

Sustainable alternative for sorption of some insecticides from water and their detection by UV/Vis spectrophotometry

Azza G. A. Reyad^a, Gehan I. Kh. Marei^a, Moustafa A. Abbassy^a, Entsar I. Rabea^a, Mohamed E. I. Badawy^b

^a Department of Plant Protection, Faculty of Agriculture, Damanhour University, Damanhour 22516, Egypt

^b Department of Pesticide Chemistry and Technology, Faculty of Agriculture, 21545-El-Shatby, Alexandria University, Alexandria, Egypt

Abstract

A study was performed to evaluate the efficacy of dry biomass from the microalgae *Nannochloropsis oculata* and *Spirogyra porticalis* in removing insecticides from water, such as fenamiphos, imidacloprid, and oxamyl. Pesticide dissipation was studied based on incubation time, pesticide concentration, and algal biomass concentration. Analyzing and quantifying pesticides through UV-Vis spectrophotometry was validated. For fenamiphos, optimum conditions were 15 minutes, 50 mg/l pesticide concentration, and 900 mg/L algal biomass with responses 68.67 and 67.27% by *N. oculata* and *S. porticalis*, respectively. The optimum conditions for imidacloprid were 15 min, 50 mg/L pesticide concentration, and 900 mg/L algal biomass, with responses of 35.55 and 28.20% by *N. oculata* and *S. porticalis*, respectively. In the same conditions, the responses were 81.31 % and 65.71 % for oxamyl by *N. oculata* and *S. porticalis*, respectively. This study proved that the microalgae *N. oculata* and *S. porticalis* were both active and biomass dependent in their ability to remove insecticides. As a result, the insecticides levels in the water samples that were tainted appeared to be potentially reduced by these algae biomass.

KEYWORDS: *Nannochloropsis oculata*; *Spirogyra porticalis*; fenamiphos; imidacloprid; oxamyl.

1. Introduction

A variety of pesticide remediation methods are available, including photocatalytic decomposition, chemical oxidation, membrane technology, electrochemical decomposition, coagulation, flocculation, biological remediation, adsorption, and hybrid technologies [1, 3]. Microorganisms that are inactive or not alive are used in the biosorption of different pollutants that bind to the cell wall of the target organism. Contaminants in aquatic environments can be removed using adsorption processes. Although it has advantages over other physical-chemical methods due to its simplicity and low cost of adsorbent materials. Adsorption is highly dependent on the properties of the adsorbent and the adsorbate, their interactions, and the conditions of operation [4]. As a result of factors such as particle size, pH, adsorbent dosage, and contact duration, pesticides adsorb to different surfaces [5, 6]. Microalgae-based processes offer the greatest nutrient removal benefits, as they simultaneously remove N and P [7]. A microalgae's cell wall consists of carbohydrates, a fibril matrix, intercellular spaces, and sulfated polysaccharides, which help adsorb organic contaminants from water [8]. *Nannochloropsis spp.* are microalgae living in freshwater and seawater that are related to diatoms and brown algae, Phylum: *Ochrophyta*, Class: *Eustigmatophyceae*, Order: *Eustigmatales*, Family: *Monodopidaceae*, Genus: *Nannochloropsis*. Biosorption of pesticides and heavy metals by *Nannochloropsis sp* have been studied [9, 11]. *Spirogyra sp* is a filamentous charophyte green algae of the Kingdom: *Plantae*, Phylum: *Chlorophyta* Class: *Zygnematophyceae*, Order: *Zygnematales*, Family: *Zygnemataceae*, Genus: *Spirogyra*.

It is high efficiency to remove malathion [12]. Fenamiphos, ethyl 3-methyl-4-(methylsulfanyl) phenyl isopropyl phosphoramidate, organophosphorus insecticide is applied to control many nematode pests [13]. However, recent studies have begun to draw attention to the harmful ecological effects of fenamiphos. In rats, LD50 values range from 1.0 to 20.0 mg/kg, while in pigs, they range from 55.0 to 95.0 mg/kg [14]. Imidacloprid, (1-[(6-Chloro-3-pyridinyl) methyl]-N-nitro-4,5-dihydro-1H-imidazol-2-amine). It is a broad-spectrum neonicotinoid insecticide is a colorless crystalline solid pesticide that melts at 136.4°C and dissolves in water at 20°C with a solubility of 0.51 g/L. As an insecticide, it is used to control beetles, insects, locusts, and termites [15]. Oxamyl, (N, N-dimethylcarbamoyloxyimino-2-(methylthio) acetamide) is a carbamate compound. It is a colorless, crystalline solid with a melting point of 100-102°C which changes to a dimorphic state at 108-110°C [16]. It causes genome DNA damage to fish and humans due to its ecotoxicology. Oxamyl is a nematicide designed to control nematodes on farms. In addition to nausea and abdominal pain, the symptoms include excessive sweating, osteoporosis, and blurred vision caused by miosis [17].

This study examined the ability of *Nannochloropsis oculata* and *Spirogyra porticalis* particles in the removal of fenamiphos, imidacloprid, and oxamyl pesticides from water. Pesticide residue concentrations were determined using UV/Vis spectrophotometry. The Plackett-Burman design was used to examine the effect of physicochemical parameters on pesticide removal, such as pH, incubation time, pesticide concentration, and algal biomass concentration. This is the first study in which *N. oculata* and *S. porticalis* powder was used as biosorbent material for the removal of pesticides from aquatic samples.

2. Materials and methods

2.1. Chemical and reagents

Analytical standard of fenamiphos (99%, (RS)-N-[Ethoxy-(3-methyl-4-methylsulfanylphenoxy) phosphoryl] propan-2-amine) was purchased from Miles Inc, Co. (Stilwell, Kansas, USA). Imidacloprid (99%, 1-[(6-chloro-3-pyridinyl) methyl]-N-nitro-4,5-dihydro-1H-imidazol-2-amine) was purchased from Bayer AG Co., (Leverkusen, Germany). Oxamyl (98.89%, methyl (1Z)-2-(dimethyl amino)-N- [(methyl carbamoyl) oxy]-2-oxoethanimido thioate) was supplied by Syngenta. Fenamiphos formulation (Nemaphos 40% EC) was obtained from Bridge Trade Co. (Cairo, Egypt). Imidacloprid formulation (Imidor® 35% SC) was obtained from Chema Industries Co. (26, 1st Industrial Zone, New Nubaria City, Behira, Egypt). A commercial formulation of oxamyl (Vydate 24% SL) was obtained from Agrimatco Egypt Co. (Giza, Egypt). The chemical structures and properties of the studied pesticides are presented in Table 1. No further purification was performed on any of the solvents or reagents used. By dissolving precisely weighted amounts of each pesticide in methanol (HPLC grade), each stock solution contained 1 mg/L of pesticide. To prepare calibration curves, the stock solutions were diluted with methanol to achieve the required concentrations for UV-Vis spectrophotometric analysis.

Table 1: Chemical structures and physicochemical properties of fenamiphos, imidacloprid, and oxamyl

Pesticide	Chemical structure	Class	Molecular formula	Molecular mass (g/mol)	Log K _{ow}	Water solubility (mg/L) at 20°C
Fenamiphos		Organophosphates	C ₁₃ H ₂₂ NO ₃ PS	303.3	3.23	400
Imidacloprid		Neonicotinoids	C ₉ H ₁₀ ClN ₅ O ₂	255.6	0.57	610
Oxamyl		Carbamates	C ₇ H ₁₃ N ₃ O ₃ S	219.2	-0.47	280

2.2. Algal culture

Biomass of microalgae *N. oculata* and *S. porticalis* were obtained from National Research Center (33 El Bohouth St, Dokki, Giza, Egypt). Algae were thoroughly washed with distilled water, shade-dried for 24 h, and then oven-dried at 50 °C until a constant weight was obtained. We pulverized the dried biomass in an analytical mill, sieved the particles with Retsh viber sieve shakers to select particles that were 500 mesh, and stored them in polyethylene bottles for later use. The characteristics of *N. oculata* and *S. porticalis* were conducted by Near Infrared Spectroscopy instrument.

