International Journal of Scientific Research Updates

Journal homepage: https://orionjournals.com/ijsru/

ISSN: 2783-0160 (Online)

(RESEARCH ARTICLE)

Check for updates

Eco-friendly products for sorption of fenamiphos, imidacloprid, and oxamyl pesticides from water and their detection by UV/VIS spectrophotometry

Azza G. A. Reyad [1,*], Moustafa A. Abbassy [1], Gehan I. Kh. Marei [1], Mohamed E. I. Badawy [2] and Entsar I. Rabea [1]

[1] *Department of Plant Protection, Faculty of Agriculture, Damanhour University, Damanhour 22516, Egypt.*
[2] *Department of Pesticide Chemistry and Technology, Faculty of Agriculture, 21545-El-Shatby, Alexandria University, Alexandria, Egypt.*

International Journal of Scientific Research Updates, 2023, 06(01), 040–058

Publication history: Received on 28 April 2023; revised on 20 June 2023; accepted on 23 June 2023

Article DOI: https://doi.org/10.53430/ijsru.2023.6.1.0045

Abstract

The present study evaluates the efficiency of the dry biomass of the microalgae *Spirogyra porticalis* and *Nannochloropsis oculata* for the removal of fenamiphos, imidacloprid, and oxamyl pesticides from water. The influence of incubation time, pesticide concentration, and algal biomass concentration on the degradation of pesticides were considered in the study. A rapid UV-Vis spectrophotometry method was developed and validated for the analysis and quantification of pesticides in the context of bioremediation with microalgae. The optimum conditions were obtained at 15 min, 50 mg/L pesticide concentration and 900 mg/L algal biomass with the response of 67.27% and 68.67 for fenamiphos by *S. porticalis* and *N. oculata*, respectively. For Imidacloprid, the optimum conditions were obtained at 15 min, 50 mg/L pesticide concentration and 900 mg/L algal biomass with the response of 28.20% and 35.55 for fenamiphos by *S. porticalis* and *N. oculata*, respectively. With the same, previse conditions the response of 65.71 and 81.31% for oxamyl by *S. porticalis* and *N. oculata*, respectively. This study confirmed that removing pesticides by the microalgae *S. porticalis* and *N. oculata* are both active and biomass of algae dependent. Consequently, these algae biomass exhibited a potential reduction of pesticides in contaminated water samples.

Keywords: Sorption; *Spirogyra porticalis*; *Nannochloropsis oculata*; Fenamiphos; Imidacloprid; Oxamyl; UV-Vis spectrophotometric method

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] .

* Corresponding author: Azza G. A. Reyad

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] .

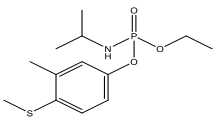
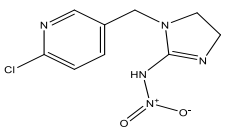
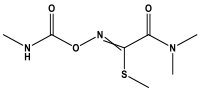
This study examined the ability of *Nannochloropsis oculata* and *Spirogyra porticalis* particles in the removal of fenamiphos, imidacloprid, and oxamyl pesticides from water. Pesticide residue concentrations were determined using UV/Vis spectrophotometry. The Plackett-Burman design was used to examine 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 Material 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**	**Chemical family**	**Molecular formula**	**Molecular mass (g mol^{-1})**	**Log K_{ow}**	**Henry's law constant (K_H) at 25°C**	**Water solubility (mgL^{-1}) at 20 °C**
Fenamiphos		Organoph-osphates	$C_{13}H_{22}NO_3PS$	303.3	3.23	9	400
Imidaclopri d		Neonicoti-noids	$C_9H_{10}ClN_5O_2$	255.6	0.57	1.65	610
Oxamyl		Carbamat es	$C_7H_{13}N_3O_3S$	219.2	-0.47	2.37	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 as shown in Table 2.

Table 2 Characteristics of *N. oculata* and *S. porticalis* biomass by NIRS instrument

Characteristics	**Percentages (%)**	
	N. oculata	***S. porticalis***
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

2.3 Experimental design

Table 3 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)

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: Y1 = A0 + A1X1 +A2X2 + A3X3 + AnXn where Y is the dependent variable, A0 the constant and A1 to An are the coefficients of the independent values and X1 to Xn 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 3. 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.

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 2. 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 2. 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] .

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 3. 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%).

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)
Removal (%) = 57.44+0.455 pH + 0.3647 incubation time -0.11111 pesticide concentration + 0.006199 algal biomass -8.17 $r^2 = 0.99$, s = 1.45398	..... (6)

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

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 (0.99and 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 $\alpha = 0.05$.

