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Modeling and optimization of independent factors influencing lead(II) biosorption from aqueous systems: A statistical approach

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ABSTRACT

Lead, [Pb(II)] is a major hazardous contaminant that exists in the soil, surface, and groundwater as a result of human activities. It is carcinogenic in nature and causes damage to the liver, kidney, and bones as well as the digestive, respiratory, and immune systems. As a result, the main purpose of this study was to prepare and employ modified powdered peanut shells as a biosorbent in the decontamination of lead(II) ions from aqueous solutions. The removal of lead(II) onto the biosorbent was modeled and optimized using the response surface methodology and the effects of three biosorption variables on two response variables were investigated using the central composite design of the response surface methodology. The optimization of lead(II) removal by the biosorbent shows that contact time, pH, and initial concentration had a significant influence on the removal efficiency and biosorption capacity of lead(II). This was shown by the response surface methodology where the interaction among the independent variables studied improved the biosorption of lead(II). Applying the central composite design, the optimized contact time (60.00 min), pH (6.00), and initial concentration (25.00 mg/L) gave a removal of 87.27% and biosorption capacity of 2.87 mg/g of lead(II) with the desirability of 1.00. The study revealed that the modified powdered peanut shells, a low-cost biosorbent was efficient in decontaminating lead(II) ions in the aqueous solutions. However, the biosorption process optimization was dependent on contact time, pH, and initial lead(II) concentration. The study recommends that the untreated form of the peanut shells should be used and the results compared with the present study.

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Introduction

Water pollution is currently a global issue, with heavy metals pollution being one of the most dangerous. As a result, scientists and engineers are particularly concerned about the removal of heavy metals due to their negative impacts on a variety of life forms [1,31,32]. Heavy metals such as lead(II), copper(II), mercury(II), chromium(VI), and nickel(II) frequently enter aquatic systems as a result of wastewater discharge from diverse manufacturing processes, causing environmental and human health problems [2,31].

Lead(II) is the most prevalent and one of the most dangerous heavy metal contaminants, entering water sources from a wide range of industrial activities such as mining, oil refining, metal plating, and finishing, and battery production [11,12]. Lead(II) is a carcinogen that damages the digestive, respiratory, and immune systems; it mostly affects the intelligence and nervous system in children [17]. The Environmental Protection Agency (EPA) and the World Health Organization (WHO) have set maximum contamination levels of lead(II) in drinking water at 15.00 and 50.00 μg/L, respectively [19].

Adsorption, precipitation, ion exchange, electrochemical treatment, flocculation, filtration, and ozonation are some of the treatment techniques and processes that have been used to remove lead(II) pollutants from water and wastewater [8,10]. These technologies, however, are costly and generate secondary wastes such as non-degradable organic contaminants and volatile compounds [37]. The adsorption using commercial activated carbon has been widely regarded as one of the most convenient and successful treatment strategies for lead(II) elimination among these several approaches. Activated carbon, on the other hand, is relatively expensive, hence this limitation motivated researchers to explore new cost-effective, long-lasting, and environmentally friendly adsorbents to replace commercial activated carbon in heavy metals removal [30].

Several studies have shown that agricultural wastes are versatile and can be used as low-cost biosorbents for the biosorption of both inorganic and organic wastes [6,8,13,29,35].

In the Northern part of Ghana, peanuts are highly produced and there are abundant peanut shells available as wastes, which are mostly stock-piled [36]. Although peanut shells as an agricultural waste are burned to produce energy for cooking, leftovers are still significant. Therefore, this study explored a biosorbent obtained from peanut shells to remove Pb(II) ions from aqueous systems by applying Response Surface Methodology (RSM) as a statistical approach. The RSM is a statistical experimental design that can be used to develop second-order polynomial equations with various factors and explain the interactive effect of the independent variables [16]. The RSM based on Central Composite Designs (CCD) is widely used in the optimization of biosorption processes and it requires a minimum number of experimentations.

This present study explores the applicability of the CCD-RSM approach to investigate the influence of independent factors such as contact time, pH, and initial concentration on lead(II) removal using modified powdered peanut shells (MPPS) as a biosorbent.

Materials and methods

Preparation of adsorbent

The peanut shells were collected from a local peanut oil processing factory in Ghana in the Upper East Region, Navrongo. To eliminate dust and other insoluble contaminants, the peanut shells were carefully washed with distilled water. The shells were then air-dried at ambient temperature for 24.00 h before being dried at 105.00 °C in an oven to achieve constant weight. The dried shells were crushed and sieved until a particle size of 3.00 mm was attained. The powdered peanut shells were chemically modified using phosphoric acid following steps specified in a study carried out by Dada et al. [18]. The acid-modified powdered peanut shells were then utilized as a biosorbent in the batch biosorption studies.

Preparation of adsorbate

All the chemicals used in this study were of analytical reagent grade, and the glassware was soaked with nitric acid (HNO_3), washed, and rinsed multiple times with distilled water before use. Procedures outlined in the study conducted by Bayuo et al. [11,12] were followed in the preparation of the stock solutions of the adsorbate, lead(II). A known weight (1.599 g) of lead nitrate, [$Pb(NO_3)_2$], was dissolved in 200.00 mL distilled water, then 10.00 mL concentrated HNO_3 was added, and the solution was diluted to the 1000 mL mark of the volumetric flask using de-ionized water. Working concentrations ranged from 15.00 to 100.00 mg/L were prepared from the stock solutions through the dilution of the stock solutions with de-ionized water to the desired concentrations.

Determination of lead(II) ions in the sample solutions

For the quantification of the concentration of lead(II) ions remaining in the liquid phase after the biosorption process, the dithizone method was used [4]. Where acidified sample solutions having microgram amount of lead(II) were combined with an ammoniacal citrate-cyanide reducing solution and extracted using dithizone in chloroform ($CHCl_3$) leading to the formation of cherry-red lead dithizonate. The absorbance of the colored solutions was then measured photometrically at a wavelength of 510.00 nm using a Cary 60 UV-Vis spectrophotometer and the corresponding concentrations were determined from the calibration curve. The calibration curve of Lead(II) is shown in Fig. 1.

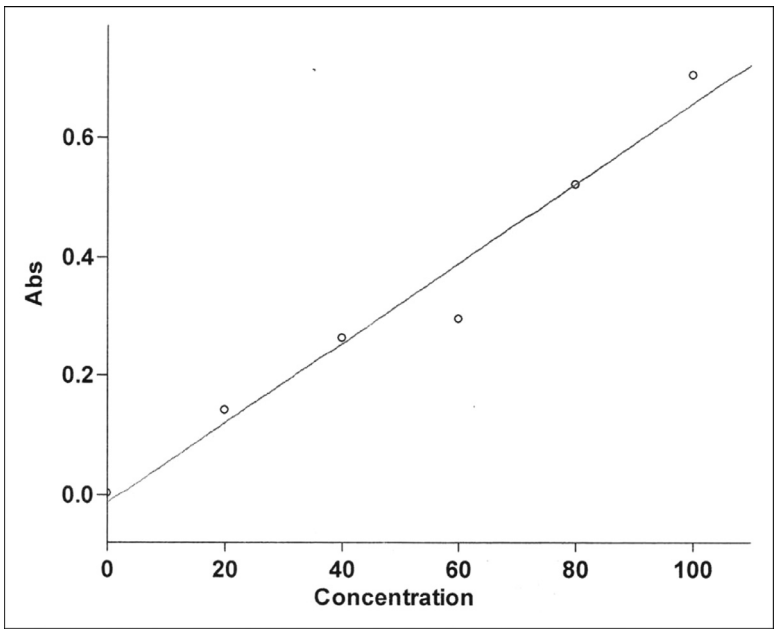

Fig. 1. Standard calibration curve used for the analysis of Pb(II).

