Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.29088

278 (2022) 147–158
December

Statistical design of experiments for biocomposite (*Zea mays* sponge/Na-alginate) preparation optimization for Pb(II) removal from aqueous media

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Received 27 July 2022; Accepted 25 October 2022

ABSTRACT

Lead ions are an efficient neurotoxic metal that results in serious disorders for human beings, including poisoning, kidney and liver disorders, hepatitis, anaemia, encephalopathy, and nephritic syndrome. The low-cost and eco-friendly biocomposite from *Zea mays* sponge (ZMS) biomass encapsulated using Na-alginate in the cross-linked matrix (ZMS/Na-alginate) as a biosorbent. A statistical approach uses full factorial design space to optimize the best conditions for preparation beads. The effect of concentrations (w/v, g/100 mL) of Na-alginate (X_1), ZMS biomass (X_2), and $CaCl_2$ cross-linker (X_3) retesting for Pb(II) ions elimination from the aquatic medium in batch mode. The supreme values optimized for X_1, X_2, and X_3 are relevant to 4.5%, 2.5%, and 1.97%. After optimization using response surface methodology, the maximum lead removal by ZMS/Na-alginate biocomposite was 97.11%. The ZMS/Na-alginate biocomposite was characterized using scanning electron microscopy and attenuated total reflection spectroscopy to investigate physical and chemical modification in the structure during the biosorption system. Therefore, the synthesized ZMS/Na-alginate beads show considerable stability during 5 consecutive adsorption–desorption cycles. This approach study demonstrates that the optimized condition affects the removal of lead ions. The findings support using the modified raw biomass as a potential absorbent for heavy metal ions removal from aqueous media.

Keywords: Biosorption; Optimization; Pb ions; Na-alginate; *Zea mays* sponge; Regeneration

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1. Introduction

The expansion of industrial activities has recently provoked an increased concentration of metallic elements in the aquatic ecosystem. Bivalent heavy metallic especially have harmful effects on the environment and threaten the health of several biological species. Lead is considered the major toxic metal in the heavy metals category, even at low levels in the aquatic medium [1]. The maximum permissible concentration of lead ions in drinking water is 0.005 ppm, according to the World Health Organization (WHO); lead ions are an efficient neuroxicin metal [2,3]. That results in serious disorders for human beings, including poisoning, kidney and liver disorders, hepatitis, anaemia, and encephalopathy syndrome [3,4]. For these reasons, various conventional methods have been reported to sequester toxic metals from the industrial fields. Some techniques to overcome this serious problem are membrane separation methods, ion exchange, chemical precipitation, flocculation, ultra-filtration, reverse osmosis, and electro-coagulation [5]. Moreover, each technique has some inconveniences, including expensive costs, cannot be feasible to use on a wide scale, and is ineffective, especially when the concentration of heavy metals in the solution is low. Whereas the adsorption technique is economically feasible for removing metals even at low concentrations, it has superior performance with high-efficiency removal utilizing a natural material at a low cost [6–8].

For this concern, some waste biomass as an adsorbent from natural origin has been carried-out for biosorption metals, such as plants, bacteria, fungi, yeast, algae, and biopolymer [9,10]. Then also using biomass immobilized in a matrix of polymers; for example, carrageenan, chitosan, cellulose, agarose, and alginate are well known and utilized in the treatment scale of removing metal ions. Such polymers received great attention from researchers due to their performance in reducing pollutants, such as biosorption in decontaminated water. Although the use of biomass as a biosorbent for the removal of pollutant (for example, toxic metals) act under various treatment like chemical treatment (chemically activated) or physical (treatment under temperature or get physical change) to increase their efficiency and performance in removing owing these toxic metal [11,12]. According to the literature, this treatment is insufficient and offers some undesirable effects on biomass. As follows, first, their stability during the biosorption process. Therefore, some of the biomasses are known within such structural proprieties, especially; low density; rigidity corresponds to poor mechanical strength, which is unstable in some operational conditions. Such properties could not serve effective adsorption, recycling, and regeneration even if it presents an opportunity to bind metals in this concern, make biomass more stable, and get suitable performance by increasing their ability for easier operation. Immobilizing the biomass *Zea mays* sponge (ZMS) on alginate polymer gel within a suitable matrix is recommended to produce ZMS beads [13]. ZMS is one of the major agricultural wastes in Algeria and it's a lignocellulosic material with carboxyl and hydroxyl functional groups, which may interact with bivalent metals as lead ions in aquatic medium. Besides that, the alginate polymer has been chosen since, according to researchers, it has a great advantage since its structural properties can be easily recoverable, nontoxic, and biocompatible. The main objective of this research is to immobilize ZMS biomass on sodium alginate to make ZMS beads as biocomposite used for Pb(II) removal. In addition, biomass immobilization in such matrix biopolymer is considered the low cost to treat contaminated water since it remains favorable, efficient, nontoxic, and beneficial. This may improve their performance application on a wide scale water treatment, and such application in the industries is competitive with activated carbon and exchange resins as the most effective process [14].

A statistical approach has been performed within the full factorial screen of design to optimize a significant variable for ZMS biomass supported on Na-alginate polymer and get immobilized for further uptake lead controlling by biosorption process [15,16]. However, it seems that there is no study has been applied to optimize the biocomposite preparation from ZMS biomass supported on Na-alginate; (ZMS/Na-alginate) for removal lead followed by applying full factorial design space.