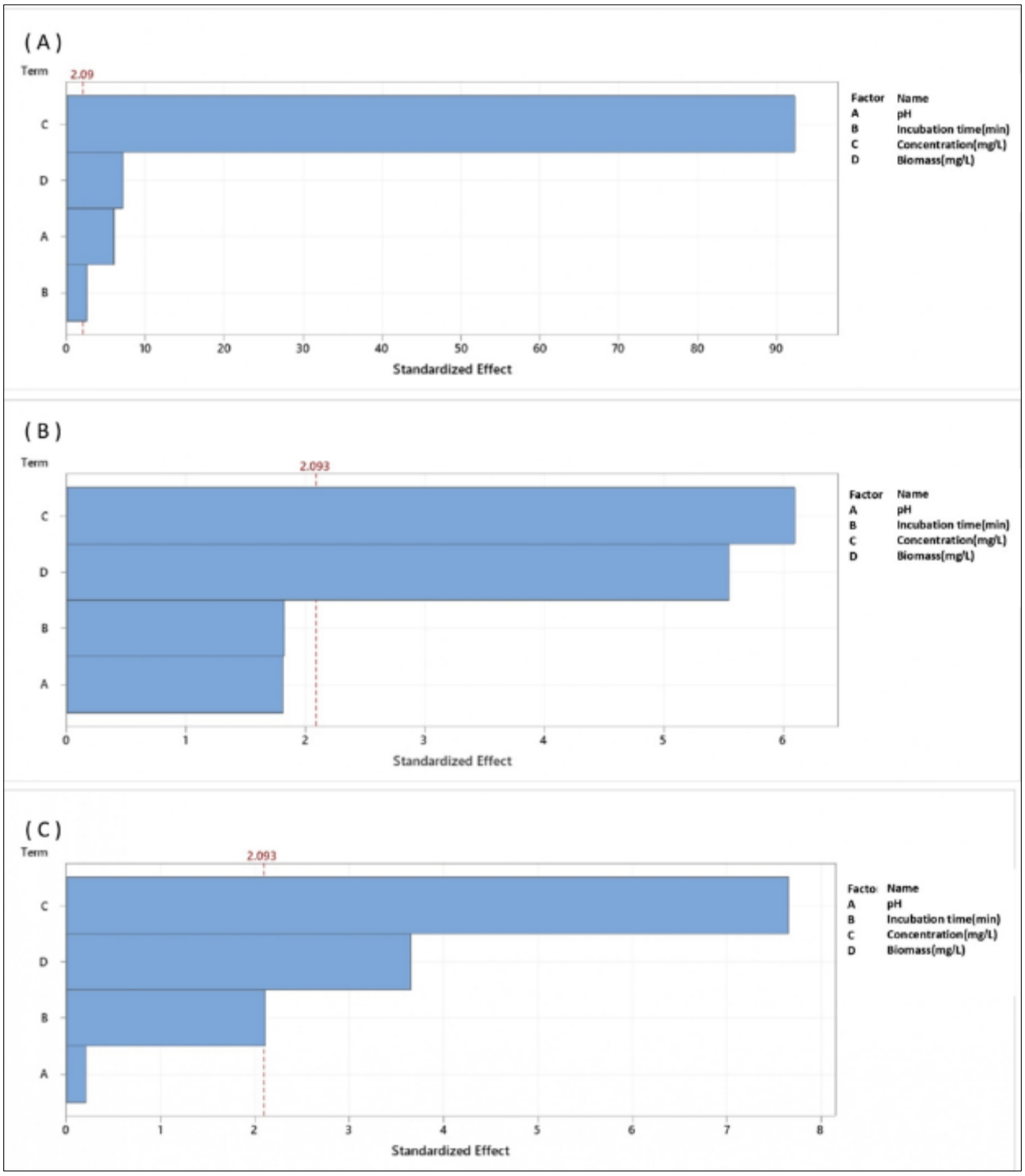


Figure 1 Pareto chart of standardized effect of *N. oculata* and incubation time and concentration disappearance of pesticides: (A) fenamiphos, (B) imidacloprid, and (C) oxamyl

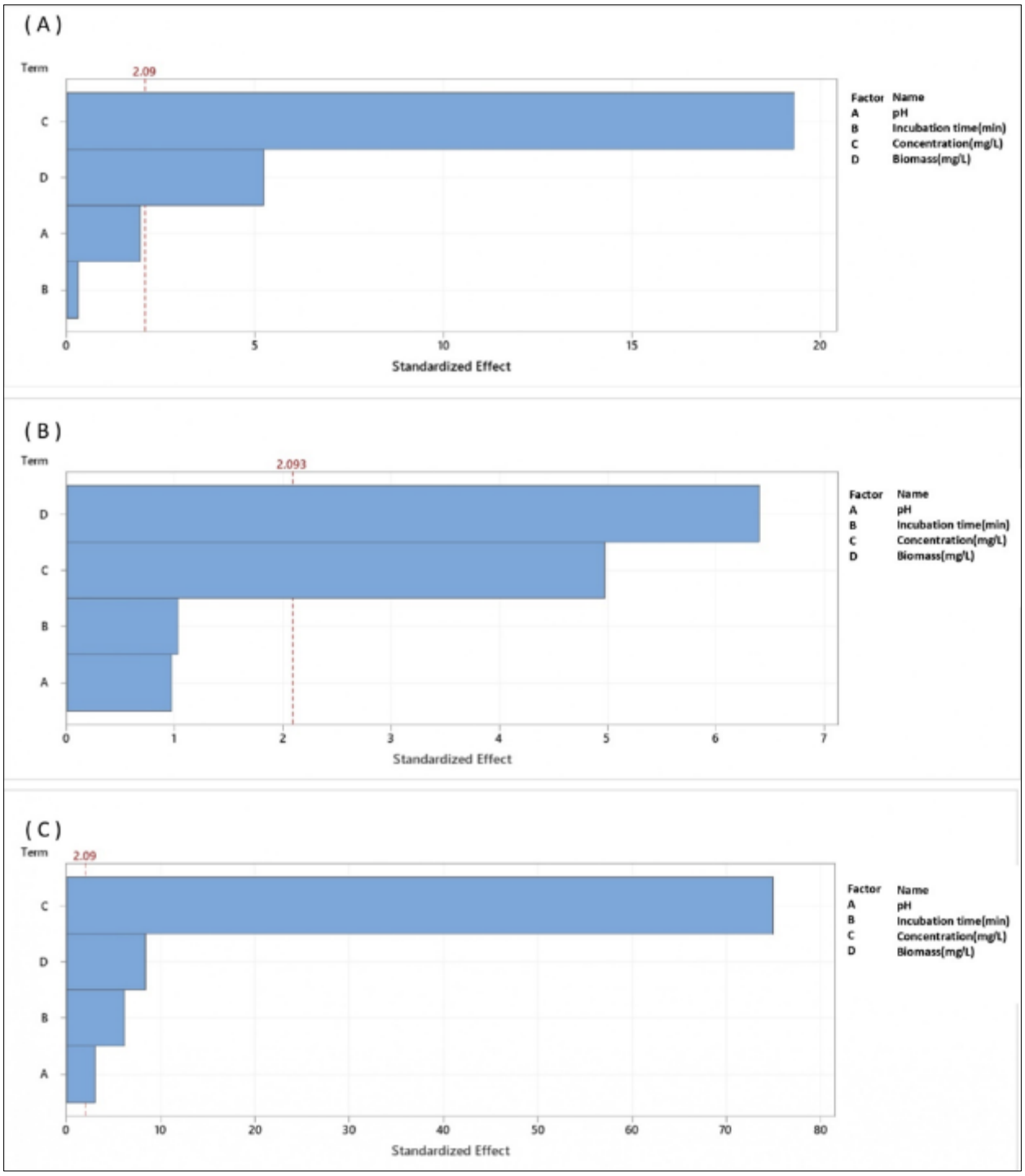


Figure 2 Pareto chart of standardized effect of *S. porticalis* and incubation time and concentration disappearance of pesticides: (A) fenamiphos, (B) imidacloprid, and (C) oxamyl