Preliminary biosorption experiments

The biosorption of lead(II) onto the MPPS was studied in a batch mode. The independent factors such as contact time, solution pH, and lead(II) concentration were optimized using the CCD-RSM approach. The batch experiments were carried out using a 250 mL conical flasks containing 100 mL solutions with varying contact time (10.00–240.00 min), solution pH (2.00–10.00), and initial lead(II) concentration (15.00–100.00 mg/L), while the other parameters (particle size of 3.00 mm, dosage of 1.00 g/100 mL and ambient temperature) were constant. The solutions were stirred at 120.00 rpm and after the biosorption, the solutions were filtered using Whatman filter paper No. 42. The filtrates were analyzed using Carry 60 UV-Vis spectrophotometer. The removal efficiency and biosorption capacity were evaluated using the following Eqs. (1) and (2) [25],[7].

$$\text{Removal efficiency (\%)} = \left(C_0 - C_e/C_0\right) \times 100 \tag{1}$$

where C_0 is the initial metal ion concentration (mg/L) and C_e is the equilibrium metal ion concentration (mg/L).

The biosorption capacity (q_e) is given by Eq. (2).

$$q_e = \left(C_0 - C_e/m\right) \times V \tag{2}$$

where q_e represents the equilibrium mass of the adsorbed substance per unit mass of adsorbent, V is the volume of solution (mL) and m is the mass of the adsorbent (g).

Experimental design, modeling, and optimization

In the present study, the Central Composite Design (CCD) was utilized to design, model, and examine the optimum process factors for lead(II) biosorption using MPPS. The CCD involves only a small number of experimentations and helps in learning how the numerous factors interact thereby influencing the process [38]. The requisite number of experiments needed is usually estimated using Eq. (3):

$$N = 2^n + 2n + n_c \tag{3}$$

where N and n are the total numbers of experimentations and independent variables (factors) required, respectively, and n_c is the number of center points.

Three independent biosorption parameters [contact time (A), solution pH (B), and initial lead(II) concentration (C)] were considered for the optimization of the biosorption process. From the preliminary biosorption experiments, an upper and a lower limit was set for each of the three independent biosorption factors in designing 20 experimental runs using Eq. (3). The dependent factors (responses) that were taken into consideration are removal efficiency and biosorption capacity.

Table 1
Experimental design, modeling, and optimization constraints set for all factors and responses for the biosorption of lead(II).

Name	Goal	Lower Limit	Upper Limit
A: Contact time	maximize	60.00	90.00
B: solution pH	maximize	6.00	8.00
C: Initial concentration	maximize	25.00	75.00
Removal efficiency	maximize	50.98	98.53
Biosorption capacity	maximize	0.14	3.70

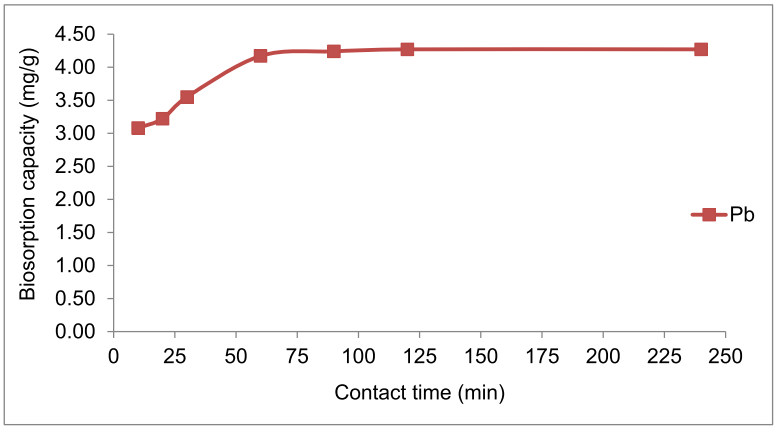

Fig. 2. Effect of contact time on the biosorption of lead(II) ions by MPPS.

The optimization process was divided into three stages: (1) statistically designing and conducting experiments, (2) developing and estimating coefficients in the regression model, and (3) response prediction and model adequacy validation. To achieve the optimum responses that equally satisfy all operating situations, numerical optimization employing the desirability function was applied [3].

In general, the desired goal of each factor and response is set in numerical optimization. For the responses, the goal is to maximize while for the factors, the goal is to set an exact value for each factor as summarized in Table 1.

Development of regression models equations and statistical analysis

Using second-order polynomial equations, each response (removal efficiency and biosorption capacity) was utilized to construct an empirical model that correlates the response to the three components of contact time (A), pH (B), and initial lead(II) concentration (C) given by Eq. (4) [26].

$$Y = b_0 + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} X_i X_j \tag{4}$$

where Y is the predicted response, b_0 is the constant coefficient, b_i is the linear coefficient, b_{ij} is the interaction coefficient, b_{ii} is the quadratic coefficient, X_i and X_j are the coded values for the factors.

The significance of the model equations and their terms were evaluated using statistical tools such as coefficient of determination (R-squared), Fisher value (F-value), probability (p-value), and residual [14].

Models validation

The models were validated by conducting a batch experiment under optimum operating conditions to compare the experimental values with predicted values under the optimum operating condition obtained.

Results and discussion

Preliminary biosorption experiments

The effect of contact time

The biosorption of lead(II) ions onto the MPPS during the variation of contact time is shown in Fig. 2. It was noted that the biosorption process occurred in two phases. The process was so quick within the first 10.00–30.00 min but at about

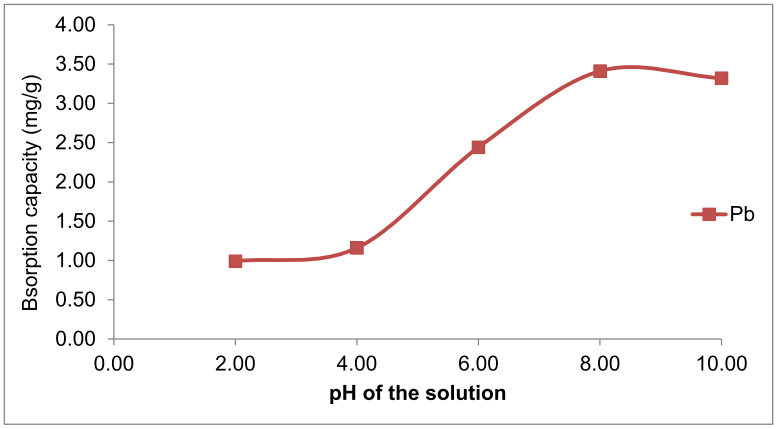

Fig. 3. Effect of solution pH on the biosorption of lead(II) ions by MPPS.