2. Materials and methods

2.1. Materials

The chemicals used, like NaOH (97%), HCl (37%), $CaCl_2$ (97%), and Na-alginate, were obtained from Sigma-Aldrich, USA. The stock solution of Pb(II) needed for the biosorption technique was prepared by dissolving salts of ($Pb(NO_3)_2$-$6H_2O$) in distilled water.

2.2. Zea mays sponge waste biomass preparation

The biomass of *Zea mays* sponge (ZMS) used in the production of biocomposite beads was taken at fresh status, collected locally from farmland in Setif (North-East of Algeria), and cut into small pieces dried in the open air for 30 days. The dried biomass was finely ground (the particle size fraction < 125 μm). Subsequently, the fine powder of ZMS was then dried in the oven at 60°C for 24 h and then stored in desiccators until used in experiments. The waste biomass dray of ZMS is used at fine powder without further treatment.

2.3. Immobilization procedure applied on ZMS biomass

Na-alginate (4.50 g) was dissolved into 100 mL of distilled water under continuous magnetic agitating for 1 h to get a viscous solution afterward. Then ZMS powder fine (2.5 g) was added carefully and homogenized under constant stirring speed with the help of a syringe [17]. The mixed solution containing ZMS and Na-alginate was immersed in 1 M $CaCl_2$ solution as droplets. The beads become formed around (3 mm) in size and were kept at 4°C for 1 h; after that, the prepared ZMS/Na-alginate beads were collected and washed twice with water and stored for treatment of Pb(II) biosorption technique from an aqueous medium. Finally, the prepared ZMS beads were stored in a desiccator till use.

2.4. Lead biosorption procedure

The efficiency of lead uptake from aqueous media using ZMS/Na-alginate biocomposite was investigated under a series of experiments conducted by the biosorption technique sets in the Batch system. The biosorption process was started with the amount of gram of such ZMS/Na-alginate biocomposite immersed into 100 mL of Pb(II) solution prepared (C = 100 mg/L) at pH close to 5.4 [18], resulting in dissolving lead nitrate in distilled water with further adjustment using 0.1 M NaOH/HCl. The mixed solution was maintained under stirring conditions (300 rpm) at 303 K. The samples were collected and filtered and the tests were performed in triplicates. The remaining concentration of lead ions left in the aqueous solution was determined using atomic absorption spectrometry (Analytik Jena AG Germany AAS NOVAA350). The percent removal of lead ions (Y_{Pb}%) was determined by the following formula [19–21]:

$$Y_{Pb}(\%)=\frac{(C_0-C_e)\times 100}{C_0} \quad (1)$$

where C_0 is the initial concentration of Pb(II) ions in the solution (mg/L), and C^e is the equilibrium concentration of Pb(II) ions (mg/L) in the solution. A systematic representation of the whole process is presented in Fig. 1.

3. Results and discussion

3.1. Statistical techniques of full factorial design at two-level

The statistical approach was made to design an experiment to select significant factors influencing the bead preparation to obtain biocomposite ZMS/Na-alginate. This one is used for the uptake of lead from the biosorption technique and investigates their influence on the percent removal of lead ions. Thus, design analysis was conducted at a three-factor combination at two-level using full factorial design 2^3 and applying the mathematical model on Minitab19 statistical software at first-degree polynomial. Further statistical screening has been considered a useful technique for analyzing and modeling to estimate the affecting variables on response [22]. For this side, the three factors variables in concentration, namely [Na-alginate (X_1); ZMS biomass (X_2); cross-linker ($CaCl_2$) (X_3)] which, range in respective (Table 1).

The selected factors could affect beads production; each varied in two levels to evaluate their performance for increasing the percentage of removal lead. It enables an increase in biosorption yield (%) of leaders considered as dependent variables (response). The design matrix, including the investigated response Y (%) is presented in Table 2. The experiment sets were performed realized in 8 runs. In this state, the statistical analysis data for 2^3 designs