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. oculate* 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 incubation time 15 min, pesticide concentration 50 mg/L and algal biomass of *N. oculate* 900 mg/L with 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 incubation time 15 min, pesticide concentration 50 mg/L and the algal biomass of *N. oculate* 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 (%) ± SE of fenamiphos	Predicated removal (%)	Experimental removal (%) ± SE of imidacloprid	Predicated removal (%)	Experimental removal (%) ± SE by oxamyl	Predicated removal (%)
1	58.64^{f}±0.13	59.12	9.17^{abc} ±1.12	13.21	44.25^{d}±0.38	47.89
2	59.77^{f}±0.26	60.45	17.22^{efg}±0.64	15.89	45.34 ^{de}±4.76	56.79
3	10.61^{a}±0.66	12.47	7.29^{a}±0.16	6.94	26.57 ^{bc}±1.38	24.46
4	15.61±0.19	16.18	14.52^{cd} ±0.07	15.08	50.12^{d}±0.16	39.87
5	18.34^{d}±0.56	19.30	12.58^{bc} ±0.19	17.73	54.15^{ef}±0.62	40.74
6	14.52^{bc}±0.14	14.86	14.80^{cd} ±0.23	12.40	18.81^{ab}±0.35	30.97
7	68.67^{i}±0.74	67.27	35.55^{j}±1.10	26.68	68.10^{g}±0.55	73.07
8	13.32^{b} ±0.25	11.15	8.56^{abc} ±0.86	4.27	17.30 ^{ab}±2.03	15.56
9	66.93^{h}±0.72	64.16	21.39^{hi}±2.09	24.03	81.31^{h}±0.21	72.20
10	15.80^{c}±0.55	15.59	7.87^{ab} ±0.11	9.60	30.59^{c}±0.12	25.33
11	17.43^{d}±0.13	17.97	13.52^{bc} ±1.51	15.06	21.11^{ab}±0.17	31.84
12	62.16^{g}±0.46	62.83	19.44^{fgh}±1.61	21.35	69.85^{g}±0.13	63.30
13	15.86^{c}±0.41	15.59	7.84^{ab} ±0.06	9.60	12.61^{a}±0.34	25.33
14	62.98^{g}±0.31	63.56	18.72^{efg}±0.41	18.55	52.86^{def}±7.16	57.66
15	14.97^{c}±0.03	14.26	7.81^{ab} ±0.04	6.92	25.58^{bc}±3.23	16.43
16	65.88^{h}±0.12	65.95	22.99^{i}±0.68	24.01	60.48^{fg}±1.10	64.17
17	61.70^{g}±0.31	62.24	16.11^{def}±1.92	15.87	61.19^{fg}±0.69	48.76
18	33.19^{e}±0.07	33.19	16.10^{def}±0.33	16.10	26.42^{bc}±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.

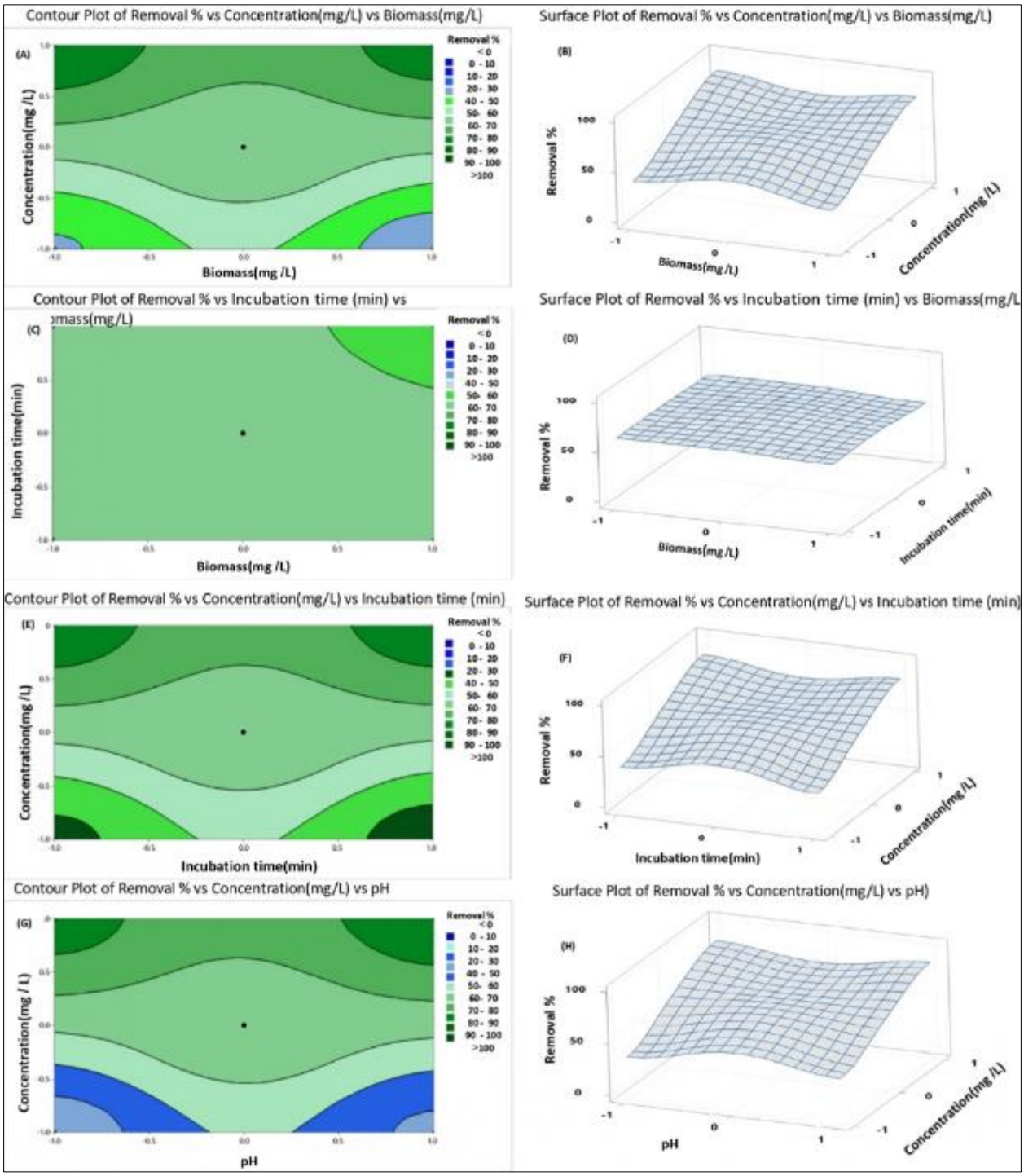


Figure 3 3D-response surface plots (left) and two-dimensional contour plots (right). (A and B): Effect of concentration and biomass (*N. oculata*) on removal of fenamiphos. (C and D): Effect of incubation time and biomass on removal of fenamiphos. (E and F): Effect concentration of fenamiphos and incubation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