40 min, the lead(II) uptake capacity continues to increase gradually until an equilibrium was reached at approximately 90.00 min attaining a maximum uptake capacity of 4.27 mg/g and percentage removal of 84.80%, respectively. The influence of contact time reveals that there was rapid removal of lead(II) ions during the early stages of the biosorption system. This could be due to the large initial concentration gradient between the metal ions in the aqueous solution and the number of vacant sites available on the biosorbent surface [10]. The equilibrium time of 90.00 min for the removal of lead(II) was consistent with the equilibrium time (90.00 min) attained for the elimination of chromium(III) by activated carbon produced from baobab shells [33].

The effect of pH of the solution

The effect of pH on the biosorption of lead(II) on MPPS at different pH values is shown in Fig. 3, which indicates that the uptake capacity augmented with increasing solution pH, attaining an optimum uptake capacity at about pH of 8.00. It was observed that lead(II) biosorption capacity was higher at a pH of 2.00 and later reduced at a pH of 4.00. After a pH of 4.80, there was a rapid augmentation in the uptake capacity of lead(II) until an equilibrium was reached at a pH of 8.00. At the optimal pH value of 8.00, the MPPS was able to adsorb 3.41 mg/g of lead(II) ions giving a removal efficiency of 68.20%. At a higher solution pH, the MPPS surface is more negatively charged; leading to more electrostatic attractions to positively charged lead(II) ions attributable to the fact that the pH (5.50) of the point of zero charge (pH_{pzc}) of the biosorbent is lower than that of the solution pH [41]. The increase in the biosorption capacity of lead(II) by the MPPS with increasing pH was found to be consistent with other studies. For instance, Feng et al. [21], Taha et al. [40], and Liang et al. [28] have all reported an increase in the biosorption of heavy metals with increasing pH using grafted copolymerized orange peels, potato peels, and orange peels, respectively .

The effect of lead(II) initial concentration

The results of the influence of lead(II) initial concentration presented in Fig. 4 show that the removal efficiency (Fig. 4a) decreased gradually when lead(II) initial concentrations were increased. It was revealed that the removal efficiency of lead(II) decreased slightly as soon as the initial concentration increased from 15.00 to 25.00 mg/L. However, at about 50.00 mg/L, maximum lead(II) removal was reached at 80.80%. The biosorption process reached equilibrium faster at lower concentrations, which is probably due to a higher rate of adsorbing the available metal ions by the active sites of the biosorbent [20]. The results also indicate that the biosorption capacity (Fig. 4b) of lead(II) increased with increasing initial metal ion concentrations. At 75.00 mg/L, the optimum uptake capacity of lead(II) ions was attained at 2.48 mg/g. Hence, the increase in the biosorption capacity with increasing lead(II) initial concentration (Fig. 4b) is considered to be a consequence of the high probability of collision between the metal ions and biosorbent surface [42]. Kumar et al. [27] affirmed a comparable situation in cadmium(II) removal where the adsorption capacity was observed to increase from 2.67 to 11.10 mg/g when the initial metal ion concentration was amplified from 10.00 to 50.00 mg/L.

Development of regression model equations using CCD

The complete design matrix of the independent factors, their ranges (in terms of coded and uncoded points), and their corresponding response values of removal efficiency (Y1) and biosorption capacity (Y2) are presented in Table 2. The removal efficiency (Y1) and biosorption capacity (Y2) ranged between 50.98 and 98.53% and 0.14 and 3.70 mg/g, respectively.

The quadratic models were chosen as recommended by the software from the model summary statistics shown in Tables 3 and 4, respectively since the additional terms were significant and the models were not aliased [34]. Based on the fact that the quadratic models for the responses Y1 and Y2 were not aliased, they could be used to characterize the relationship between the responses Y1 and Y2 and the interactive variables (factors).

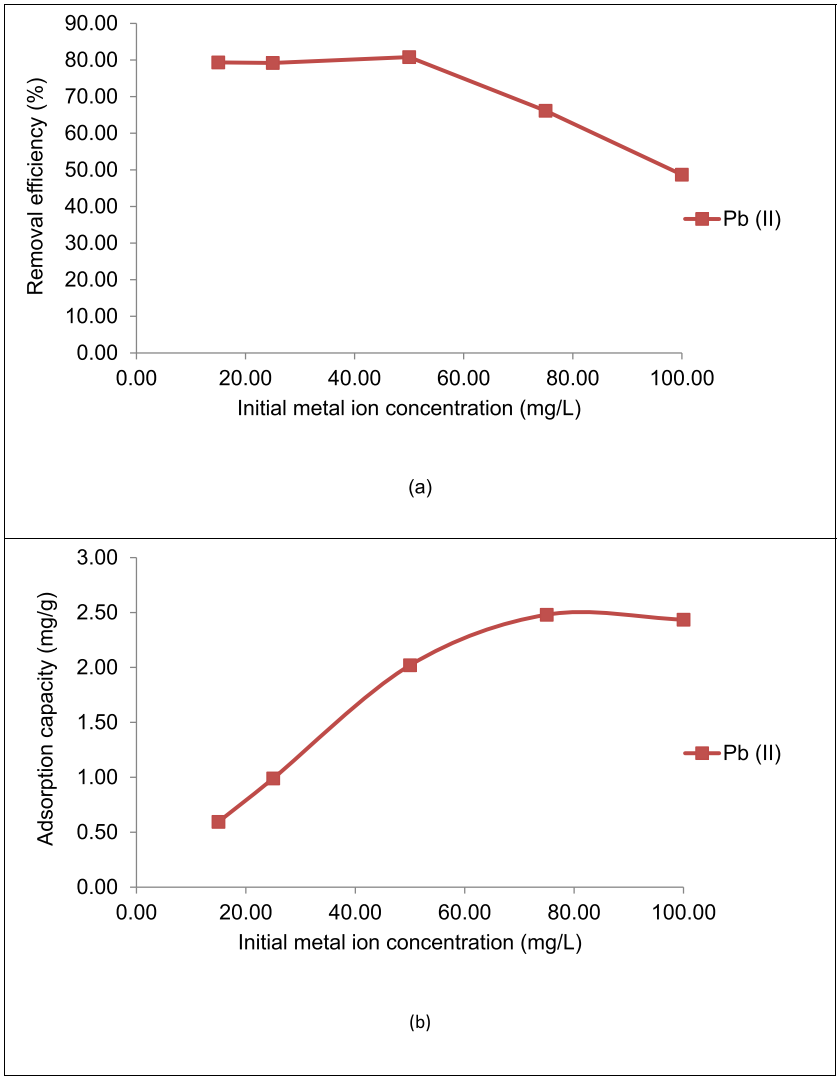

Fig. 4. Effect of initial concentration on the biosorption of lead(II) ions by MPPS.

Table 5 (response Y1) shows that the quadratic model had a small standard deviation of 6.22 and high R^2 (0.9624) with predicted R^2 (0.8745) that is in reasonable agreement with adjusted R^2 (0.9238). More so, in Table 6 (response Y2), the quadratic model had a small standard deviation of 0.63, high R^2 (0.9798), predicted R^2 (0.8972), and adjusted R^2 (0.9576). The R^2 values of both responses were close to unity with smaller standard deviations indicating the suitability of the models in predicting the responses [3]. However, a high R^2 value does not always mean that the regression model is good, and such inferences may only be made if the corrected R^2 value is also high [14]. Basically, the difference between the adjusted R^2 and predicted R^2 should be within 0.20 for the regression model to be in good agreement. This criterion was met in this investigation because the difference between the adjusted R^2 and predicted R^2 values for both responses is less than 0.20. This indicates that the model for each response is extremely significant and that the experimental and predicted values of removal efficiency and biosorption capacity are in good agreement. From Tables 5 and 6, both responses had appropriate precisions of larger than 4.00, indicating that the models were in good agreement and highly significant. The predicted R^2 values of 0.8745 and 0.8972 for responses Y1 and Y2, respectively, show that the models were adequate and offer 87.45% and 89.72% variability in the prediction of the removal efficiency and biosorption capacity beyond the experimental range of process conditions during lead(II) biosorption. The R^2 values of 0.9624 and 0.9798 also suggest that 96.24% and 97.98% of the variation in removal efficiency and biosorption capacity, respectively could be due to the three independent factors considered.