2.3. Experimental design

The experimental design enables the study of the influence of several variables with a limited number of experiments. Statistical analysis of the results will reveal which variables are significantly influencing the desired response and how polynomial equations relate the variables and the desired response. The Plackett-Burman factorial design was used to identify the most principal factors early in the experimentation phase when all the facts about the system are unknown. Minitab 19.1 software (Minitab Inc. State College, PA) (Minitab 2019). This experimental design was generated for four factors of the current study. The Plackett-Burman factorial design [18] employed in this study to correlate dependent and independent variables using the following polynomial model: $Y_1 = A_0 + A_1X_1 + A_2X_2 + A_3X_3 + A_nX_n$ where Y is the dependent variable, A₀ the constant and A₁ to A_n are the coefficients of the independent values and X₁ to X_n are the independent factors. Eighteen experimental trials involving four independent variables were generated by Minitab software. The independent variables screened were the concentration of pesticide (X₁), the concentration of biomass (X₂), incubation time (X₃), and pH (X₄). Each variable was examined at three levels, including low(-), high (+), and basal (0) as shown in Table 2. A dependent variable (response data) was determined as the removal of pesticides. The final data were entered into the worksheet after designing, conducting, and analyzing the experiment (biosorption or removal %), followed by statistical analysis through Stat > DOE > Factorial > Analyze Factorial Design.

Table 2. Experimental design by Plackett-Burman factorial design for removal of pesticides by *N. oculata* and *S. porticalis*

Experimental number	pH	Incubation time (min)	Pesticide (mg/L)	Biomass (mg/L)
1	9 (+)	5 (-)	50 (-)	100 (-)
2	9 (+)	15 (+)	50 (-)	100 (-)
3	9 (+)	15 (+)	450 (+)	100 (-)
4	9 (+)	15 (+)	450 (+)	900 (+)
5	5 (-)	15 (+)	450 (+)	900 (+)
6	9 (+)	5 (-)	450 (+)	900 (+)
7	5 (-)	15 (+)	50 (-)	900 (+)
8	9 (+)	5 (-)	450 (+)	100 (-)
9	9 (+)	15 (+)	50 (-)	900 (+)
10	5 (-)	15 (+)	450 (+)	100 (-)
11	5 (-)	5 (-)	450 (+)	900 (+)
12	9 (+)	5 (-)	50 (-)	900 (+)
13	5 (-)	15 (+)	450 (+)	100 (-)
14	5 (-)	15 (+)	50 (-)	100 (-)
15	5 (-)	5 (-)	450 (+)	100 (-)
16	5 (-)	5 (-)	50 (-)	900 (+)

17	5 (-)	5 (-)	50 (-)	100 (-)
18	7(0)	10(0)	250(0)	500(0)

The sign in parentheses indicates the level of each factor as low (-), high (+), and basal (0).

2.4. Sorption experiment

The biosorption experiments were conducted by adding 100, 500, and 900 mg/L of alga to Erlenmeyer flasks containing pesticide aqueous solutions (50, 250, and 450 mg/L) pesticide concentrations were selected according to field application, and 0.1 from field application. Various pH values (5, 7, and 9) were used in the experiments. Using a magnetic multi-stirrer (Velp Scientific, Italy), Erlenmeyer flasks containing pesticide solution and alga were stirred (200rpm) for different periods (5, 10, and 15 minutes) at 27°C. Samples were collected from the stirrer at certain points and filtered (0.22 m). In the supernatant, the remaining pesticide in the water had been absorbed by the algae. Using a UV/Vis Spectrophotometer, pesticides were measured. Maximum absorbencies of 220, 252, and 234 nm were used for fenamiphos, imidacloprid, and oxamyl, respectively.

2.5. Statistical analysis

Statistical analysis was performed using the IBM SPSS software version 25.0 (SPSS, Chicago, IL, USA) (IBM 2017). Means and standard error (SE) were obtained from three independent replications performed for each treatment. Analysis of variance (ANOVA) was conducted and means property values were separated ($p \leq 0.05$) with Student-Newman-Keuls (SNK). Minitab 19.1 software (Minitab Inc. State College, PA) (Minitab 2019) was used to design the experiments and modeling. Model adequacy checks were conducted by examining various plots (scatter, histograms, and normal probability) of the residuals.

3. Results and Discussion

3.1. Characteristics of *N. oculata* and *S. porticalis*

Algal samples were analyzed by Near Infrared Spectroscopy (NIRS) instrument with significant accuracy. This spectroscopic method can be used to analyze algae rapidly and inexpensively. A single spectrum can provide values for multiple analytes within minutes at most with these methods [19]. The powder of the microalgae *N. oculata* was characterized by NIRS instrument and the data are shown in Table 3. The percentage of protein content was found to be 44.26% while the carbohydrate content and fat were 17.21% and 11.99%, respectively. The powder contains 17.21% nitrogen and 5.03% crude fiber. The moisture and ash were 10.22% and 11.29%, respectively. Microalgae, *N. oculata* ash content was 24.47 %, volatile matter content was 67.45%, and lipid 11.44% [20].

The powder of the microalgae *S. porticalis* was characterized by NIRS instrument and the data are shown in Table 3. The percentage of protein content was found to be 40.95% while the carbohydrate content and fat were 21.12% and 2.5%, respectively. The powder contains 21.12% nitrogen and 14.3% crude fiber. The moisture and ash were 8.66% and 12.48%, respectively. *S. porticalis* exhibited total protein content of 12.46-16.89%, carbohydrate content of 34.72-39.25%, 12.97-16.75% moisture, fat was 20.17-22.03% fat, and 10.78-15.98% ash content based on the dry weight [21].

Table 3: Characteristics of *N. oculata* and *S. porticalis* biomass by NIRS instrument

Characteristics	Percentages (%)	
	<i>N. oculata</i>	<i>S. porticalis</i>
Ash	11.29	12.48
Carbohydrates	17.21	21.12
Fat	11.99	2.50
Fiber	5.03	14.30
Moisture	10.22	8.66
Nitrogen	17.21	21.12
Protein	44.26	40.95

3.2. Optimization of pesticide removal by algal biomass

The efficiency of *N. oculata* and *S. porticalis* biosorbents was evaluated at three diverse levels of concentrations of the tested pesticides, incubation time (min), and pH according to Plackett-Burman factorial design. The number of experimental runs (17) and center point (medium level) were determined as shown in Table 2. This protocol will investigate the interactions among the variables and determine the optimum concentration of each factor for maximizing the response. Tables 4 and 5 represent the design matrix of the coded variables together with the experimental results for the removal of fenamiphos, imidacloprid, and oxamyl, by *N. oculata* and *S. porticalis*, respectively. Generally, the data revealed a great deal of variation in the removal (%) according to the level of the four independent variables.

The results of fenamiphos, imidacloprid, and oxamyl removal (%) by *N. oculata* biomass at different parameters are shown in Table 4. The results of fenamiphos showed that the highest removal data (68.67 and 66.93%) were obtained with experiments 7 and 9 which used the highest algal biomass (900 mg/L) and the lowest pesticide concentration (50 mg/L) with pH 5 and incubation time (15 min). Experiments 16, 14, 12, and 17 proved 65.88, 62.98, 62.16, and 61.70%, respectively. However, trials 3 and 8 exhibited the lowest removal efficiency (10.61-13.32%). The experiment of the center point (18) which used a median algal biomass (500 mg/L) and the median pesticide concentration (250 mg/L) with incubation for 10 min proved 33.19% removal. The results of imidacloprid showed that the highest removal (35.55%) was obtained with experiment 7 which used the highest algal biomass (900 mg/L) and the lowest pesticide concentration (50 mg/L) with incubation for 15 min. It was followed by trial 16 with the removal of 22.99%. However, trials 3, 15, and 13 exhibited the lowest removal efficiency (7.29, 7.81 and 7.84%, respectively). The experiment of the center point (18) exhibited 16.10% removal. The removal data of oxamyl are shown in Table 4. The highest removal value was obtained with experiment 9 (81.31%).

The results of fenamiphos, imidacloprid, and oxamyl removal (%) by *S. porticalis* biomass at different parameters as shown in Table 5. The results of fenamiphos showed that the highest removal percentages (67.27 and 64.59%) were obtained with experiments 7 and 16 that used the highest algal biomass (900 mg/L) and the lowest pesticide concentration (50 mg/L) with an incubation time of 15 min. Experiments 9 and 12 proved 60.11 and 60.23%, respectively. However, trials 3 and 13 exhibited the lowest removal efficiency (5.91-7.40%). The experiment of the center point (18) which used median algal biomass (500 mg/L) and the median pesticide concentration (250 mg/L) with incubation for 10 min proved 24.96% removal. In general, this algal biomass is not suitable for the removal of imidacloprid where the removal % was very low and ranged from 4.17% to 28.20%. The results of imidacloprid showed that the highest removal (28.20%) was obtained with experiment 7, which used the highest algal biomass (900 mg/L), and the lowest pesticide concentration (50 mg/L) with incubation for 15 min. However, trials 1 and 10 exhibited the lowest removal efficiency (4.17 and 4.81%, respectively). The experiment of the center point (18) exhibited 15.20% removal. The removal data of oxamyl are shown in Table 5. The highest removal value was obtained with experiment 7 (65.71%).

As a result of these quantitative data, the first-order polynomial equations (1-6) and their coefficients for each response factor were derived.