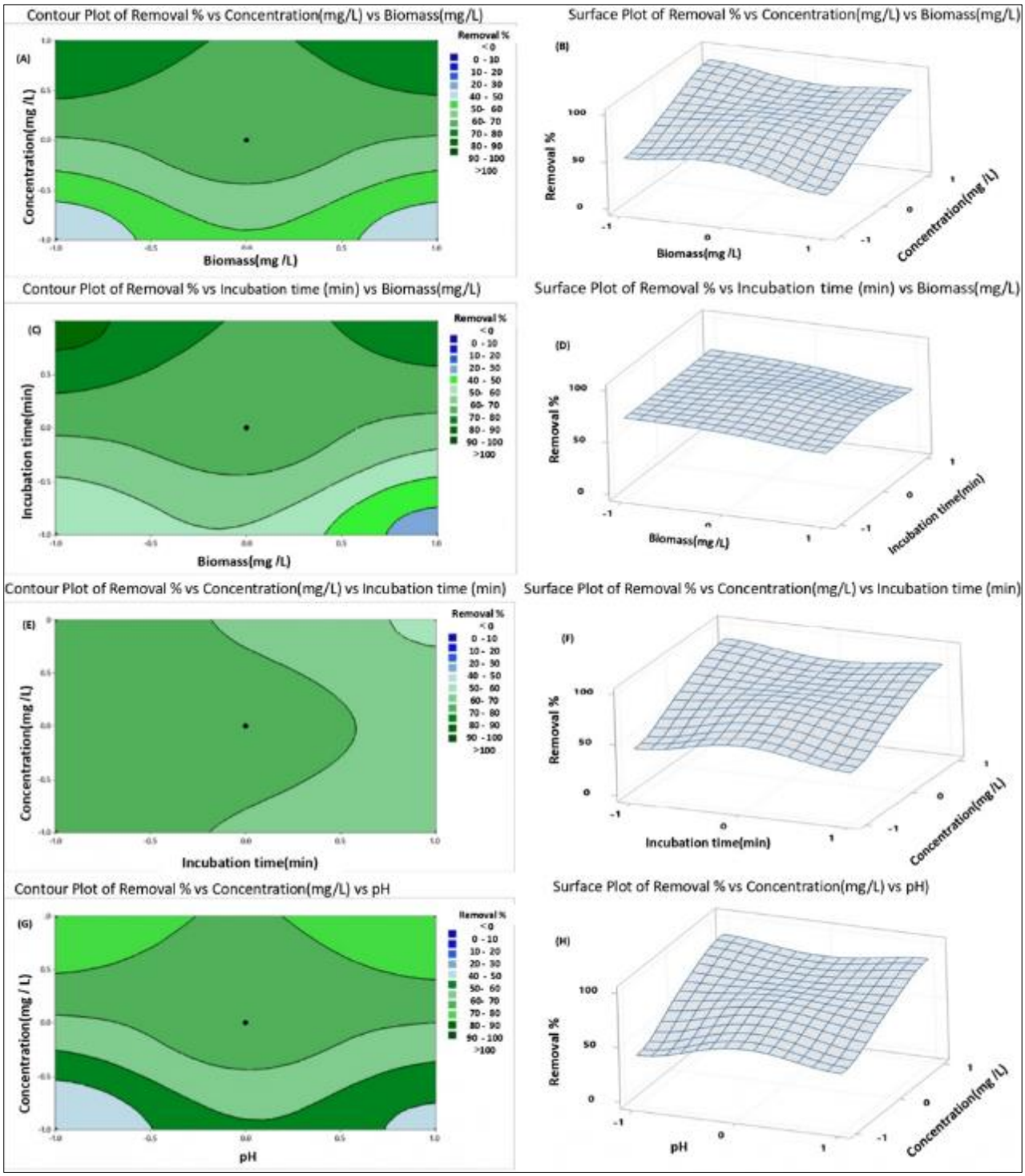


Figure 4 3D-response surface plots (left) and two-dimensional contour plots (right). (A and B): Effect of concentration and biomass (*S. porticalis*) on removal of fenamiphos. (C and D): Effect of incubation time and biomass on removal of fenamiphos. (E and F): Effect concentration of fenamiphos and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