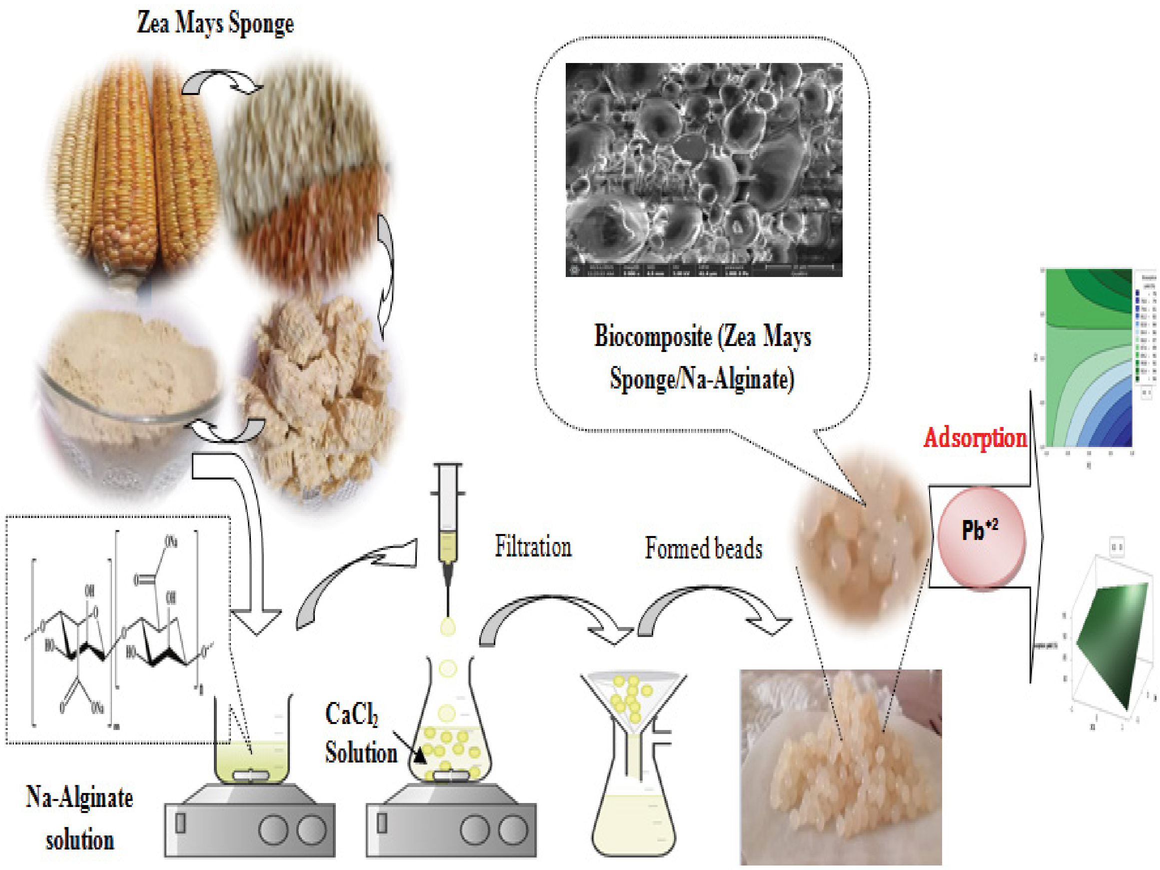

Fig. 1. Systematic representation of the whole process.

Table 1
Conditions of experimental design

Factor name	Factor	Range/Level	
		–1	+1
Concentration of Na-alginate	X_1	2.5	4.5
Concentration of biomass (*Zea mays* sponge)	X_2	1.5	2.5
Concentration of cross-linker ($CaCl_2$)	X_3	1	2

Table 2
Experimental design matrix for preparation of ZMS/Na-alginate biocomposite

Test	Independent variable code	Response Y_{3h} (%)	Predicted Y_{3h} (%)	Residuals	Test	Independent variable code
	X_1	X_2	X_3			
1	–1	–1	–1	88.804	88.825	0.021
2	1	–1	–1	75.890	75.5375	0.3525
3	–1	1	–1	89950	89.929	0.021
4	1	1	–1	93.790	94.1425	–0.3525
5	–1	–1	1	88.050	88.029	0.021
6	1	–1	1	77.800	78.1525	–0.3525
7	–1	1	1	89.112	89.113	–0.021
8	1	1	1	97.110	96.7575	0.3525

are illustrated in Table 3. The experimental data sets were fitted on a mathematical model, further obtained and checked as the following equation:

$$Y = a_0 + \sum_{i=1}^{n} a_i X_i + \sum_{i=1}^{n-1}\sum_{j-i+1}^{n} a_{ij} X_i X_j + \sum_{i=1}^{n-2}\sum_{j-i+1}^{n-1}\sum_{k-j+1}^{n} a_{ijk} X_i X_j X_k \quad (2)$$

where Y is considered as the predicted response (yield of Pb(II) uptake on biosorption technique for 3 h), a_0 as a constant coefficient; a^i a^j the linear coefficients; a^i_{-1} selected as the interaction coefficients; X^i, X^j, and X^k which are taken as coded values of ZMS/Na-alginate beads preparation variables. In the same trend, when substituting each of the coefficients, a^i at Eq. (2), by their employed values illustrated in Table 3, the empirical model results for Pb(II) removal are also based on analyzing experimental data as given in Eq. (3).

$$\text{Y3h} = 87.563 - 1.416X_1 + 4.927X_2 + 0.455X_3 + 4.375X_1X_2 + 0.853X_1X_3 + 0.166X_2X_3 \quad (3)$$

Table 2 represents the percentage of Pb(II) removal from ZMS beads in aqueous media conducted in 8 runs experiments. In each run, the data were tested at two levels from the combination of dependent variables. It can be remarked that the percentage of lead ions removal % varied from 75.89 to 97.11 in 8 trials. From this variation, it was essential to apply the optimization process to identify a significant variable influencing the percentage of lead ions attaining their maximum removal. As shown in Table 2, the highest percent of Pb(II) removal can be observed in run number 8 attain 97.11%.

Table 3
Fitting the parameters and their interactions followed on the general model

Terms	Coefficient	Effect	*p*-value
X_1	–1.416	–2.831	0.083
X_2	4.927	9.854	0.024[a]
X_3	0.455	0.909	0.248
X_1X_2	4.375	8.751	0.027[a]
X_1X_3	0.853	1.705	0.137
X_2X_3	0.166	0.331	0.538
R^2	0.9900		
R^2_{Adj}	0.9947		
$R^2_{predict}$	0.9519		
S	0.528209		

[a]Significant

According to Table 3, applying the full experimental design to analyze the relationship between Pb(II) removal and independent variable indicates the effect on each factor's percent uptake Pb(II). With regards to their coefficient of each factor also reveals an effect extent for Pb(II) uptake, then also it can be seen that the analysis of the regression coefficient controlling under three factors (Table 3) displayed a positive effect on response (Y) % as a percent of lead removal% for either of two factors which ZMS biomass (X_2) and cross-linker ($CaCl_2$) with coefficient value 4.927 and 0.455, respectively. The positive effect means that the increase in the concentration of ZMS biomass and cross-linker ($CaCl_2$) enables a positive effect on the percent of Pb(II) removal on the biosorption technique. At the same time, the Na-alginate (X_1) had a negative effect and gave a coefficient close to (–1.416 in value), which means that the decrease in the concentration of X_3 factor leads to exert a positive effect on the biosorption of Pb(II).