Removal (%) = 29.00 + 0.778 pH - 0.1323 incubation time + 0.11993 pesticide concentration - 0.004638 algal biomass + 6.02 $r^2 = 0.99, s = 1.273669$ (1)
Removal (%) = 39.27+1.102 pH -0.067 incubation time +0.10951 pesticide concentration - 0.01484 algal biomass +8.77 $r^2 = 0.95, s = 5.56691$ (2)
Removal (%) =17.95- 0.664 pH +0.268 incubation time -0.02237 pesticide concentration + 0.01017 algal biomass +0.63 $r^2 = 0.79, s = 3.59708$ (3)
Removal (%) =13.92- 0.346 pH +0.146 incubation time -0.01772 pesticide concentration + 0.01140 algal biomass +0.97 $r^2 = 0.78, s = 3.49435$ (4)
Removal (%) = 47.51- 0.22 pH + 0.890 incubation time -0.0808 pesticide concentration + 0.01927 algal biomass -17.9 $r^2 = 0.80, s = 10.3390$ (5)

$$\text{Removal (\%)} = 57.44 + 0.455 \text{ pH} + 0.3647 \text{ incubation time} - 0.11111 \text{ pesticide concentration} + \dots \dots \dots (6)$$

$$0.006199 \text{ algal biomass} - 8.17$$

$$r^2 = 0.99, s = 1.45398$$

Models were developed to investigate how individual parameters affect the algal biomass removal efficiency of pesticides. As seen in these six equations, the pH (X_1), the incubation time (min) (X_2), pesticide concentration (mg/L) (X_3), and algal biomass (mg/L) (X_4) had a significant effect on the pesticide removal (%). Both the incubation time and algal biomass should be high since the regression coefficients are positive, whereas the pesticide concentration and pH should be as low as possible since the regression coefficients are negative. Furthermore, the correlation coefficient of the incubation time is higher in four models (0.268, 0.146, 0.890, and 0.3647 in Equations 3, 4, 5, and 6, respectively) indicating that it has a greater influence. The goodness of fit of the model was evaluated using the determination coefficient (R^2). In this case, (R^2) value was calculated to be fenamiphos (0.99 and 0.95 (equations 1 and 2) for *N. oculata* and *S. porticalis*, respectively), imidacloprid (0.79 and 0.78 (equations 3 and 4) for *N. oculata* and *S. porticalis*, respectively) and oxamyl (0.80 and 0.99 (equations 5 and 6) for *N. oculata* and *S. porticalis*, respectively). A regression model with an R^2 close to 1.0 is thought to have a high correlation. As a result, the current R^2 value demonstrated a particularly good fit between the observed and predicted responses, implying that the model is trustworthy for predicting fenamiphos, imidacloprid, and oxamyl removal. (%)

The results presented in **Tables 4 and 5**, indicate that the models are valid and can theoretically be used in the calculation and prediction of pesticide removal (%). Additionally, the influence of each factor on the pesticide removal by algal biomass was also evaluated with Pareto charts (**Figures 1 and 2** for *N. oculata* and *S. porticalis*, respectively). **Figures 1 A, B, and C** illustrate the Pareto charts for the removal (%) of fenamiphos (A), imidacloprid (B), and oxamyl (C) at $\alpha = 0.05$. A visualization of the factors' effects on fenamiphos removal can be seen in these charts, which show that pH, incubation time, pesticide concentrations, and algal biomass all play significant roles at $\alpha = 0.05$ (**Figure 1A**) as indicated by their magnitude greater than the limit of the line label. **Figure 1B** represents the Pareto chart for the removal efficacy of imidacloprid. This chart demonstrates that pesticide concentration and the algal biomass had the highest significant effects on the removal efficiency at $\alpha = 0.05$. Other factors pH and incubation time showed significant values lower than the reference line (2.093 at $\alpha = 0.05$). The Pareto pattern for oxamyl removal in **Figure 1C** shows that the pesticide concentration had the highest significant effect, followed by the algal biomass and incubation time. pH showed values lower than the reference line (2.093 at $\alpha = 0.05$).

Figures 2A, 2B, and 2C (for *S. porticalis*) illustrate the Pareto charts for the removal (%) of fenamiphos (A), imidacloprid (B), and oxamyl (C) at $\alpha = 0.05$. These charts indicate that pesticide concentration and algal biomass were significant in their effect on the removal of fenamiphos at $\alpha = 0.05$. Other factors pH and incubation time showed significant values lower than the reference line (2.093 at $\alpha = 0.05$). **Figure 2B** represents the Pareto chart for the removal efficacy of imidacloprid. This chart demonstrates that the algal biomass and pesticide concentration had the highest significant effects on the removal efficiency at $\alpha = 0.05$. Other factors (pH and the incubation time) showed significant values lower than the reference line (2.093 at $\alpha = 0.05$). The Pareto pattern for oxamyl removal in **Figure 2C** shows that the pesticide concentration had the highest significant effect, followed by the algal biomass, the incubation time, and pH all play significant roles at $\alpha = 0.05$.

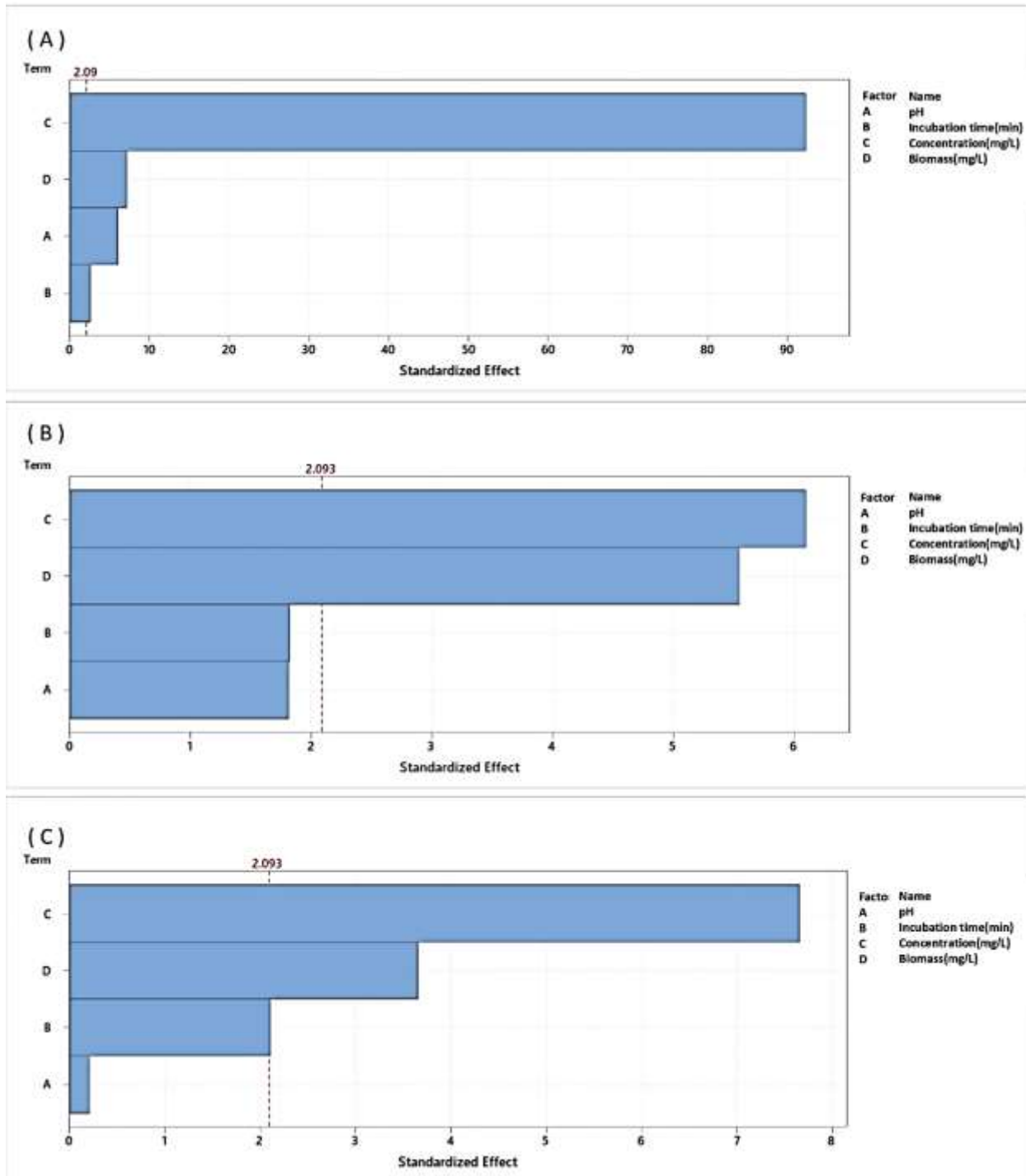


Figure 1. Pareto chart of standardized effect of *N. oculata* biomass, pH, incubation time, and concentration of pesticides on the removal of fenamiphos (A), imidacloprid (B), and oxamyl (C).