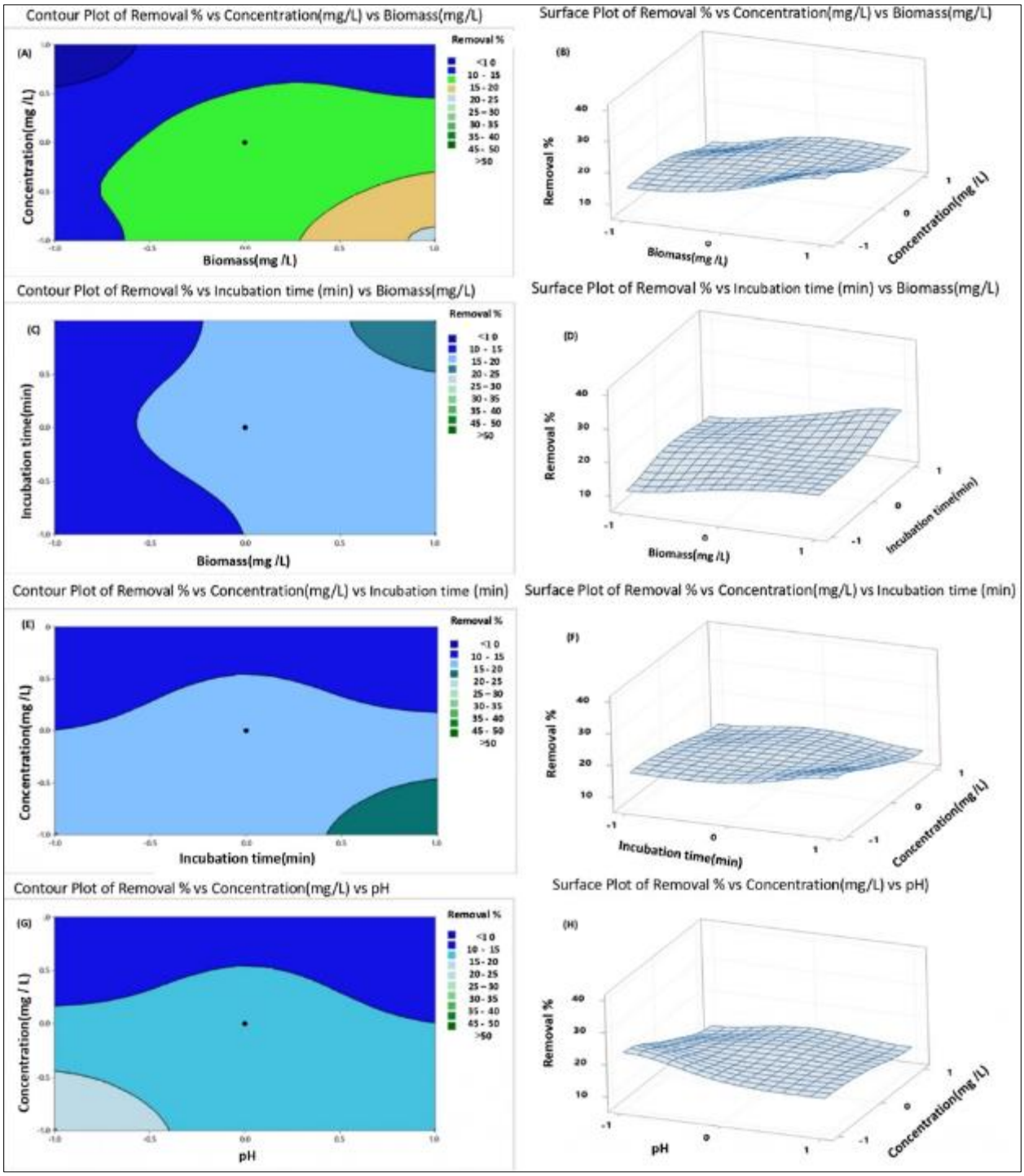


Figure 5 3D-response surface plots (left) and two-dimensional contour plots (right). (A and B): Effect of concentration and biomass (*N. oculata*) on removal of imidacloprid. (C and D): Effect of incubation time and biomass on removal of imidacloprid. (E and F): Effect concentration of imidacloprid and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

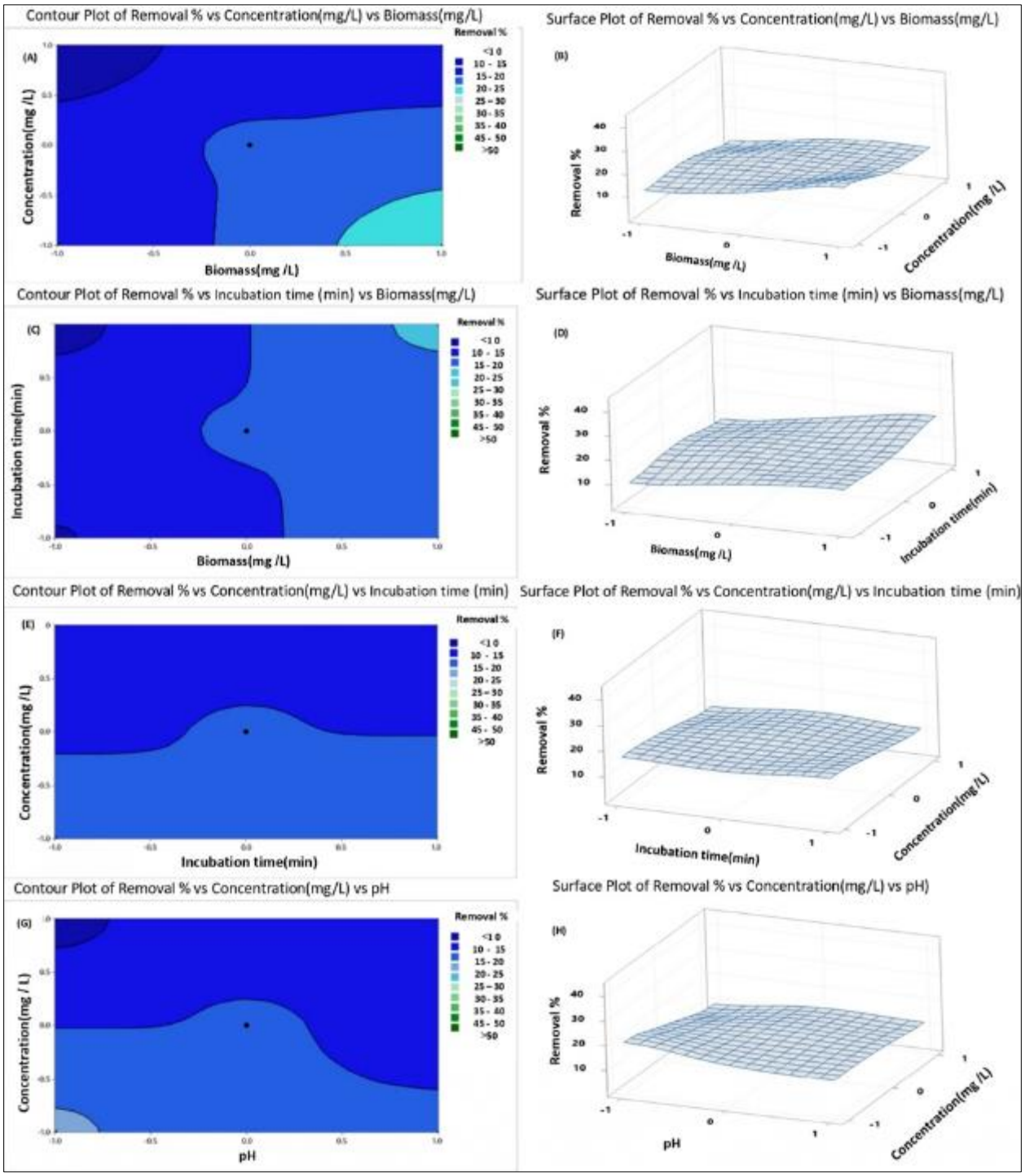


Figure 6 3D-response surface plots (left) and two-dimensional contour plots (right). (A and B): Effect of concentration and biomass (*S. porticalis*) on removal of imidacloprid. (C and D): Effect of incubation time and biomass on removal of imidacloprid. (E and F): Effect concentration of imidacloprid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