Therefore, Table 3 reveals the extent of the effect of each variable on response, such as the percent of Pb(II) removal, and estimate who have a large effect, then also display the positive or negative effect. These demonstrate that the relationship between them significantly impacts the biosorption of lead. For this purpose, the method of descendant regression named (backward technical) has been applied [23]. The best quality model can be selected when the R^2 is close to unity, which means the choice of the best model is based on high correlation coefficients in statistical analysis such as analysis of regression; therefore, it will be evaluated in this survey such as in predicted responses [23,24]. In addition, the determination of the highest correlation R^2 when close to (0.9) considers the as best model. On the other hand, when R^2 was obtained to be 0.75, it stayed as an appropriate model, but it should not be under this value [25,26], according to Koocheki et al. [27], which reported that it's necessary to estimate the adjusted R^2 because the high R^2 is not to be enough to select the best one of the models. From this purpose, it can be concluded that the best model is made well based on high adjusted (R^2_{Adj}) [28]. Further, in the present work, the highest value of both correlation R^2 and adjusted (R^2_{Adj}) have been taken after applying screening design to check each model as will reveal between main effect and their interaction chosen at two levels and almost related to the probability (P) which should be under 0.05 in value; these could be on coordinator with using technical of backward.

By applying this last one to get the model general, then start to remove the interaction effect of ZMS biomass and cross-linker (X_2, X_3) who had insignificant probability (p), which is close to 0.538 in value as shown in Table 3 after this elimination, it is revealed that the adjusted (R^2_{Adj}) get an increase with a significant probability to attain 0.000 as cited in Table 4. Then also, at this stage, the main effect which seems to be the most influential in parameters is ZMS biomass (X_2). From these obtained results, it can be proved the use of ZMS as biosorbent and check their responsibility first as compared with another effect for removal Pb(II) by biosorption system, which demonstrates that ZMS biomass containing the absorbed sites responsible for uptake Pb(II) as bivalent metal toxic use in this study. Based on these results, the interaction effect of (X_2, X_3) is rejected as followed by their adjusted p-value; hence after checking the mathematical equation [Eq. (3)] of the model and taking into consideration the probability parameters P less to 0.05 in value, then also the model represents on Table 4 is considered as the best one use to calculate the experimental data, the similar view was discussed in the previous study [17].

$$Y_{3h\ Pb(II)} = 87.563 - 1.416X_1 + 4.927X_2 + 0.455X_3 + 4.375X_1X_2 + 0.853X_1X_3 \quad (4)$$

Table 4
Effect of the parameters and their interaction after applying backward technical to estimate the best model

Terms	Coefficient	Effect	p-value
X_1	–1.416	–2.831	0.015[a]
X_2	4.927	9.854	0.001[a]
X_3	0.455	0.909	0.123
X_1X_2	4.375	8.751	0.002[a]
X_1X_3	0.853	1.705	0.040[a]
R^2	0.9987		
R^2_{Adj}	0.9953		
$R^2_{predict}$	0.9785		
S	0.499394		

[a]Significant

3.2. Student's t-test for the influent model

To evaluate the experimental data and to get information between the main effect and interaction effect which should not be zero, the student t-test was performed. Pareto chart of each effect on the percent of Pb(II) removal as the response is displayed in Fig. 2. The analysis of data points was found to be around 95 in confidence level within 2° of freedom at a t-value equal to 4.303. It means that each effect is significant when having a t-value above 4.303. From the analysis of obtained results, the main effects of X_1 (Na-alginate) and X_2 (ZMS biomass) are the most influential parameters in this survey design.

3.3. Variance analysis (ANOVA) to check the optimum model

It is very necessary to apply ANOVA to verify the validity of such experimental data sets against the zero hypotheses within illustrate all parameters (Table 5), such as degrees of freedom (D-F); The sum squares (SS); mean of square (MS), F-test and p-value, as known, the analysis of regression model recorded by ANOVA demonstrate that the model considers significant if their calculated parameters such as F-value and the probability (P) level to 0.05 [29,30]. The analysis of ANOVA on model selection gives a high coefficient of R^2-value (0.9987), adjusted R^2_{Adj}-value (0.9953), and predictive $R^2_{predict}$ (0.9785)as shown in

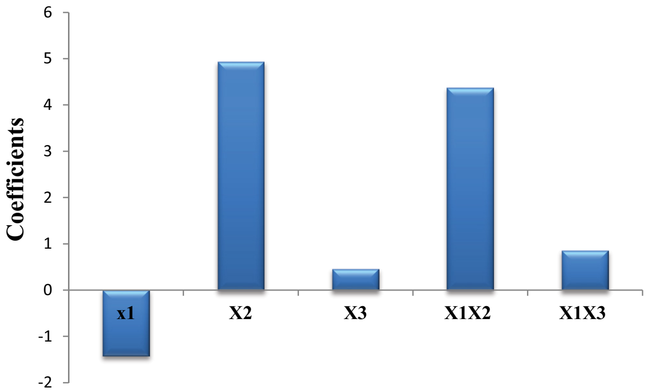

Fig. 2. Pareto chart of the effects variable for building ZMS bead used for removal Pb(II) plot.