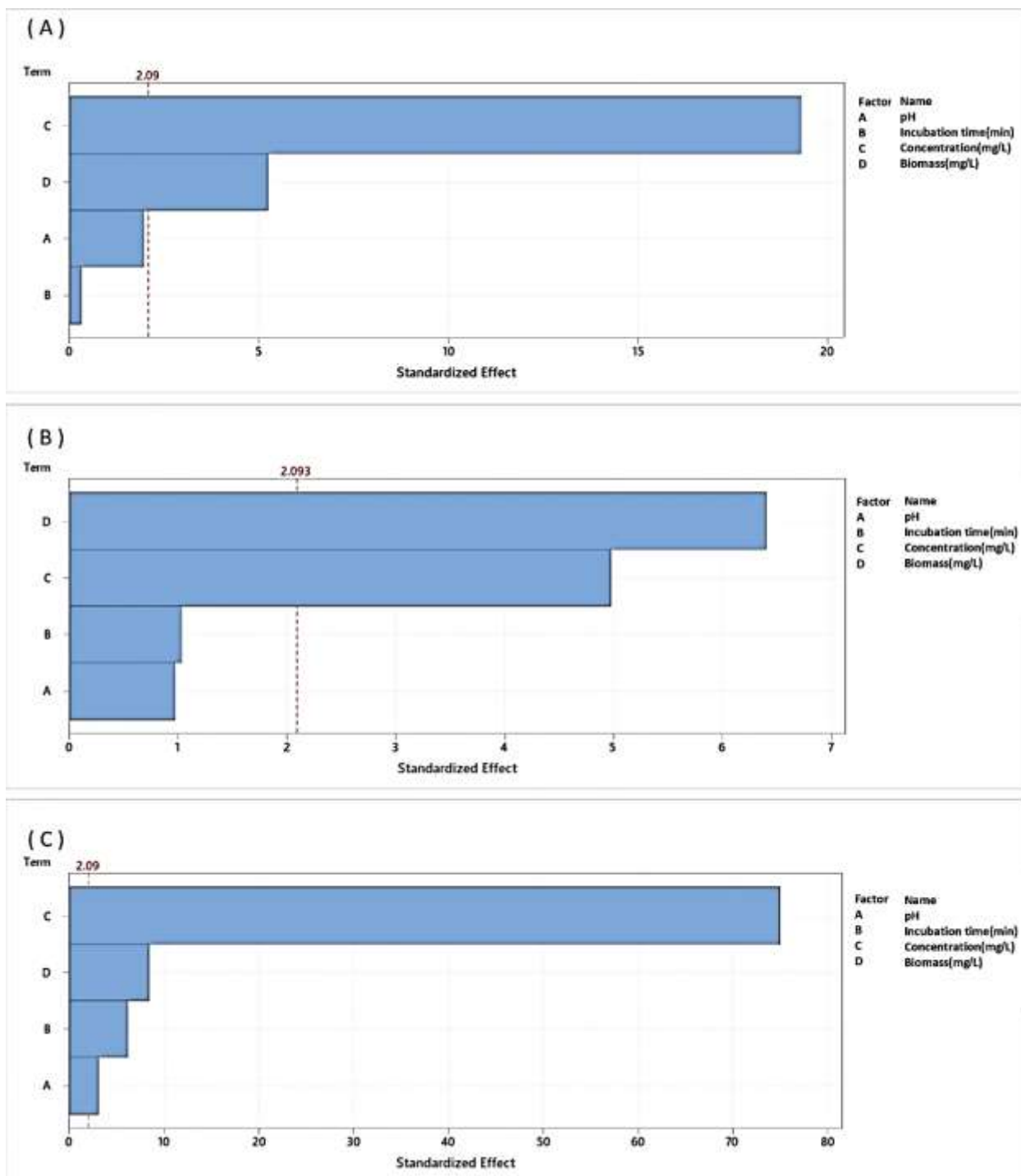


Figure 2. Pareto chart of standardized effect of *S. porticalis* biomass, pH, incubation time, and concentration of pesticides on the removal of fenamiphos (A), imidacloprid (B), and oxamyl (C).

Expression of the experimental results in the form of surface plots reflects the interactive effects of examined independent variables (Figures 3-8). The three-dimensional response surface diagram is the graphical representation of the regression equation, in which the removal (%) is generated to form the wise pair of the three factors, with one variable constant at the optimal level. The other two variables vary within the experimental range. The optimum value of each variable was located based on the hump in the three-dimensional plot. Figure 3 shows that the optimum fenamiphos removal (%) emerged at basal levels of the three variables. Solving the model according to the data obtained from Table 4 revealed an optimum response at the incubation time of 15 min, pesticide concentration 50 mg/L, and the algal biomass of *N. oculata* 900 mg/L with a response of 68.67%. Figure 4 shows that the optimum imidacloprid removal (%) emerged at basal levels of these three variables. Solving the model according to the data obtained from Table 4 revealed an optimum response at an incubation time 15 min, pesticide concentration 50 mg/L, and algal biomass of *N. oculata* 900 mg/L with a response of 35.55%. Figure 5 shows that the optimum oxamyl removal (%) emerged at basal levels of these three variables. Solving the model according to the data obtained from Table 4 revealed an optimum response at an incubation time 15 min, pesticide concentration 50 mg/L, and the algal biomass of *N. oculata* 900 mg/L with a response of 81.31%.

Table 4. Removal (%) of fenamiphos, imidacloprid, and oxamyl by *N. oculata* biomass at different parameters

Experimental number	Experimental removal (%) of fenamiphos \pm SE	Predicated removal (%)	Experimental removal (%) of imidacloprid \pm SE	Predicated removal (%)	Experimental removal (%) of oxamyl \pm SE	Predicated removal (%)
1	58.64 ^f \pm 0.13	59.12	9.17 ^{abc} \pm 1.12	13.21	44.25 ^d \pm 0.38	47.89
2	59.77 ^f \pm 0.26	60.45	17.22 ^{efg} \pm 0.64	15.89	45.34 ^{de} \pm 4.76	56.79
3	10.61 ^a \pm 0.66	12.47	7.29 ^a \pm 0.16	6.94	26.57 ^{bc} \pm 1.38	24.46
4	15.61 \pm 0.19	16.18	14.52 ^{cd} \pm 0.07	15.08	50.12 ^d \pm 0.16	39.87
5	18.34 ^d \pm 0.56	19.30	12.58 ^{bc} \pm 0.19	17.73	54.15 ^{ef} \pm 0.62	40.74
6	14.52 ^{bc} \pm 0.14	14.86	14.80 ^{cd} \pm 0.23	12.40	18.81 ^{ab} \pm 0.35	30.97
7	68.67 ⁱ \pm 0.74	67.27	35.55 ^j \pm 1.10	26.68	68.10 ^g \pm 0.55	73.07
8	13.32 ^b \pm 0.25	11.15	8.56 ^{abc} \pm 0.86	4.27	17.30 ^{ab} \pm 2.03	15.56
9	66.93 ^h \pm 0.72	64.16	21.39 ^{hi} \pm 2.09	24.03	81.31 ^h \pm 0.21	72.20
10	15.80 ^c \pm 0.55	15.59	7.87 ^{ab} \pm 0.11	9.60	30.59 ^c \pm 0.12	25.33
11	17.43 ^d \pm 0.13	17.97	13.52 ^{bc} \pm 1.51	15.06	21.11 ^{ab} \pm 0.17	31.84
12	62.16 ^g \pm 0.46	62.83	19.44 ^{fgh} \pm 1.61	21.35	69.85 ^g \pm 0.13	63.30
13	15.86 ^c \pm 0.41	15.59	7.84 ^{ab} \pm 0.06	9.60	12.61 ^a \pm 0.34	25.33
14	62.98 ^g \pm 0.31	63.56	18.72 ^{efg} \pm 0.41	18.55	52.86 ^{def} \pm 7.16	57.66
15	14.97 ^c \pm 0.03	14.26	7.81 ^{ab} \pm 0.04	6.92	25.58 ^{bc} \pm 3.23	16.43
16	65.88 ^h \pm 0.12	65.95	22.99 ⁱ \pm 0.68	24.01	60.48 ^{fg} \pm 1.10	64.17
17	61.70 ^g \pm 0.31	62.24	16.11 ^{def} \pm 1.92	15.87	61.19 ^{fg} \pm 0.69	48.76
18	33.19 ^e \pm 0.07	33.19	16.10 ^{def} \pm 0.33	16.10	26.42 ^{bc} \pm 0.32	26.42

Values in the column with different letters (a-l) are significantly different at $p \leq 0.05$ using one-way analysis of variance (ANOVA) followed by the Student-Newman-Keuls. * Predicted removal calculated from models 1,3 and 5.

