal%	Maximize	41	89.83	1	1	5

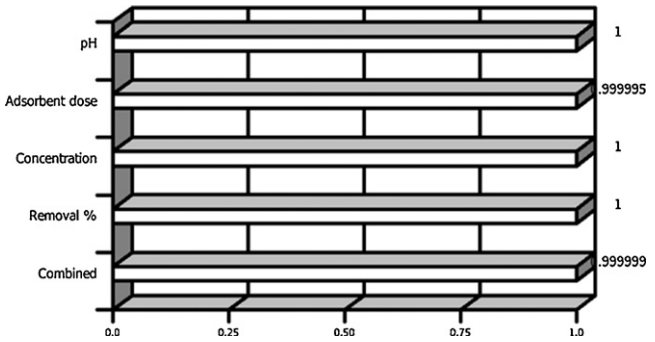

Fig. 6. Bar graph representing individual desirability of all responses (d_i) in correspondence with combined desirability (D).

and concentration 1 mg L^{-1}, reduced removal% (74.09%) observed. Therefore, for the interaction effect of pH and initial concentration, the latter was mostly responsible for removal efficiency and the pH effect becomes less important when the concentration level increases.

3.4. Optimization using desirability functions

The numerical optimization of the software has been chosen in order to find the specific point that maximizes the desirability function. The desired goal was selected by adjusting the weight or importance that might alter the characteristics of a goal. The goal fields for response have five options: none, maximum, minimum, target and within range. The criteria for the optimization of all studied factors in correspondence with removal% are shown in Table 4. From the (Eq. (7)), it has been seen that the main effect of pH was negatively significant, therefore, the goal for pH was assigned as 'within range' with corresponding 'importance' 1. As higher concentration is usually preferred for removal% of QP and 'maximize' for goal was selected with importance '5'. Used tea leaves, as a low-cost material, consequently, the goal for dose was 'maximize' with medium priority of importance. The removal% and its value were assigned as 'maximize' for goal with the highest importance. The lower limit and upper limit values of all responses are taken from the Box–Behnken design levels. The optimization procedure was conducted under these settings and boundaries. The individual desirability functions (d_i) for each of the responses, and the calculated geometric mean as maximum over all desirability (D = 0.999) is represented in Fig. 6. Our main objective was to maximize the removal% with recalculating all responsible factors by using desirability functions. By using this desirability function with all pre-selected goal for each factors, gave the specific value for all responses that are presented in Fig. 7. The software optimized 96.31% removal of QP with calculating the optimized model factors of pH 8.83, concentration 7 mg L^{-1} and dose 0.4 g for used tea leaves. Finally, for their validation, duplicate confirmatory experiments were conducted using the optimized parameters. The results are closely related with the data obtained from optimization analysis using desirability functions, indicating Box–Behnken design in corporate with desirability functions could be effectively used to optimize the adsorption parameters for the removal of QP by used tea leaves.

3.5. Adsorption isotherms of pesticides

In order to assess the potential adsorption capacity of the used tea leaves toward the pesticide studied, adsorption isotherms at room temperature were derived on the basis of batch analysis with constant dose (0.40 g) and pH (8.83) obtained from the statistical optimization by desirability functions. Adsorption isotherm studies were carried out in 15 mL polypropylene centrifuge tubes with 10 mL of the different pesticide initial concentrations (0.5, 1.0, 2.5, 5.0 and 7 μg ml^{-1}). The extraction and analysis procedures were followed according to the previously discussed in Sections 2.3 and 2.4. The amount adsorbed by the selected adsorbents was calculated by the following equation (Eq. (8))

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{8}$$

where, C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}), V is the volume of solution (ml) and m is the mass of the used tea leaves (g)

All the adsorption isotherms were constructed by the linearized Freundlich (Eq. (9)) and Langmuir (Eq. (10)) isotherm equation, by plotting log (q_e) vs. log (C_e) and $1/q_e$ vs. $1/C_e$ respectively.

$$\log q_e = \log(K_F) + \frac{1}{n}\log(C_e) \tag{9}$$

$$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \tag{10}$$

where, q_e is the adsorbed amount (μg g^{-1}), C_e is equilibrium concentration (μg ml^{-1}), K_F is the Freundlich coefficient that represents the degree or strength of adsorption. While n is an exponential coefficient that reflects the curvature in the isotherm. q_m (μg g^{-1}) is the maximum adsorption capacity of the adsorbent; K_a is the Langmuir's constant.