Table 5
Variance analysis (ANOVA) for model use to build ZMS/Na-alginate biocomposite

Parameters	Freedom degree	Sum squares	Mean square	F-value	p-value
Constant	1	61,338.582	61,338.582		
Total corrected	7	371.370	53.053		
Regression	5	370.871	74.174	297.42	0.003
Residual	2	0.499	0.249		
Total	8	61,709.952	7,713.744		

R^2 = 99.87%; R^2_{Adj} = 99.53%; $R^2_{predict}$ = 97.85%

Table 4 either after checking the test F, the zero hypotheses becomes reject within F-value close to 297.42 (larger than corresponding critical value as 2.356 cited in the table of Fischer and p-value level to 0.003, therefore according to Table 5, all value of P seems at level confidence of 95% which shows that both main effect and interaction effect had a p-value less to 0,05, based on predicting the optimal condition sets under a range of variable utilized to prepare ZMS beads which serve to increase the percent of Pb(II) removal from biosorption system. These results show that the present model (optimize) is considered adequate to predict the optimal condition within ranging of such variables examined in the preparation of ZMS beads for increasing percent of Pb(II) removal in the biosorption system.

Furthermore, the suitability of the model was shown between experimental data and predicted of each response fitting as shown in Fig. 3. As regarding this plot represented, it appears a satisfactory correlation between predicted and experimental obtained response for percent of Pb(II) removal, either the points around on diagonal line displays great fit of model state, since the deviation(s) becomes less among of them, the similar observation [31,32].

3.4. Main interaction effects plot on the optimized model

To recognize the relative strength of the main effect in each of the three factors and compare them, potting of main effects (X_1, X_2, X_3) to give their response at two levels of design screening under respective variables in the process. Fig. 4 represents the main effect of Na-alginate (X_1), ZMS biomass (X_2), and $CaCl_2$ (X_3), all tested on concentration to get the percent of Pb(II): yield in biosorption technique. As can be seen that the ZMS biomass is considered the most influent variables providing the largest coefficient (4.93) and has a positive effect which means that the removal of Pb(II) (response yield of biosorption%) is more favored at a high level of ZMS biomass concentration 2.5 w/v%. Hence, Pb(II) removal increases when ZMS biomass concentration ranges from low to high; this seems reasonable because when ZMS biomass increases from 1.5 to 2.5, it will provide more exchangeable sites onto their surface, which is responsible for removing metals like lead. The second main effect, which also has had a considerable effect, is, Na-alginate (X_2), classed as the third effect and had a negative effect due to that Na-alginate becomes less significant at a higher level of concentration, it means the percent of Pb(II) removal increases in lesser level 2.5%. Whereas the $CaCl_2$ (X_3) classed on the third effect on removal Pb(II) follows on response yield within positively affecting due that $CaCl_2$ concentration is more favored at (2%) as high level. In addition, the interaction of two factors is almost influential in this screening design X_1X_2 plotting their all-possible combination as shown in Fig. 5, from this graphical interaction. Besides this observation, it can imply that the ZMS/Na-alginate biocomposite synthesized as biosorbent becomes more affecting in removal under this respective condition of preparation; therefore, it can be concluded that there is a significant relationship between the condition of ZMS/Na-alginate preparation as biocomposite and uptake of lead.

3.5. Residual normal probability retesting and checking the validity of the model

The normal probability (N.P.P. plot) was performed to test the normality of the model, which means checking if empirical data points are normally distributed [33]. The N.P.P of residual is considered one of the methods used to explore the adequacy of such a model [34]. As shown in (Fig. 6), all point of experimental data sets seems to fall in a straight line for recovery of Pb(II); this is because such a model fits well and suggests a normal distribution.

3.6. Response surface at three-dimensional and contour plotting

To explain better the influence of parameters sets as independent variables X_1, X_2, X_3 within their interaction on dependent variable followed by X_1X_2, X_1X_3, and X_2X_3 to show the best response (Pb(II) removal percent %), 3D of response surface and corresponding contour plots for a measured response which has been extracted on the model above based on Eq. (4). plotting the surface at a three-dimensional view can help see the desirable response extract in this study [17,29]. From Fig. 7, it can be seen that increase in combination with increasing both ZMS biomass (X_2) and cross-linker (X_3) concentration further the contour plots seem to have a linear relation between ZMS biomass (X_2) and cross-linker (X_3) for all measured response. Thus two variable considered independent variable gives a good combination.

3.7. Optimize the preparation conditions of ZMS/Na-alginate

In the final part, to check the optimal condition for preparation of the ZMS/Na-alginate) biocomposite affecting to remove Pb(II) as toxic metal, the screening design was made in Minitab to suggest the maximum uptake of lead; the analysis between the predict response (Y)% and experimental