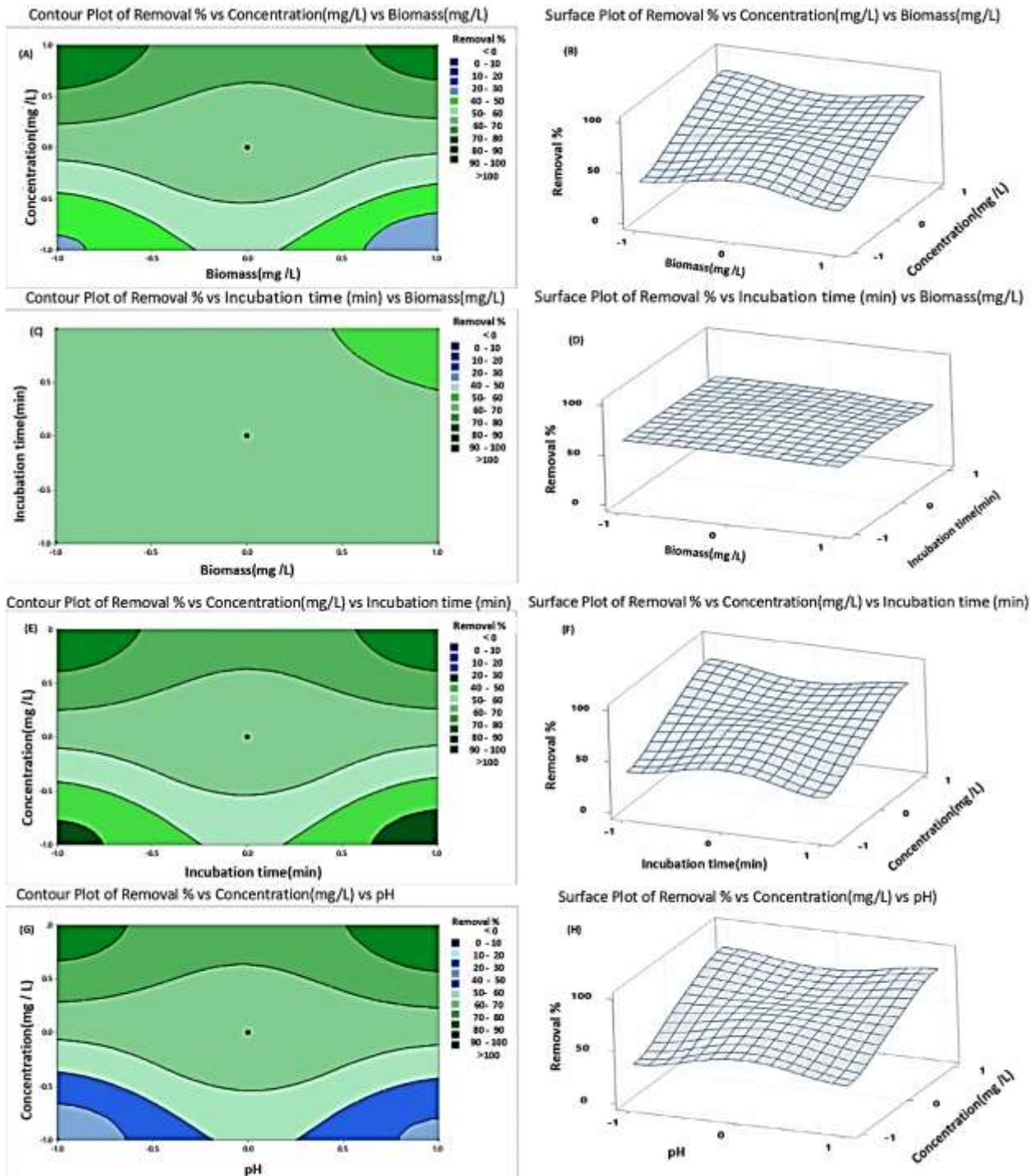


Figure 3. 3D-response surface plots (left) and two-dimensional contour plots (right). A and B: Effect of concentration and biomass (*N. oculata*) on the removal of fenamiphos. C and D: Effect of incubation time and biomass on the removal of fenamiphos. E and F: Effect concentration of fenamiphos and incubation time and biomass on the removal of fenamiphos.

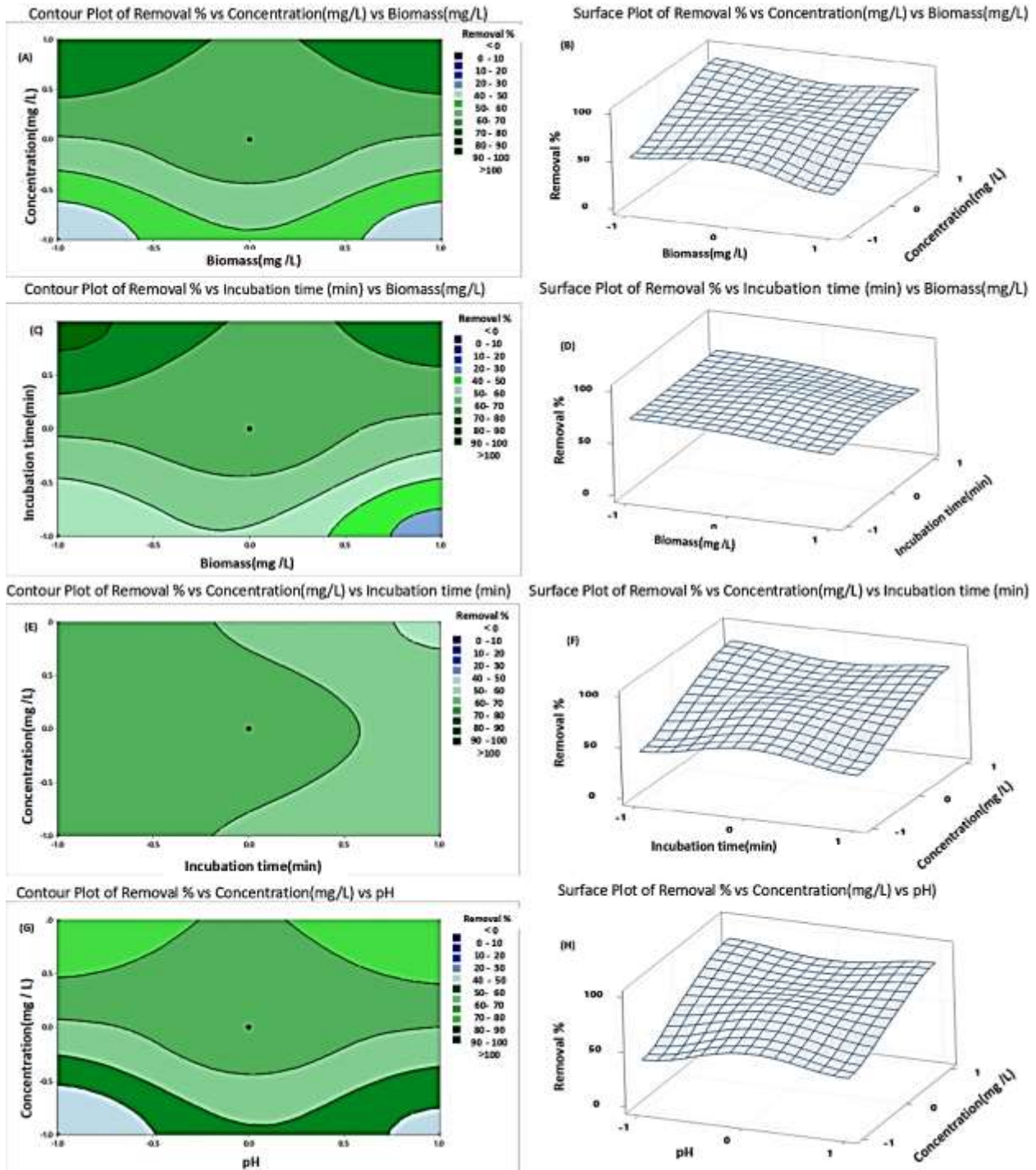


Figure 4. 3D-response surface plots (left) and two-dimensional contour plots (right). A and B: Effect of concentration and biomass (*S. porticalis*) on the removal of fenamiphos. C and D: Effect of incubation time and biomass on the removal of fenamiphos. E and F: Effect of concentration of fenamiphos and incubation time and biomass on the removal of fenamiphos.