Table 2
Design matrix of lead(II) biosorption factors and their respective responses from the experiments.

	Coded factors			Uncoded factors			Y 1	Y 2
Run	A (min)	B	C (mg/L)	A (min)	B	C (mg/L)	Removal efficiency %	Biosorption capacity mg/g
1	1.000	−1.000	1.000	90.00	6.00	75.00	53.20	1.33
2	1.000	1.000	−1.000	90.00	8.00	25.00	57.20	0.72
3	0.000	0.000	0.000	75.00	7.00	50.00	79.20	2.97
4	1.000	1.000	1.000	90.00	8.00	75.00	84	1.05
5	−1.000	−1.000	−1.000	60.00	6.00	25.00	98.53	3.70
6	−1.000	1.000	−1.000	60.00	8.00	25.00	51.20	0.64
7	1.000	−1.000	−1.000	90.00	6.00	25.00	55.40	0.14
8	−1.000	1.000	1.000	60.00	8.00	75.00	76.67	2.88
9	0.000	0.000	0.000	75.00	7.00	50.00	60.60	1.52
10	−1.000	−1.000	1.000	60.00	6.00	75.00	92.00	1.05
11	0.000	0.000	−1.682	75.00	7.00	7.96	65.00	1.63
12	0.000	1.682	0.000	75.00	8.68	50.00	81.33	3.05
13	0.000	0.000	1.682	75.00	7.00	92.04	61.40	1.54
14	1.682	0.000	0.000	100.23	7.00	50.00	75.60	1.89
15	0.000	0.000	0.000	75.00	7.00	50.00	77.20	1.93
16	0.000	0.000	0.000	75.00	7.00	50.00	82.51	2.80
17	0.000	−1.682	0.000	75.00	5.32	50.00	50.98	0.20
18	−1.682	0.000	0.000	49.77	7.00	50.00	70.80	1.77
19	1.000	−1.000	1.000	90.00	6.00	75.00	53.20	1.33
20	1.000	1.000	−1.000	90.00	8.00	25.00	57.20	0.72

Table 3
Model summary statistics for removal efficiency (response Y1).

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	Comment
Linear	21.34	0.6423	0.4567	0.0933	9654.12	
2FI	16.78	0.5876	0.3420	−0.6983	1454.65	
Quadratic	6.22	0.9624	0.8745	0.9238	4794.15	Suggested
Cubic	9.11	0.9476	0.8932	−18.3429	1.8765E+07	Aliased

Table 4
Model summary statistics for biosorption capacity (response Y2).

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	Comment
Linear	0.4823	0.8423	0.8108	0.7553	5.42	
2FI	0.5340	0.8454	0.7681	0.4310	12.59	
Quadratic	0.6341	0.9798	0.8972	0.9596	3.02	Suggested
Cubic	0.1876	0.9654	0.9478	−3.1120	81.28	Aliased

Table 5
Fit Statistics for removal efficiency (response Y1).

Std. Dev.	6.22	R^2	0.9624
Mean	70.96	Adjusted R^2	0.9238
C.V.%	8.77	Predicted R^2	0.8745
		Adequate Precision	14.5428

Table 6
Fit Statistics for biosorption capacity (response Y2).

Std. Dev.	0.6341	R^2	0.9798
Mean	3.85	Adjusted R^2	0.9596
C.V.%	16.47	Predicted R^2	0.8897
		Adequate Precision	36.5120

Considering the results in Table 7, the quadratic models were selected as suggested by the software and Eqs. (5) and (6) gave the response surface model equations in their coded values.

$$Y1 = +58.30 - 5.61\,A + 0.70\,B + 5.51\,C + 1.55\,AB + 9.62\,AC + 1.25\,BC + 6.36\,A^2 + 7.00\,B^2 + 3.80\,C^2 \quad (5)$$

$$Y2 = +1.77 - 0.0964\,A - 0.3074\,B + 0.7169\,\mathrm{C} + 0.5894AB + 0.6744\,AC + 0.0906\,BC \quad (6)$$

Table 7
ANOVA for Quadratic model for removal efficiency (response Y1).

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value	Remark
Block	23.42	1	23.42			
Model	2893.06	9	321.45	3.48	0.0385	significant
A-Contact time	429.30	1	429.30	4.65	0.0593	significant
B-pH	6.76	1	6.76	0.07	0.7928	
C-Initial concentration	415.17	1	415.17	4.50	0.0629	
AB	19.22	1	19.22	0.21	0.6589	
AC	739.84	1	739.84	8.02	0.0197	significant
BC	12.50	1	12.50	0.14	0.7213	
A^2	583.26	1	583.26	6.32	0.0331	significant
B^2	705.73	1	705.73	7.65	0.0219	significant
C^2	207.73	1	207.73	2.25	0.1677	
Residual	830.27	9	92.25			
Lack of Fit	737.92	5	147.58	6.39	0.682	Not significant

Table 8
ANOVA for Quadratic model for biosorption capacity (response Y2).

Source	Sum of Squares	df	Mean Square	*F*-value	*p*-value	Remark
Block	0.0295	1	0.0295			
Model	14.920	6	2.4900	4.90	0.0094	significant
A-Contact time	0.1268	1	0.1268	0.25	0.6263	
B-pH	1.2900	1	1.2900	2.54	0.1368	
C-Initial concentration	7.0200	1	7.0200	13.83	0.0029	significant
AB	2.7800	1	2.7800	5.47	0.0374	significant
AC	3.6400	1	3.6400	7.17	0.0201	significant
BC	0.0657	1	0.0657	0.13	0.7253	
Residual	6.0900	12	0.5076			
Lack of Fit	4.6600	8	0.5831	1.64	0.3339	Not significant

From response Y1 model Eq. (5), it can be seen that the factors that have a positive effect on the removal efficiency of lead(II) are B, C, AB, AC, BC A^2, B^2 and C^2. Whilst for response Y2 model Eq. (6), factors like AB, AC, and BC have a positive influence on the biosorption capacity of lead(II). The negative values in both responses (Y1 and Y2) model equations indicate an inverse relationship and positive values favored the optimization of the process conditions.

Statistical and graphical analysis

The ANOVA component of the CCD was used to assess the importance and suitability of the model equations selected for removal efficiency (response Y1) and biosorption capacity (response Y1). From Tables 7 and 8, the model terms for both responses (Y1 and Y2) have *p*- values less than 0.05 and *F*-values of 3.48 and 4.90, respectively. The higher *F*-values indicate that the model terms have the most significant effect on the response function, while $p < 0.05$ suggests that the models were very significant.