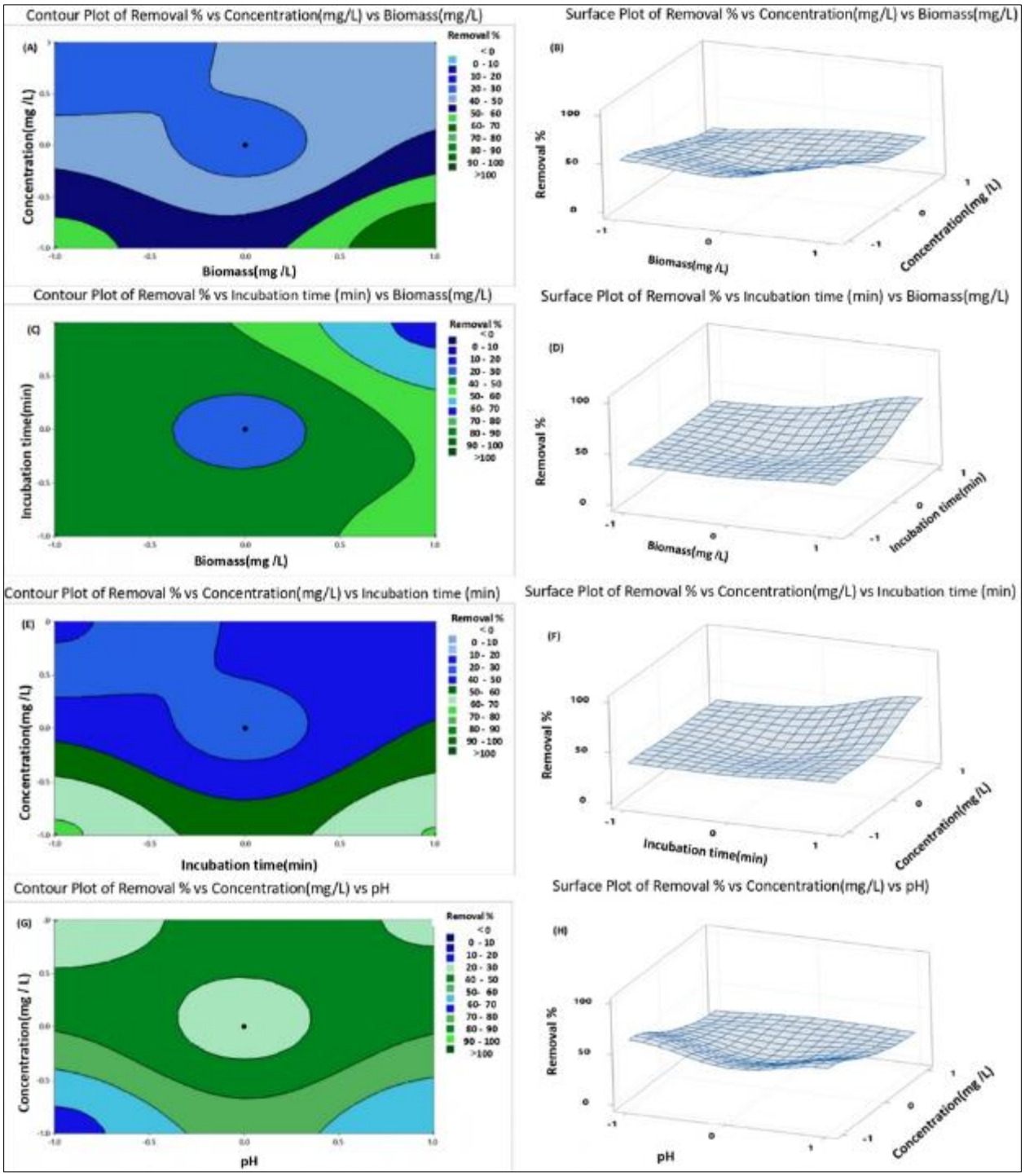


Figure 7 3D-response surface plots (left) and two-dimensional contour plots (right). (A and B): Effect of concentration and biomass (*N. oculata*) on removal of oxamyl. (C and D): Effect of incubation time and biomass on removal of oxamyl. (E and F): Effect concentration of oxamyl and incubation time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