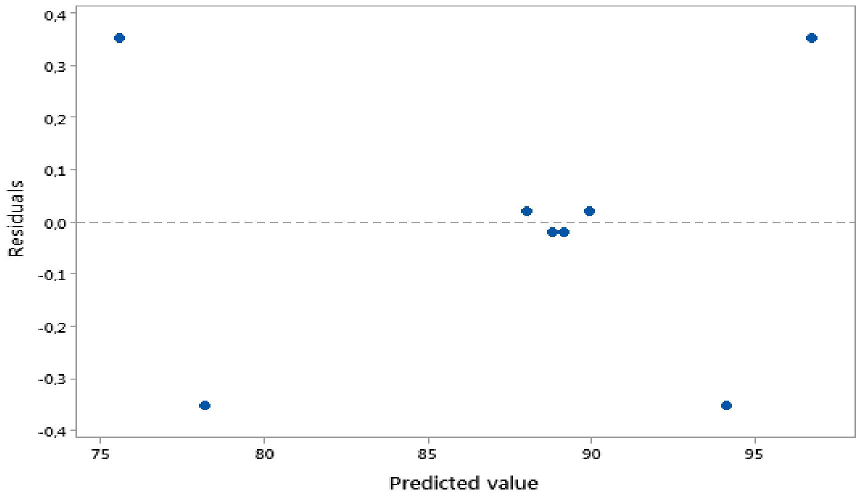

Fig. 3. The percentage of removal Pb(II), predicted vs. residual, on ZMS/Na-alginate biocomposite used for Pb(II) removal.

data point in Table 6 show that the experimental response gives (97.11%) which considerate as higher removal. It seems near to their predicted response (96.75%). From these screens of design, the optimum response level was explored at a concentration of (4.5) Na-alginate, (2.5) ZMS biomass, and (2) $CaCl_2$ with 97.11% of Pb(II) removal onto ZMS/Na-alginate biocomposite. In the final view of this design, and besides the percentage of error obtained on a mathematical model, it can be concluded that such variable data tested by full factorial design 2^3 had a good fitting.

3.8. Scanning surface morphology of ZMS/Na-alginate biocomposite

Scanning electron microscopy (SEM) scanning analysis has been considered a quiet analysis for displaying the modification onto the surface of biosorbents. The surface morphology of optimized ZMS/Na-alginate beads was scanned at different steps of magnifications (Fig. 8) from the (SEM) analysis in an attempt to explore the morphology of such ZMS/Na-alginate) beads before the sorption and after loaded Pb(II). The graphical picture appears somewhat spherical-shape within the irregular structure. This might be related to the particle size of ZMS biomass when reacting with alginate polymer during the preparation procedure of ZMS biomass beads. SEM pictures provide a significant change on the surface of ZMS biomass beads which seems to become more parous after being loaded with cations of Pb(II) due to their sorption onto ZMS/Na-alginate biocomposite. Biosorption of lead and it is also getting more existent space with very distinction; this change can be ensured and justified by taking lead cations into pores on surface ZMS/Na-alginate bead biomass.

3.9. Attenuated total reflection analysis of ZMS/Na-alginate biocomposite for uptake Pb(II)

The analysis of attenuated total reflection (ATR) under spectrometer (equipped with the Two UATR, PerkinElmer (USA) within range (500–4,000 cm^{-1})). The ATR has been

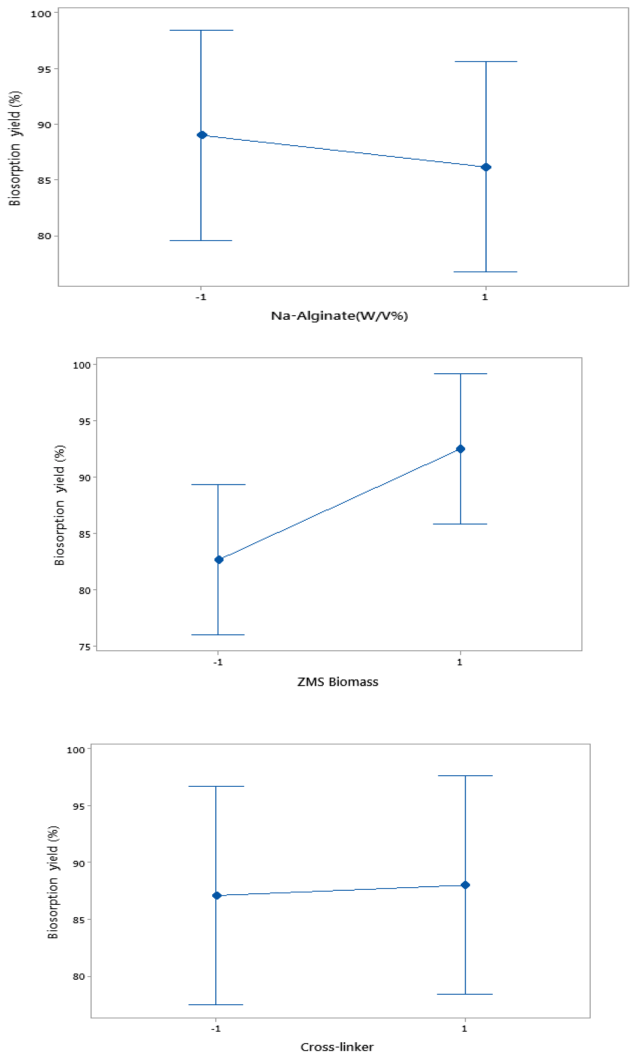

Fig. 4. The main effect of Na-alginate (X_1), ZMS biomass, and (X_3) cross-linker.