In the response surface quadratic model for removal efficiency (response Y1), the significant model terms were discovered to be A, AC, A^2 and B^2 and the model term AC was found to have the greatest influence on the response with an *F*-value of 8.02. The influence of the model terms is in the order of $AC > B^2 > A^2 > A$. Also, the quadratic model for the biosorption capacity (response Y2) was found to have significant model terms as C, AB, and AC and the model term with the most significant influence on the response is C having an *F*-value of 7.02. The effect of the model terms is in the order of $C > AB > AC$. The lack of fit *F*-values of the responses Y1 and Y2 were found to be insignificant because the *p*-values were greater than 0.05, showing that the models were accurate.

Interactive effect of the independent factors

The combined effect between the three independent variables (A- contact time, B- solution pH, and C- initial concentration) and two dependent variables (Y1- removal efficiency and Y2- biosorption capacity were studied. The actual versus predicted values of responses Y1 and Y2 of lead(II) were plotted. Fig. 5 depicts the relationship between the predicted and actual values of the quadratic model, from the graph it is observed that the data points were mostly positioned close together around the straight line of best fit. This development shows orderliness between the predicted and experimental data, thereby confirming the significance of the regression models [23]. A similar observation was made by Shafaghat and Ghaemi [39] who conducted a comparative study on Pb(II) removal using ground granulated blast-furnace and phosphorus slags as adsorbents, where the data points on the plot were found to fall within the straight line.

Furthermore, from the 3-D surface plot presented in Fig. 6, it is observed that as both contact time and pH of the solution increase at a constant initial concentration (25.00 mg/L), the removal efficiency and biosorption capacity also upsurge. This

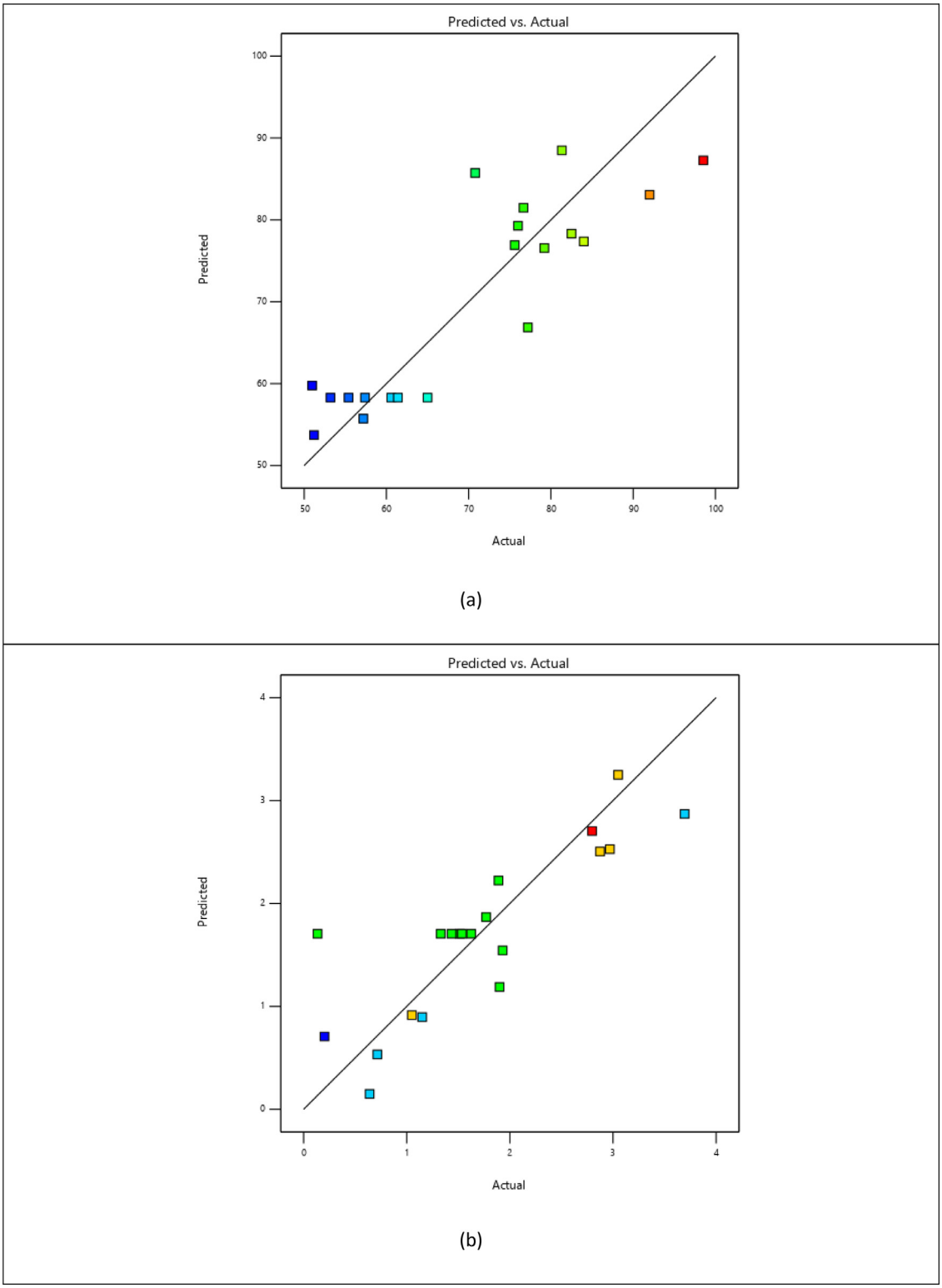

Fig. 5. Predicted versus Actual values of response Y1 (a) and response Y2 (b).