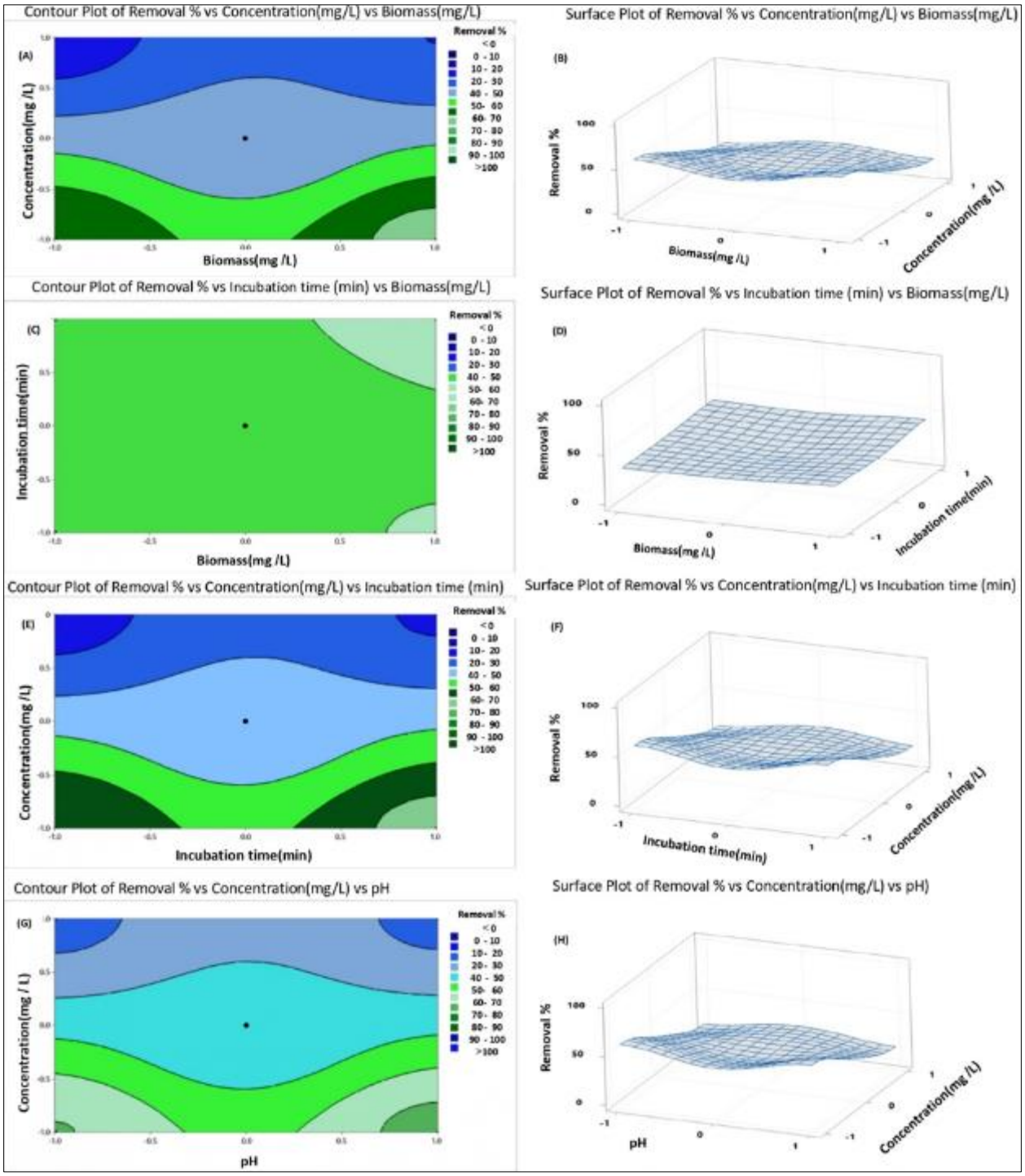


Figure 8 3D-response surface plots (left) and two-dimensional contour plots (right). (A and B): Effect of concentration and biomass (*S. porticalis*) on removal of oxamyl. (C and D): Effect of incubation time and biomass on removal of oxamyl. (E and F): Effect concentration of oxamyl and incubation time and biomass on 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 O_2, sequestration of CO_2, 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 Cu^{2+} ions from aqueous solutions. To determine the maximum amount of Cu^{2+} ions adsorbed onto *Nannochloropsis oculata* biomass, initial Cu^{2+} 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 $CaCl_2$ 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 sorbet 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].

4 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.

Compliance of ethical standard

Acknowledgments

I would like to extend my sincere thanks to Moustafa A. Abbassy, Entsar I. Rabea, Gehan I. Kh. Marei and Mohamed E. I. Badawy, they generously provided knowledge and expertise.

Disclosure of conflict of interest

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

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.

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 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.

Funding

This research did not receive any grant or specific funding from funding agencies in the public, commercial, or not-for-profit sectors.

References

[1] Cosgrove, S.; Jefferson, B.; Jarvis, P. J. E. T. R., Pesticide removal from drinking water sources by adsorption: a review. Environmental Technology Reviews, 8:1, 1-24, DOI: https://doi.org/10.1080/21622515.2019.1593514

[2] Ghanbarlou, H.; Nasernejad, B.; Fini, M. N.; Simonsen, M. E.; Muff, J. J. C. E. J., Synthesis of an iron-graphene based particle electrode for pesticide removal in three-dimensional heterogeneous electro-Fenton water treatment system. Chemical Engineering Journal. 2020, 395, 125025. DOI: https://doi.org/10.1016/j.cej.2020.125025

[3] Vacca, A.; Mais, L.; Mascia, M.; Usai, E.M.; Palmas, S. Design of Experiment for the Optimization of Pesticide Removal from Wastewater by Photo-Electrochemical Oxidation with TiO2 Nanotubes. Catalysts 2020, 10, 512. DOI: https://doi.org/10.3390/catal10050512

[4] Moradeeya, P. G.; Kumar, M. A.; Thorat, R. B.; Rathod, M.; Khambhaty, Y.; Basha, S. J. C., Nanocellulose for biosorption of chlorpyrifos from water: chemometric optimization, kinetics and equilibrium. Cellulose. 2017, 24,1319-1332. DOI: https://doi.org/10.1007/s10570-017-1197-x

[5] Trivedi, N. S.; Mandavgane, S. A. J. S.; Reviews, P., Fundamentals of 2, 4 dichlorophenoxyacetic acid removal from aqueous solutions. Separation & Purification Reviews. 2018, 47:4, 337-354.DOI: https://doi.org/10.1080/15422119.2018.1450765

[6] Joshiba, G. J.; Kumar, P. S.; Govarthanan, M.; Ngueagni, P. T.; Abilarasu, A. J. E. P., Investigation of magnetic silica nanocomposite immobilized Pseudomonas fluorescens as a biosorbent for the effective sequestration of Rhodamine B from aqueous systems. Environmental Pollution. 2021, 269, 116173.DOI: https://doi.org/10.1016/j.envpol.2020.116173

[7] Wang, J.-H.; Zhang, T.-Y.; Dao, G.-H.; Xu, X.-Q.; Wang, X.-X.; Hu, H.-Y. J. A. m.; biotechnology, Microalgae-based advanced municipal wastewater treatment for reuse in water bodies. Appl Microbiol Biotechnol. 2017, 101, 2659-2675. DOI: https://doi.org/10.1007/s00253-017-8184-x

[8] Hammed, A. M.; Prajapati, S. K.; Simsek, S.; Simsek, H. J. A., Growth regime and environmental remediation of microalgae. ALGAE , The Korean Society of Phycology. 2016, 31, 189-204. Crossref , Doi: https://doi.org/10.4490/algae.2016.31.8.28.

[9] Dirbaz, M.; Roosta, A. J. J. o. E. C. E., Adsorption, kinetic and thermodynamic studies for the biosorption of cadmium onto microalgae Parachlorella sp. Journal of Environmental Chemical Engineering. 2018,2302-2309. DOI: https://doi.org/10.1016/j.jece.2018.03.039

[10] Kiswandono, A.; Suharso, S.; Buhani, B.; Tugiyono, T.; Sumekar, D. W., Study of Water Quality of Way Umpu River, Way Kanan Regency, Lampung Province, Indonesia, Based on Differences of TSS, DO, BOD, COD, and Phosphate Levels in Mining Locations. LPPM-UNILA-IR.2021,1-13.DOI: http://repository.lppm.unila.ac.id/id/eprint/35617

[11] Encarnação, T.; Santos, D.; Ferreira, S.; Valente, A. J.; Pereira, J.; Campos, M.; Burrows, H. D.; Pais, A. A. J. B. o. E. C.; Toxicology, Removal of imidacloprid from water by microalgae Nannochloropsis sp. and its determination by a validated RP-HPLC method Bull Environ Contam Toxicol. 2021,107, 131–139. DOI: https://doi.org/10.1007/s00128-021-03228-1

[12] Liani, C.; Katoch, S. J. I. J. o. E.; Research, A., Biosorption of Malathion pesticide using Spirogyra sp. IJOEAR.2017, 15-20.