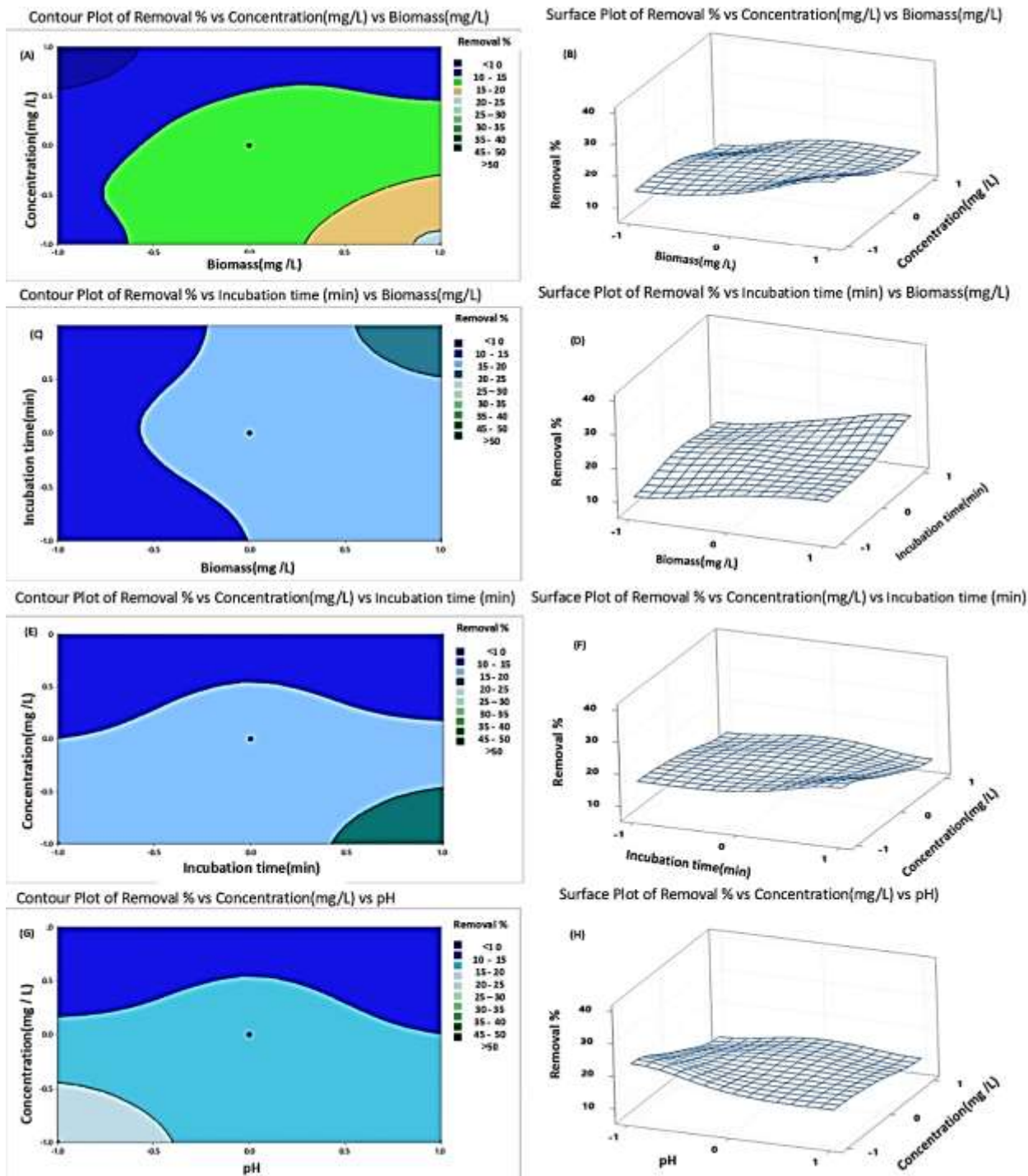


Figure 5. 3D-response surface plots (left) and two-dimensional contour plots (right). A and B: Effect of concentration and biomass (*N. oculata*) on the removal of imidacloprid. C and D: Effect of incubation time and biomass on the removal of imidacloprid. E and F: Effect concentration of imidacloprid and incubation time and biomass on the removal of imidacloprid.

Figure 6 shows that the optimum fenamiphos removal (%) emerged at basal levels of the four variables. Solving the model according to the data obtained from Table 5 (for *S. porticalis*) revealed an optimum response at an incubation time 15 min, pesticide concentration 50 mg/L, and, the algal biomass of *S. porticalis* 900 mg/L with a response of 67.27%. Figure 7 shows that the optimum imidacloprid removal (%) emerged at pH 5, incubation time 15 min, pesticide concentration 50 mg/L, and, algal biomass of *S. porticalis* 900 mg/L with a response of 28.20% (the data obtained from Table 5). Figure 8 shows that the optimum oxamyl removal (%) emerged at basal levels of these four variables. Solving the model according to the data obtained from Table 5 revealed an optimum response at pH 5, incubation time 5 min, pesticide concentration 50 mg/L, and the algal biomass of *S. porticalis* 900 mg/L with a response of 65.71%.

Table 5. Removal (%) of fenamiphos, imidacloprid, and oxamyl by *S. porticalis* biomass at different parameters

Experimental number	Experimental removal (%) of fenamiphos \pm SE	Predicated removal (%)	Experimental removal (%) of imidacloprid \pm SE	Predicated removal (%)	Experimental removal (%) of oxamyl \pm SE	Predicated removal (%)
1	36.82 ^f \pm 2.63	47.15	4.17 ^a \pm 1.77	11.79	60.09 ^h \pm 0.00	58.42
2	58.86 ^{ij} \pm 0.66	47.82	15.56 ^{def} \pm 0.64	13.25	63.23 ^{hi} \pm 0.06	62.07
3	7.58 ^{ab} \pm 0.14	4.01	7.94 ^{abc} \pm 0.14	6.17	17.10 ^{abc} \pm 0.09	17.62
4	16.08 ^c \pm 0.08	15.89	17.49 ^{def} \pm 0.36	15.29	20.90 ^{de} \pm 0.17	22.58
5	18.91 ^d \pm 0.03	20.30	14.77 ^{def} \pm 0.34	16.67	24.00 ^e \pm 0.59	20.76
6	14.46 ^c \pm 0.17	15.22	11.35 ^{bcd} \pm 0.75	13.83	20.00 ^{cd} \pm 0.35	18.94
7	67.27 ^l \pm 0.81	64.10	28.20 ^j \pm 2.33	23.76	65.71 ⁱ \pm 1.93	65.21
8	5.91 ^a \pm 0.36	3.35	8.75 ^{bcd} \pm 0.68	4.70	13.78 ^a \pm 0.34	13.98
9	60.11 ⁱ \pm 0.72	59.70	18.06 ^{efg} \pm 0.80	22.38	65.00 ⁱ \pm 0.41	67.03
10	10.00 ^b \pm 0.50	8.42	4.81 ^b \pm 0.17	7.55	15.54 ^{ab} \pm 0.34	15.80
11	15.43 ^c \pm 0.40	19.63	12.32 ^{bcd} \pm 0.41	15.21	18.18 ^{bcd} \pm 1.19	17.12
12	60.23 ⁱ \pm 0.66	59.03	22.22 ^{hij} \pm 6.42	20.92	64.64 ⁱ \pm 1.88	63.38
13	7.40 ^{ab} \pm 0.31	8.42	5.48 ^{ab} \pm 0.56	7.55	15.54 ^{ab} \pm 0.68	15.80
14	43.13 ^g \pm 0.62	52.23	13.03 ^{def} \pm 0.96	14.64	60.12 ^h \pm 0.34	60.25
15	8.83 ^{ab} \pm 0.51	7.76	7.32 ^{abc} \pm 0.24	6.09	13.13 ^a \pm 0.86	12.16
16	64.59 ^k \pm 0.25	63.44	24.17 ^{hij} \pm 2.74	22.30	60.71 ^h \pm 0.69	61.56
17	56.87 ^{hi} \pm 1.12	51.56	15.40 ^{def} \pm 0.41	13.17	55.24 ^g \pm 1.79	56.60
18	24.96 ^e \pm 0.91	24.96	15.20 ^{def} \pm 0.46	15.20	31.42 ^f \pm 0.27	31.42

Values in the column with different letters (a-h) are significantly different at $p \leq 0.05$ using one-way analysis of variance (ANOVA) followed by the Student-Newman-Keuls. * Predicted removal calculated f