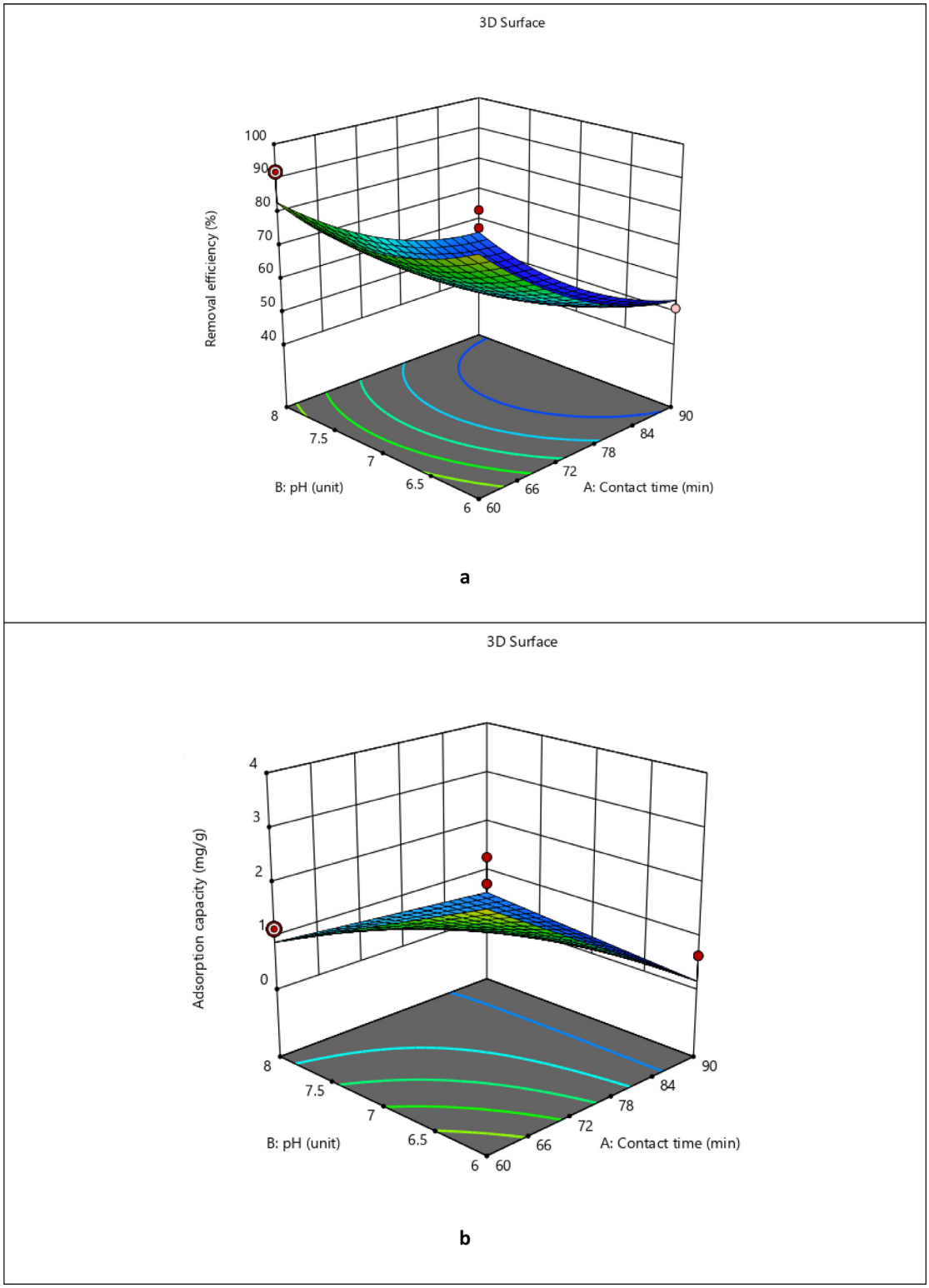

Fig. 6. The combined effect of factors A-B on responses Y1 (a) and Y2 (b) on lead(II) biosorption.

Table 9
36 Solutions for the optimization of lead(II) biosorption.

Number	Contact time	pH	Initial concentration	Removal efficiency(%)	Biosorption capacity(mg/g)	Desirability	Selected
1	60.000	6.000	25.000	87.270	2.870	1.000	
2	60.108	6.000	25.000	87.059	2.860	0.999	
3	60.000	6.008	25.000	87.135	2.862	0.999	
4	60.000	6.000	25.228	87.152	2.869	0.998	
5	60.000	6.017	25.028	86.977	2.853	0.997	
6	60.000	6.000	25.463	87.027	2.867	0.997	
7	60.296	6.000	25.000	86.692	2.843	0.997	
8	60.001	6.020	25.000	86.946	2.850	0.997	
9	60.000	6.000	25.736	86.892	2.865	0.995	
10	60.116	6.023	25.000	86.682	2.837	0.995	
11	60.309	6.000	25.251	86.539	2.841	0.995	
12	60.522	6.001	25.000	86.236	2.822	0.994	
13	60.000	6.039	25.000	86.653	2.832	0.993	
14	60.000	6.052	25.000	86.454	2.819	0.991	
15	60.000	6.066	25.000	86.245	2.806	0.989	
16	60.002	6.000	26.722	86.392	2.858	0.988	
17	61.061	6.000	25.000	85.215	2.774	0.988	
18	60.000	6.084	25.000	85.964	2.787	0.986	
19	61.404	6.000	25.000	84.565	2.743	0.984	
20	61.670	6.000	25.000	84.064	2.719	0.981	
21	60.001	6.121	25.000	85.420	2.751	0.979	
22	60.000	6.000	28.235	85.658	2.848	0.978	
23	62.029	6.000	25.000	83.396	2.686	0.977	
24	60.000	6.000	28.429	85.566	2.847	0.977	
25	60.000	6.181	25.000	84.584	2.691	0.969	
26	60.000	6.000	29.684	84.977	2.838	0.968	
27	62.912	6.000	25.000	81.783	2.606	0.967	
28	60.000	6.000	30.004	84.830	2.836	0.965	
29	61.173	6.169	25.057	82.470	2.604	0.958	
30	60.000	6.257	25.002	83.596	2.617	0.955	
31	60.000	6.070	30.811	83.392	2.763	0.948	
32	64.540	6.000	25.000	78.923	2.459	0.947	
33	60.000	6.000	34.599	82.858	2.804	0.931	
34	65.790	6.000	25.000	76.831	2.345	0.931	
35	63.801	6.000	30.068	78.228	2.525	0.922	
36	60.000	6.117	42.070	78.505	2.645	0.853	

suggests the combined effect of varying contact time and pH of the solution at the same time during lead(II) removal while keeping initial concentration constant. The combined effect was higher at greater values of the two independent factors. It is found that equilibrium is more likely to be attained at increasing contact time, which may result in maximal removal of the heavy metal ions from the aqueous phase [5]. Also, the increase in the removal efficiency and biosorption capacity with increasing pH is due to the upsurge of the negative charges on the biosorbent surface, which enhances the adsorption of the cation, Pb(II) [24].

More so, the 3-D surface plot presented in Fig. 7 shows that at constant pH of the solution (6.00), both the removal efficiency and biosorption capacity rise with increasing contact time and initial lead(II) concentration indicating the combined influence of these biosorption parameters on the decontamination of lead(II) ions from the aqueous systems. A decrease in the values of any of the factors significantly reduces the responses and vice versa. This is because a decrease in the initial metal ion concentration leads to a decline in the driving force for mass transfer, which is attributable to the lower uptake capacity of Pb(II) ions [43].

Besides, Fig. 8 of the 3-D surface plot demonstrates the same trend. Where at a constant contact time (60.00 min), both responses (removal efficiency and biosorption capacity) increase with rising pH of the solution and lead(II) initial concentration. The removal efficiency and uptake capacity show dependence on both factors and the collective influence was higher at greater values of the two independent factors.

Optimization of the biosorption process

The goal of optimization is to find the optimal operating condition for removing lead(II) ions from aqueous systems by the MPPS. The major goal is to maximize removal efficiency and biosorption capacity to achieve the optimum possible percentage removal and uptake capacity. The best condition for getting optimal results was determined using the desirability function. To optimize the biosorption process of lead(II) removal, the software selected and confirmed the most desirable experimental setting as presented in Fig. 9. The optimal operating condition for the decontamination of lead(II) by the MPPS was attained as follows: A- Contact time = 60.00 min, B- Solution pH = 6.00, and C-Initial concentration = 25.00 mg/L with the desirability of 1.00 after seeking 36 solutions (Table 9) to optimize the operating variables affecting lead(II) removal. The