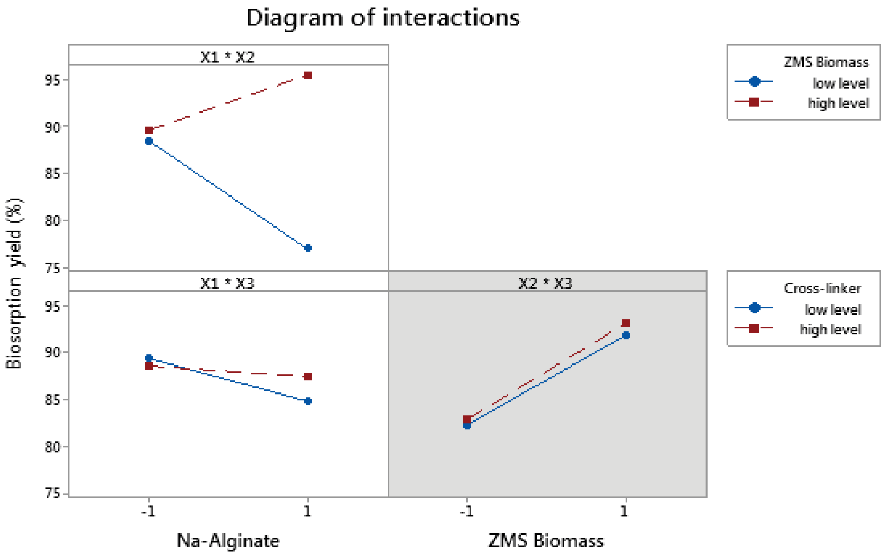

Fig. 5. Plotting the interactions effect for Pb(II) removal.

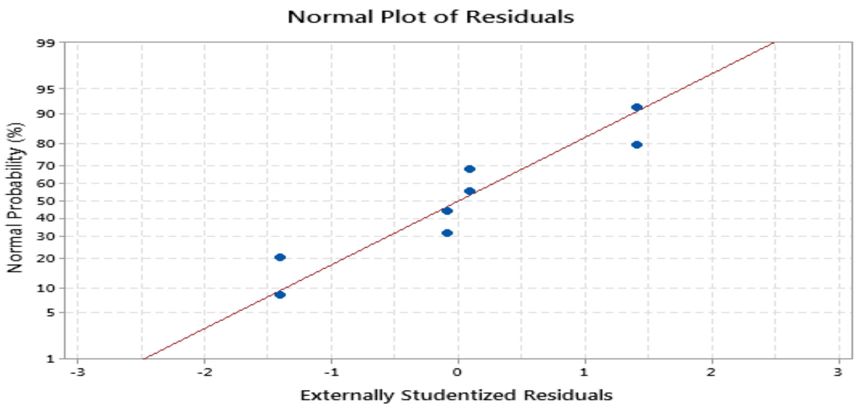

Fig. 6. The normal plot of the studentized residuals vs. normal probability for Pb(II) removal.

Table 6
Optimal preparation conditions of ZMS/Na-alginate biocomposite

Coded variable tested	Factors	Response removal Y_{3h} (%)		
		Predicted	Experimental	Error
X_1 [Na-alginate (w/v %)]	4.5	96.75	97.11	0.35
X_2 [Biomass ZMS (w/v %)]	2.5			
X_3 [Cross-linker (w/v %)]	2			

realized to explore the chemical functional groups presented in ZMS biomass, Na-alginate, and ZMS/Na-alginate biocomposite before/after loading with Pb(II). Among these functional groups are considered significant to remove Pb(II).

Regarding ATR spectra (Fig. 9) of ZMS biomass and Na-alginate, some functional groups have appeared. The broad band at 3,324 and 3,307 cm^{-1} give from ZMS biomass and Na-alginate, indicating the presence of (–OH stretching) [17]. Hence the peaks found on ZMS biomass spectra at 2,923; 1,646 and 1,237 cm^{-1} could be corresponded to (–CH stretching of alkane groups), (–C=O ring stretching vibration of amide), and (–OH ring stretching of secondary alcoholic groups) respectively [35,36]. Moreover, the two peaks at 1,596 and 1,412 cm^{-1} in Na-alginate spectra were attributed to –C=O stretching vibration of carboxylate anions presented in alginate polymer [37]. Then also, the spectra (Fig. 9a and b) for both (ZMS biomass and Na-alginate) show a similarity approximative in peak at