[13] Megharaj, M.; Singh, N.; Kookana, R. S.; Naidu, R.; Sethunathan, N. J. A. m.; biotechnology, Hydrolysis of fenamiphos and its oxidation products by a soil bacterium in pure culture, soil and water. Appl Microbiol Biotechnol . 2003, 61, 252-256. Doi: https://doi.org/10.1007/s00253-002-1206-2

[14] Qader, B.; Hussain, I.; Baron, M.; Jimenez-Perez, R.; Gonzalez-Rodriguez, J.; Gil-Ramírez, G. J. E., A Molecular Imprinted Polymer Sensor for Biomonitoring of Fenamiphos Pesticide Metabolite Fenamiphos Sulfoxide. Electroanalysis.2021, 33, 1129-1136. DOI: https://doi.org/10.1002/elan.202060599

[15] Cobas, M.; Meijide, J.; Sanromán, M.; Pazos, M. J. J. o. t. T. I. o. C. E., Chestnut shells to mitigate pesticide contamination. Journal of the Taiwan Institute of Chemical Engineers. 2016, 61, 166-173. DOI: https://doi.org/10.1016/j.jtice.2015.11.026

[16] Mohammad, S. G.; Ahmed, S. M.; Badawi, A. F. M. J. D.; Treatment, W., A comparative adsorption study with different agricultural waste adsorbents for removal of oxamyl pesticide. Desalination and Water Treatment . 2015, 55, 2109-2120. DOI: https://doi.org/10.1080/19443994.2014.930797

[17] Agarwal, S.; Sadeghi, N.; Tyagi, I.; Gupta, V. K.; Fakhri, A. J. J. o. c.; science, i., Adsorption of toxic carbamate pesticide oxamyl from liquid phase by newly synthesized and characterized graphene quantum dots nanomaterials. Journal of colloid and interface science. 2016, 478, 430-438.DOI: https://doi.org/10.1016/j.jcis.2016.06.029

[18] Vanaja, K.; Shobha Rani, R. J. C. r.; affairs, r., Design of experiments: concept and applications of Plackett Burman design. Clinical Research and Regulatory Affairs. 2007, 24, (1), 1-23.DOI: https://doi.org/10.1080/10601330701220520

[19] Liu, J.-Y.; Zeng, L.-H.; Ren, Z.-H. J. A. S. R., Recent application of spectroscopy for the detection of microalgae life information: A review. Applied Spectroscopy Reviews. 2020, 55, 26-59. DOI: https://doi.org/10.1080/05704928.2018.1509345

[20] Hamidi, N.; Yanuhar, U.; Wardana, I. J. I. J. o. E.; Engineering, E., Potential and properties of marine microalgae *Nannochloropsis oculata* as biomass fuel feedstock. Int J Energy Environ Eng 2014, 5, (4), 279-290. DOI: https://doi.org/10.1007/s40095-014-0138-9

[21] Haroun, A.; Matazu, I.; Abdulhamid, Y.; Sani, J. J. N. A. O. P.; SCIENCES, A., Molecular Identification of Green Algae, *Spirogyra porticalis*, along Parts of River Kaduna and its Potential for Singlecell Protein (SCP) Production. NIGERIAN ANNALS OF PURE AND APPLIED SCIENCES. 2018, 1, 38-43.DOI: https://doi.org/10.46912/napas.61

[22] López-Pacheco, I. Y.; Silva-Núñez, A.; García-Perez, J. S.; Carrillo-Nieves, D.; Salinas-Salazar, C.; Castillo-Zacarías, C.; Afewerki, S.; Barceló, D.; Iqbal, H. N.; Parra-Saldívar, R. J. J. o. E. M., Phyco-remediation of swine wastewater as a sustainable model based on circular economy. Journal of Environmental Management. 2021, 278, 111534.DOI: https://doi.org/10.1016/j.jenvman.2020.111534

[23] Mustafa, S.; Bhatti, H. N.; Maqbool, M.; Iqbal, M. J. J. o. W. P. E., Microalgae biosorption, bioaccumulation and biodegradation efficiency for the remediation of wastewater and carbon dioxide mitigation: Prospects, challenges and opportunities. Journal of Water Process Engineering.2021, 41, 102009.DOI: https://doi.org/10.1016/j.jwpe.2021.102009

[24] Nie, J.; Sun, Y.; Zhou, Y.; Kumar, M.; Usman, M.; Li, J.; Shao, J.; Wang, L.; Tsang, D. C. J. S. o. T. T. E., Bioremediation of water containing pesticides by microalgae: mechanisms, methods, and prospects for future research. Science of The Total Environment . 2020, 707, 136080.DOI: https://doi.org/10.1016/j.scitotenv.2019.136080

[25] Rizwan, M.; Mujtaba, G.; Memon, S. A.; Lee, K.; Rashid, N. J. R.; Reviews, S. E., Exploring the potential of microalgae for new biotechnology applications and beyond: a review. Renewable and Sustainable Energy Reviews. 2018, 92, 394-404.DOI: https://doi.org/10.1016/j.rser.2018.04.034

[26] Gîlcă, E.; Tănăselia, C.; Miclean, M.; Roman, C. J. A.-R. d. Ş. ş. P. A., Removal of Cu2+ ions from aqueous solutions using *Nannochloropsis oculata* biomass. Agricultura-Revistă de Ştiinţă şi Practică Agricolă . 2016, (3/4), 64-68.DOI: http://journals.usamvcluj.ro/index.ph...

[27] Cheng, Y.; Wang, H.; Deng, Z.; Wang, J.; Liu, Z.; Chen, Y.; Ma, Y.; Li, B.; Yang, L.; Zhang, Z. J. C., Efficient removal of Imidacloprid and nutrients by algae-bacteria biofilm reactor (ABBR) in municipal wastewater: Performance, mechanisms and the importance of illumination. Chemosphere. 2022, 135418. DOI: https://doi.org/10.1016/j.chemosphere.2022.135418

[28] Li, H.-B.; Cheng, K.-W.; Wong, C.-C.; Fan, K.-W.; Chen, F.; Jiang, Y. J. F. c., Evaluation of antioxidant capacity and total phenolic content of different fractions of selected microalgae. Food chemistry. 2007, 102, (3), 771-776. DOI: https://doi.org/10.1016/j.foodchem.2006.06.022

[29] Bishnoi, N. R.; Kumar, R.; Kumar, S.; Rani, S. J. J. o. H. M., Biosorption of Cr (III) from aqueous solution using algal biomass spirogyra spp. Journal of Hazardous Materials. 2007, 145, (1-2), 142-147.DOI: https://doi.org/10.1016/j.jhazmat.2006.10.093

[30] Mohan, S. V.; Ramanaiah, S.; Sarma, P. J. B. E. J., Biosorption of direct azo dye from aqueous phase onto Spirogyra sp. I02: Evaluation of kinetics and mechanistic aspects. Biochemical Engineering Journal. 2008, 38, (1), 61-69.DOI: https://doi.org/10.1016/j.bej.2007.06.014