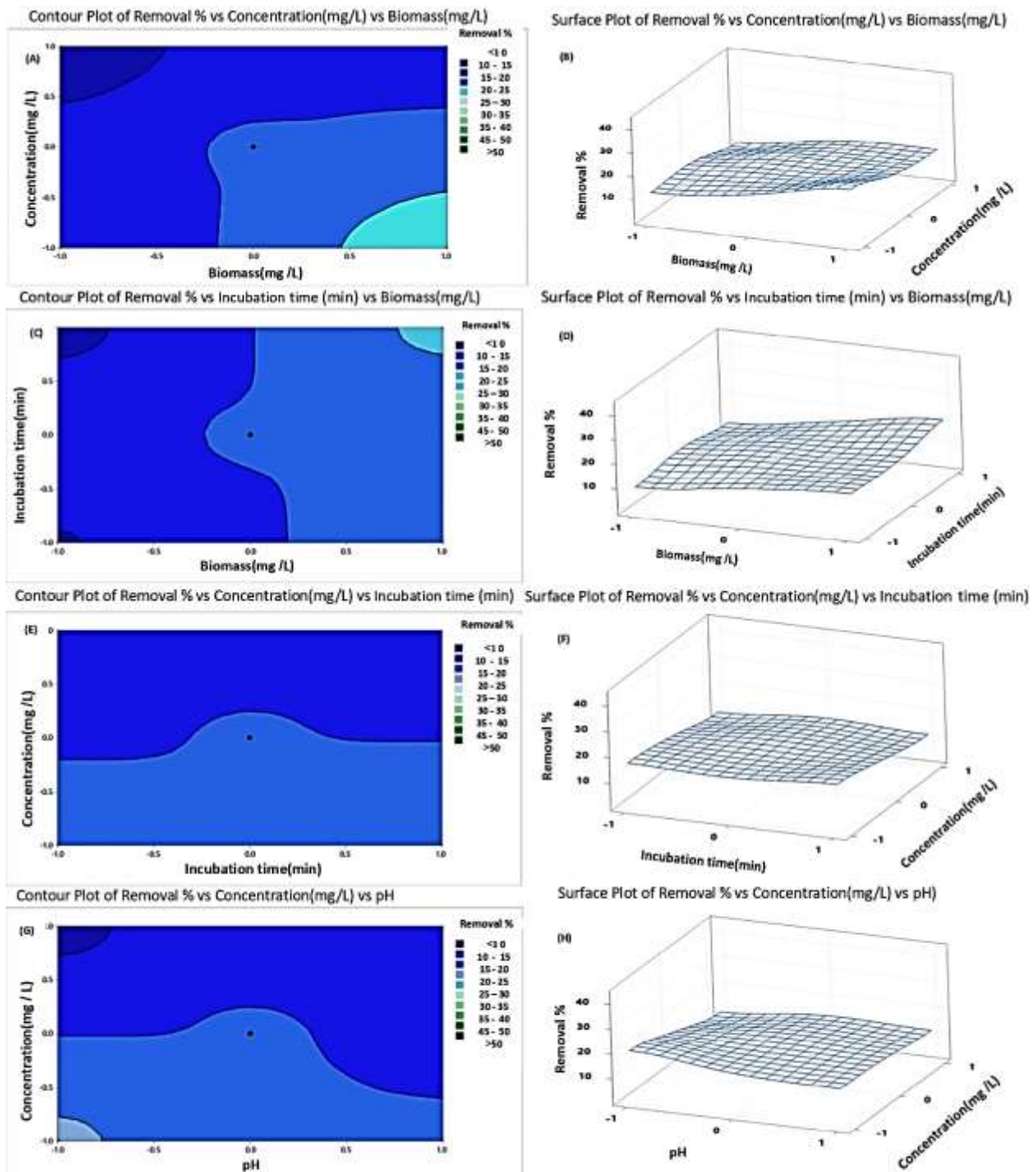


Figure 6. 3D-response surface plots (left) and two-dimensional contour plots (right). A and B: Effect of concentration and biomass (*S. porticalis*) on the removal of imidacloprid. C and D: Effect of incubation time and biomass on the removal of imidacloprid. E and F: Effect concentration of imidacloprid and incubation time and biomass on the removal of imidacloprid.

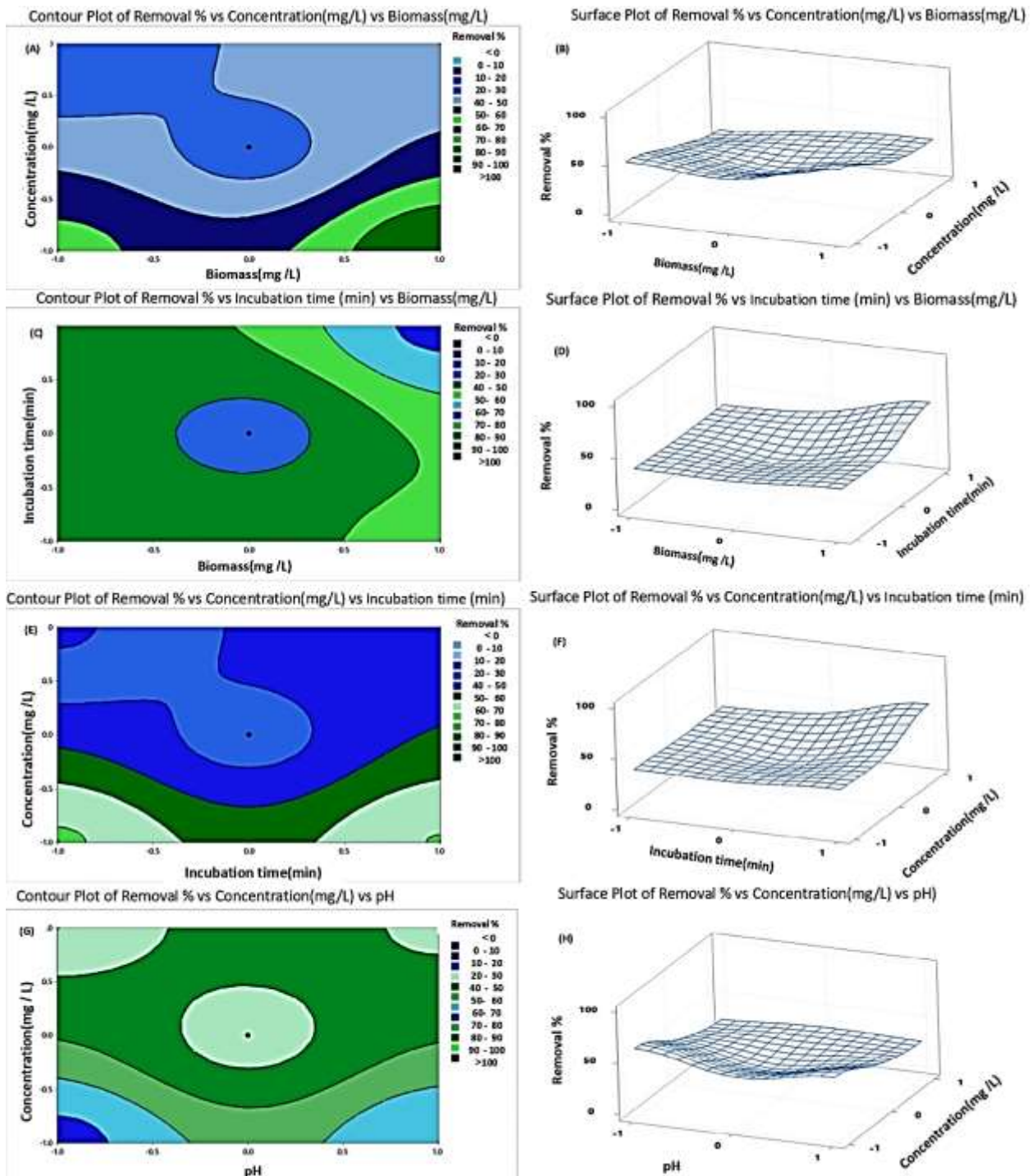


Figure 7. 3D-response surface plots (left) and two-dimensional contour plots (right). A and B: Effect of concentration and biomass (*N. oculata*) on the removal of oxamyl. C and D: Effect of incubation time and biomass on the removal of oxamyl. E and F: Effect concentration of oxamyl and incubation time and biomass on the removal of oxamyl.