The experimental isotherm data to Langmuir and Freundlich equations seems to be quite good regarding linearity and very close

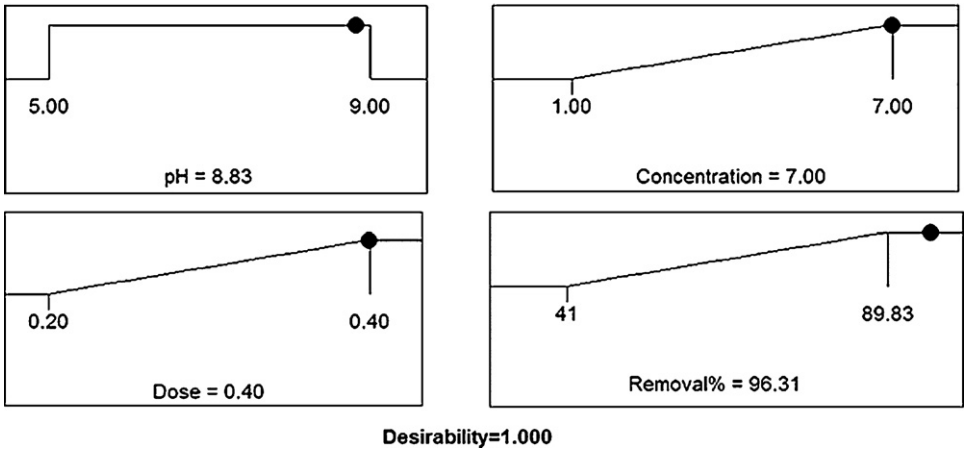

Fig. 7. Desirability ramp for numerical optimization of four selected goals.

Table 5
Adsorption isotherm values of quinalphos by Freundlich and Langmuir models.

Freundlich		Langmuir	
K_F ($\mu g\,g^{-1}$ ($\mu g\,ml^{-1}$)$^{-1/n}$)	9.4	q_m ($\mu g\,g^{-1}$)	196.07
$1/n$	1.04	K_a (ml μg^{-1})	0.520
R^2	0.985	R^2	0.997
F_{error} (function error)	0.3144	F_{error} (function error)	0.1245

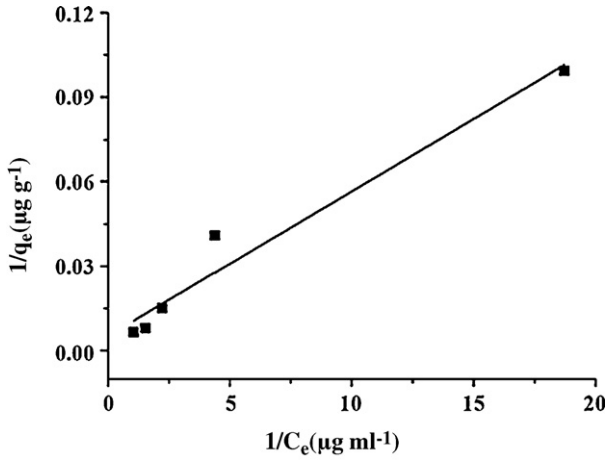

Fig. 8. Langmuir isotherms plot for quinalphos onto used tea leaves.

to target pesticide (Table 5). But only R^2 values might not predict well for all model parameters. For this reason, all models were evaluated by error function [29] in order to find out the best fit isotherm model. The error function can be expressed (Eq. (11)) as:

$$F_{error} = \sqrt{\frac{\sum_i^p ((q_i\,cal - q_i\,exp)/q_i\,exp)^2}{p}} \quad (11)$$

where, q_i cal is each value of q_e predicted by the fitted model and q_i exp is each value of q_e measured experimentally, and p is the number of experiments conducted.

By comparing the results of the values of error function presented in Table 5, it can be concluded that the Langmuir model (Fig. 8) fits best the QP adsorption isotherm data indicating the surface homogeneity of the used tea leaves. Similar observation was also found by Akhter et al. [21] for methyl parathion adsorption on different agricultural waste materials. The monolayer adsorption capacity of used tea leaves, q_m, were found to be 196.07 $\mu g\,g^{-1}$.

4. Conclusion

The Box–Behnken design was applied as a suitable response surface method to determine the effects of different adsorption parameters (pH, concentration and adsorbent dose) and their interactions, for removal of QP and under optimal values of process parameters. The simultaneous optimization of the multi-response system by desirability function indicated that 96.31% removal of QP can be possible by using the optimal conditions of pH 8.83, concentration of 7 mg L^{-1} and dose of 0.40 g. The adsorption isotherm was well fitted by the Langmuir model indicated homogenous surface structure. The used tea leaves used in this study are locally available as well as economically feasible and there have no alternative use, moreover, proposed adsorbent do not require any pretreatments but showed high removal capacity. Although, single step of experiments did not remove 100% of selected compound from aqueous solution but 100% of removal may be possible by increasing dose or treatment of aqueous solution doubly. The used tea leaves can be use for the daily water treatments where this adsorbents are the most common and available and industrial treated water is beyond the capacity of common village people. Finally, it may be concluded that RSM with desirability function can provide a further insight for potential use of other processes, especially industrial waste water treatment system.

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