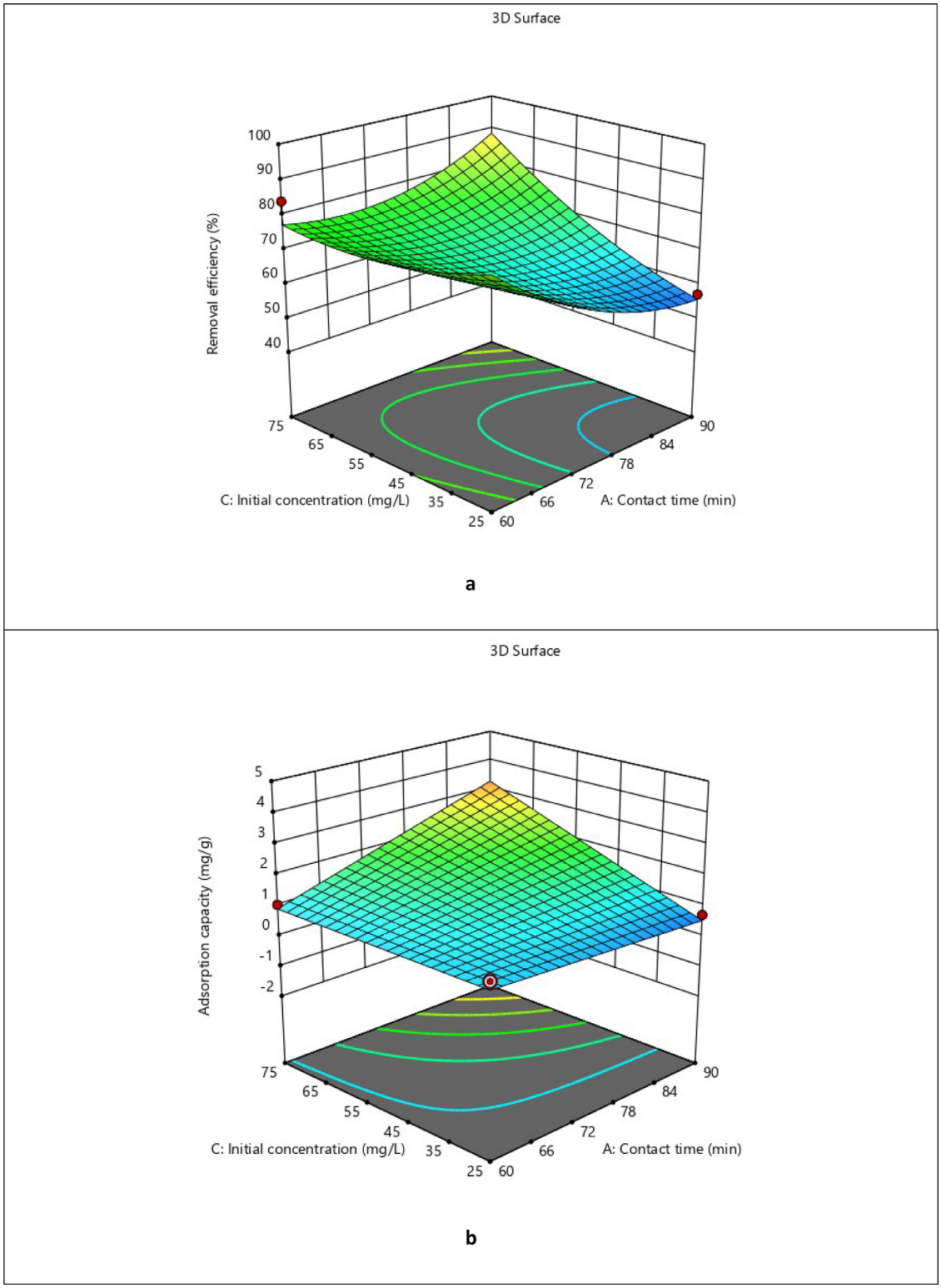

Fig. 7. The combined effect of factors A-C on responses Y1 (a) and Y2 (b) on lead(II) biosorption.

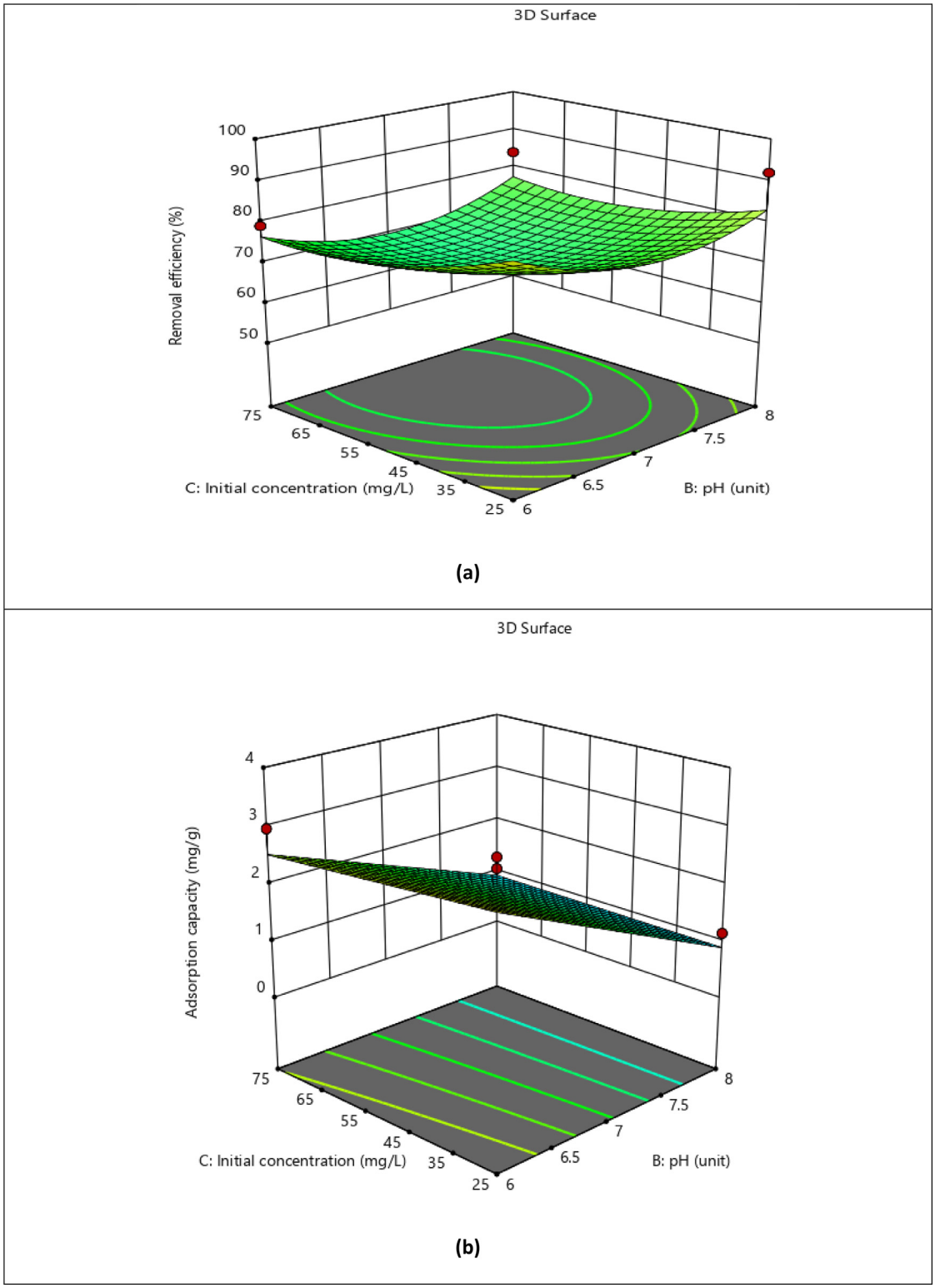

Fig. 8. The combined effect of factors B-C on responses Y1 (a) and Y2 (b) on lead(II) biosorption.