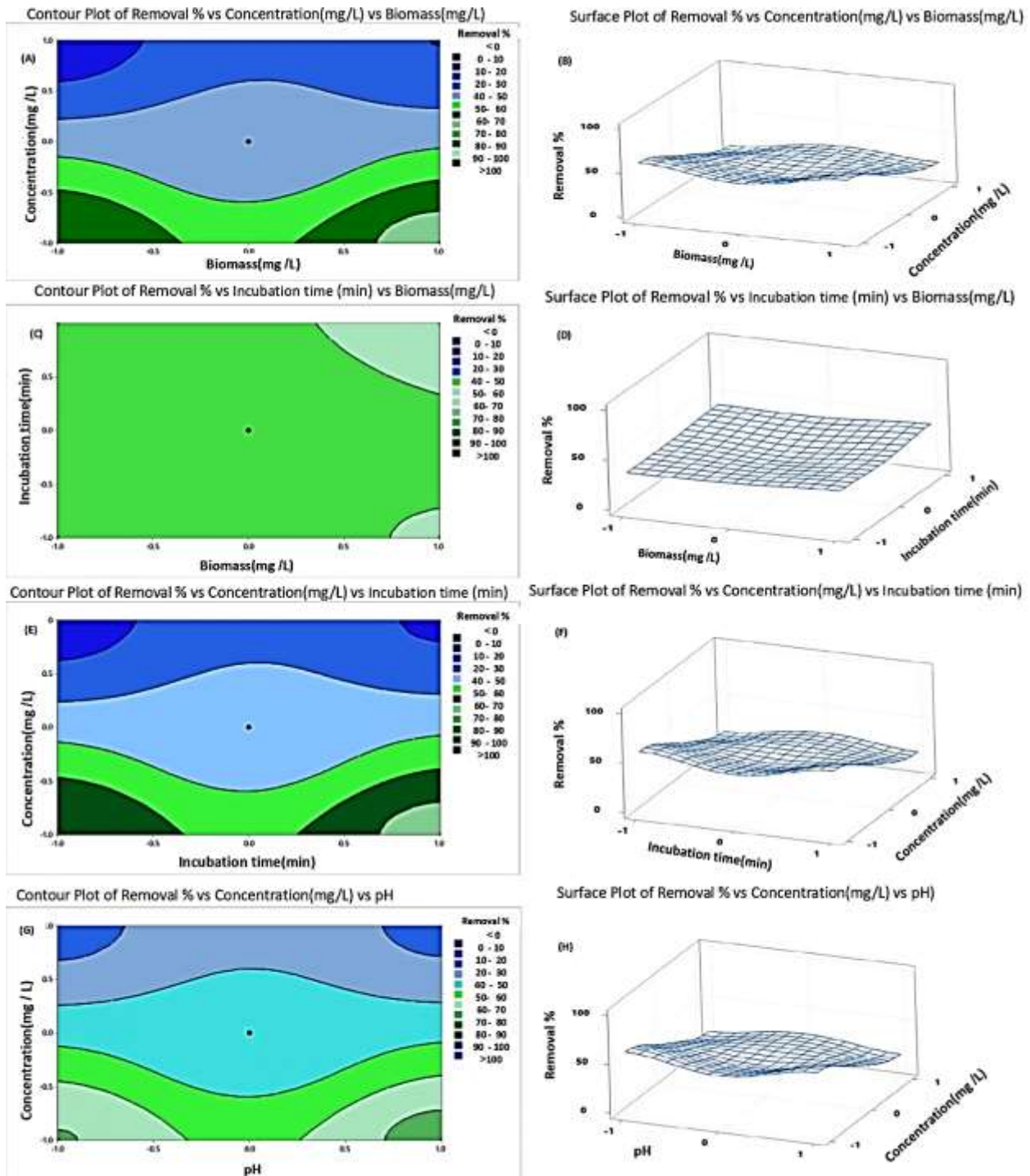


Figure 8. 3D-response surface plots (left) and two-dimensional contour plots (right). A and B: Effect of concentration and biomass (*S. porticalis*) on the removal of oxamyl. C and D: Effect of incubation time and biomass on the removal of oxamyl. E and F: Effect concentration of oxamyl and incubation time and biomass on the removal of oxamyl

Phycoremediation refers to the combination of the words “phyco” meaning “algae” and “remediation” which means, “to treat or bring back to the original state.” the process of phyto-remediation seems to be a sustainable and environmentally friendly way to remove nitrogen, phosphorus, and some metal ions from wastewater [22]. Microalgae can remove distinct types of contaminants through different methods such as biosorption, bioaccumulation and biodegradation. Microalgae have been found to remove pollutants from domestic effluents, agricultural runoffs, textiles, leather, pharmaceuticals, and electroplating industries [23]. The most advantageous method for advanced nutrient removal is based on microalgae, which exhibit outstanding properties such as simultaneous removal of N and P, extra-chemical-free treatment, generation of O₂, sequestration of CO₂, reduction of metal ions, and production of value-added compounds [7]. Microalgae can remove pesticides via different methods such as screening and domesticating effective strains, the co-cultivation of microalgae and bacteria, and the immobilization of microalgae are considered effective approaches. These methods are critically evaluated [24]. In the last few years, microalgae biotechnology has grown exponentially in parallel with the rapid appearance of facilities and microalgae-based products. It includes both eukaryotic microalgae and prokaryotic cyanobacteria [25]. *N. oculata*, the microalgae remove imidacloprid from water rapidly, 50% in the first 20 h. Their efficiency increases with light, while aeration may also contribute to the process [11]. Using *Nannochloropsis oculata* biomass to remove Cu²⁺ ions from aqueous solutions. To determine the maximum amount of Cu²⁺ ions adsorbed onto *Nannochloropsis oculata* biomass, initial Cu²⁺ ion concentrations varied from 10 mg/L to 50 mg/L [26]. It was demonstrated that a novel algae-bacteria biofilm reactor (ABBR) was capable of removing imidacloprid from municipal wastewater as well as conventional nutrients. ABBR achieved 74.9% removal of imidacloprid under 80 μmol m⁻²·s⁻¹ light, higher than photobioreactor without biofilm (61.2%) or ABBR under 40 μmol m⁻²·s⁻¹ light (48.4%) after 16 days of operation [27]. *S. porticalis* is a group of microalgae belonging to the family Zygnemataceae. Based on the diverse target compounds, growth rate, cultivation simplicity, greater biodiversity, and other allied factors, the micro-algal community represents a hitherto untapped resource of natural antioxidants [28]. Removal of Cr (III) removal from aqueous solution by *spirogyra* spp. Maximum metal uptake (Q_{max}) was observed as 30.21 mg/g with 0.2 M CaCl₂ treated algal biomass indicating good biosorbents than other treated and untreated biomass [29]. *Spirogyra* sp. is used to remove malathion. It was discovered that 76.34 percent of malathion was removed from a starting concentration of 100 mg/L [12]. Using non-viable algal *Spirogyra* I02 as biosorbent, the azo dye was sorbed from the aqueous phase. Algal biosorbents were found to be capable of adsorbing azo dye in agitated batch sorption measurements. Biosorption is dependent on the pH of the aqueous phase, and the functional groups on the algal cell wall and their ionic states (at particular pHs) determine its extent [30]. Adsorption of oxamyl from the liquid phase by newly synthesized and characterized graphene quantum dots nanomaterials. The effects of agitation speed, pH, adsorbent dose, contact time, temperature, and initial concentration on sorption efficiency were studied and optimized using batch adsorption experiments. The optimal pH for maximum oxamyl adsorption was found to be 8.0 and the optimal adsorbent dose of 0.6 g was found to be optimum for adsorption within 25 minutes [17].

Conclusion

The effectiveness of dry biomass of microalgae *N. oculata* and *S. porticalis* for removal of pesticides from the water was demonstrated UV/Vis spectrophotometric method. The characterization of the algal biomass was achieved by NIRS instrument. Screening and optimization of varied factors on the removal of fenamiphos, imidacloprid, and oxamyl by these microalgae were premeditated in detail using Plackett-Burman design analysis. Incubation time, pesticide concentration, and algal biomass all contributed to the proximate optimum conditions of removal (%). Algal biomass and pesticide concentration were the greatest significant factors. Consequently, the dry biomass of the microalgae *N. oculata* and *S. porticalis* can be used to remove fenamiphos, imidacloprid, and oxamyl from polluted water very rapidly and diminish environmental contamination.

Ethical approval

Not applicable

Availability of data and materials

All data generated or analyzed during this study are included in this article. Also, the related datasets are available from the corresponding author on reasonable request.

Conflict of interest

The authors confirm no known conflicts of interest associated with this publication.

Author's contributions

All authors contributed to the study's conception and design. They performed material preparation, data collection, and analysis. Azza G. A. Reyad performed the experiments, data collection, and analysis. Moustafa A. Abbassy, Entsar I. Rabea, and Gehan I. Kh. Marei shared in the experimental section, statistical analysis, and wrote the draft of the manuscript. Mohamed E. I. Badawy performed UV-Vis spectrophotometric analysis of pesticide residues and revised the data. All authors participated in manuscript writing and proofreading and approved the final manuscript.

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