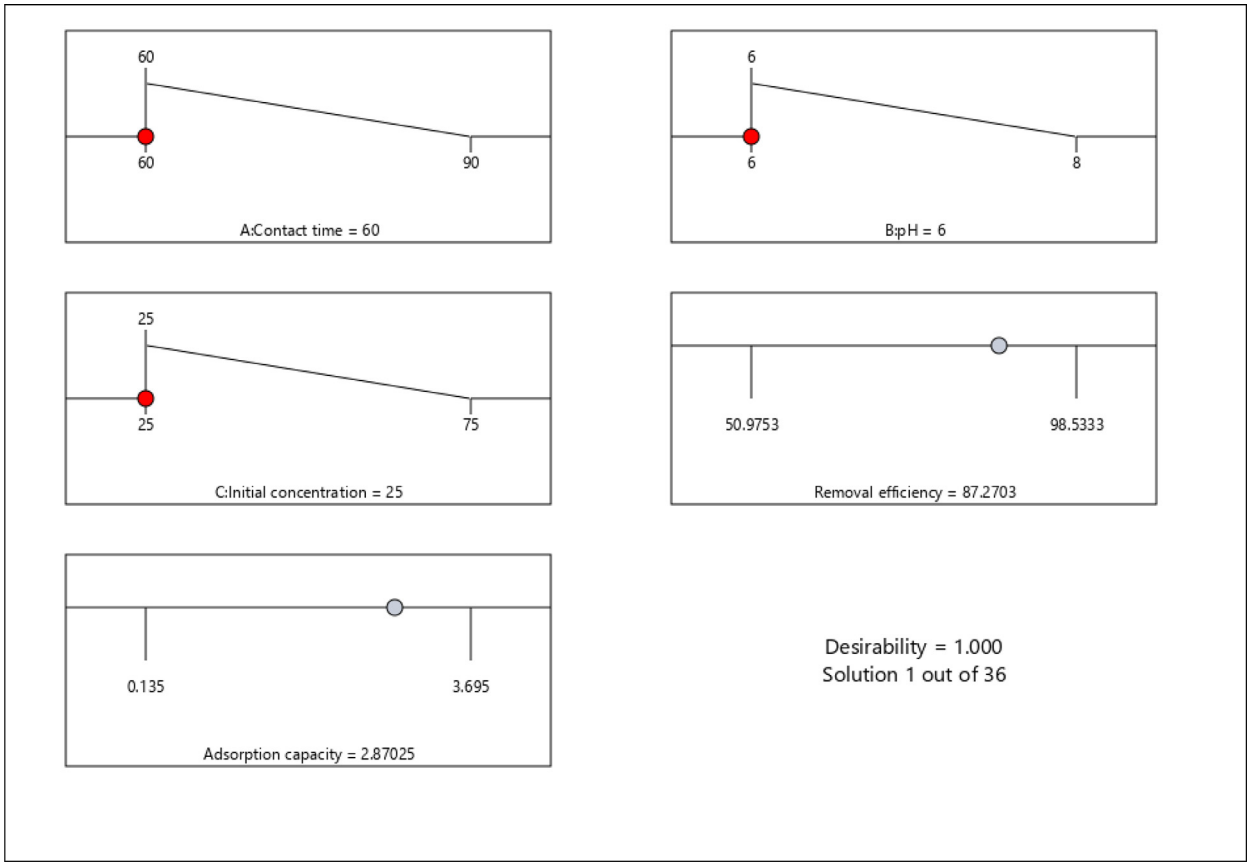

Fig. 9. Desirability ramps for lead(II) biosorption.

Table 10
Point prediction, observed values and confirmation of predicted responses for lead(II) biosorption.

Run 11 Response	Predicted Mean	Predicted Median	Observed	Std Dev	SE Mean	SE Pred	95% PI low	Data Mean	95% PI high
Removal efficiency	87.27	87.27	98.53	9.60	7.87	12.42	59.18	83.45	115.36
Biosorption capacity	2.87	2.87	3.70	0.66	0.53	0.84	1.03	2.79	4.71

removal efficiency and biosorption capacity of lead(II) under this optimized operating condition were determined as 87.27% and 2.87 mg/g, respectively.

Model validation

Table 10 compares the predicted values to the actual values under the ideal operating condition. For the removal efficiency and biosorption capacity of the lead(II), the standard error (SE) mean of predicted against actual values was determined to be 7.87 and 0.53, respectively. Furthermore, the standard error prediction (SE Pred) of the removal efficiency and biosorption capacity was found to be 12.42 and 0.84, respectively, when the predicted results shown in Table 11 were confirmed through further laboratory experimentations. The confirmatory experiments show optimum lead(II) removal efficiency and biosorption capacity of 83.45% and 2.79 mg/g, respectively. These results demonstrate that the quadratic models and the optimal operating condition developed were accurate and applicable in predicting response variables.

Comparison to literature

When a comparison was made between different adsorbents used to remove Pb(II) from synthetic wastewater, it was discovered that the removal efficiency of the acid-modified powdered peanut shells used as biosorbent in this study was lower with short equilibrium contact time and low initial metal ion concentration than most of the other adsorbents in the literature. Although most adsorbents outperform the utilized sorbent in terms of removal efficiency, they require a

Table 11
Comparison of Lead, [Pb(II)] removal efficiency using modified peanut shells with other studies reported in the literature.

Adsorbent	Contact time (min)	pH	Initial metal ion concentration (mg/L)	Removal efficiency (%)	Reference
Modified peanut shells	60.00	6.00	25.00	87.27	Present study
Tamarind fruit shell powder	33.11	6.98	26.44	83.50	[9]
Groundnut shells	90.00	8.00	75.00	90.26	[11]
Peanut hull-g-methyl methacrylate biopolymer	63.75	5.70	76.25	99.30	[15]
Chitosan/rice husk ash/nano-γ alumina	105	5.00	30.00	90.98	[22]

long contact period and a high starting concentration with lower pH values. Table 11 summarizes the various reported experimental conditions compared to the present studied conditions.

Conclusion

The influence of the different biosorption parameters indicates that the uptake capacity of lead(II) by the MPPS increased with an increase in contact time, solution pH, and initial lead(II) concentration. On the contrarily, the percentage removal of lead(II) decreased with an increase in initial concentration and increased with increasing contact time and initial pH of the solution. From the preliminary biosorption studies, the best contact time, pH, and lead(II) initial concentration were found as 90.00 min, 8.00, and 50.00 mg/L, respectively. More so, the optimization of lead(II) biosorption from the aqueous solutions indicates that the contact time, solution pH and initial lead(II) concentration had a significant effect on the removal efficiency and biosorption capacity of MPPS in lead(II) elimination from the aqueous solutions. This was discovered by the RSM where the combined effect of the parameters studied improved the decontamination of lead(II) from the aqueous phases. Using the CCD-RSM approach, the optimum removal efficiency (87.27%) and biosorption capacity (2.87 mg/g) were achieved at the best optimized operating condition of 60.00 min time of contact, pH of 6.00 and 25.00 mg/L lead(II) initial concentration, with the desirability of 1.00.

Declaration of Competing Interest

The authors report no conflict of interest.

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