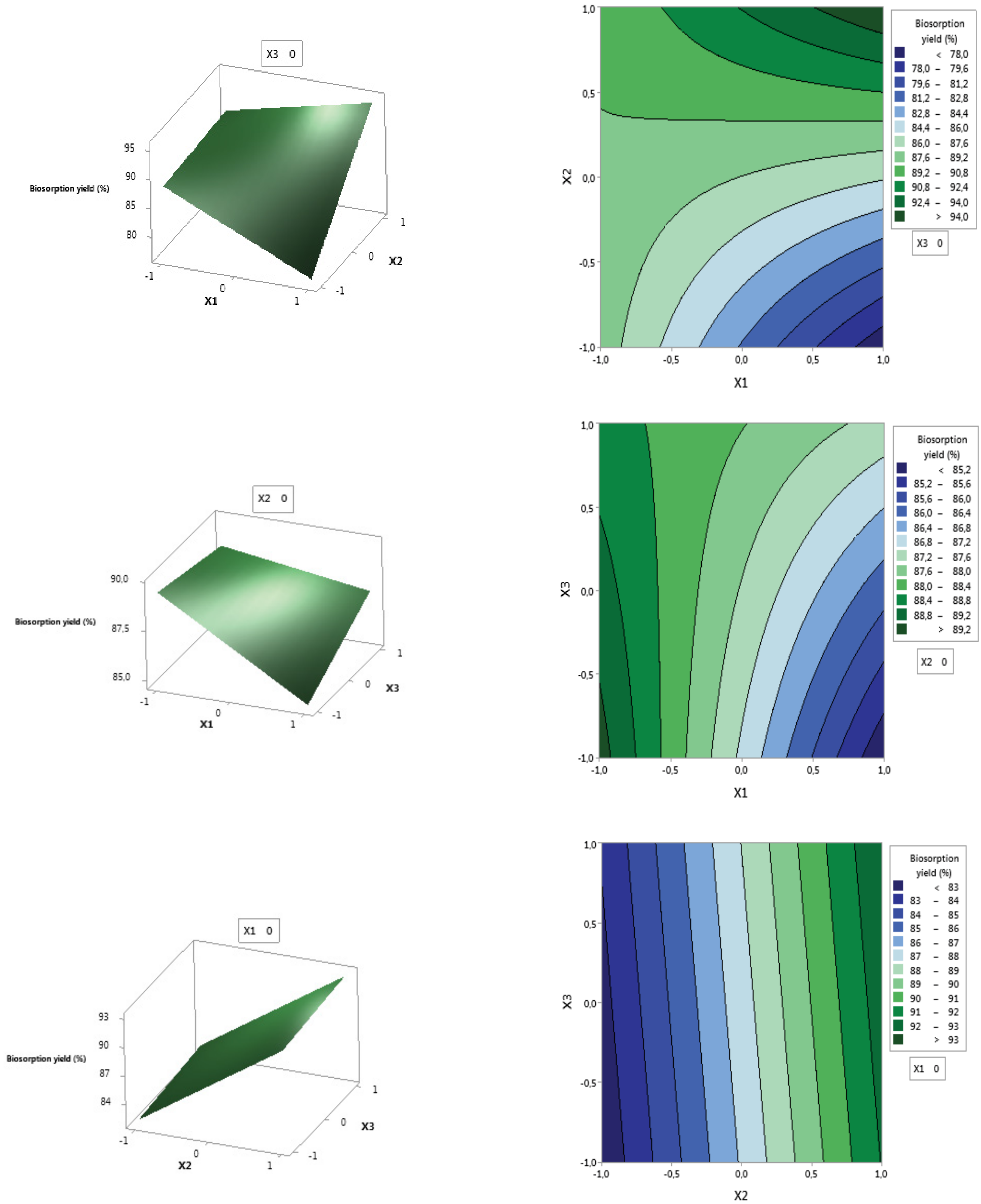

Fig. 7. Typical contour and surface plot graphic for Pb(II) removal.

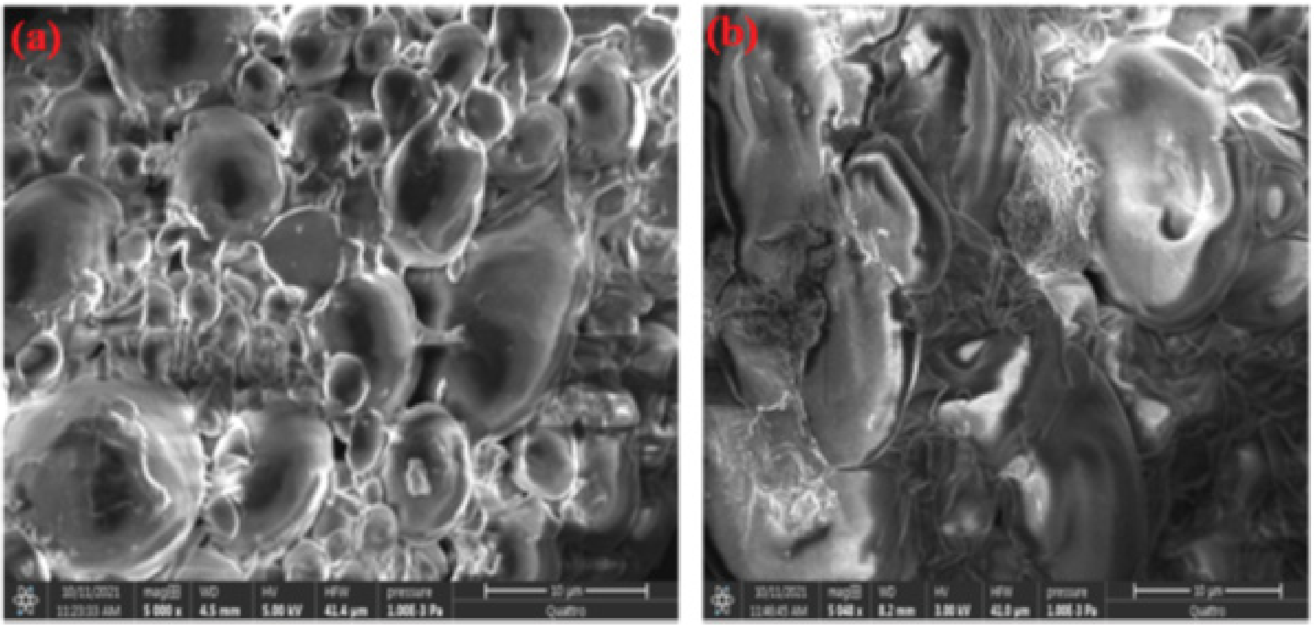

Fig. 8. Scanning electron microphotograph images of (a) biocomposite beads ZMS/Na-alginate before biosorption and (b) SEM physical image of the beads ZMS/Na-alginate, Pb(II).

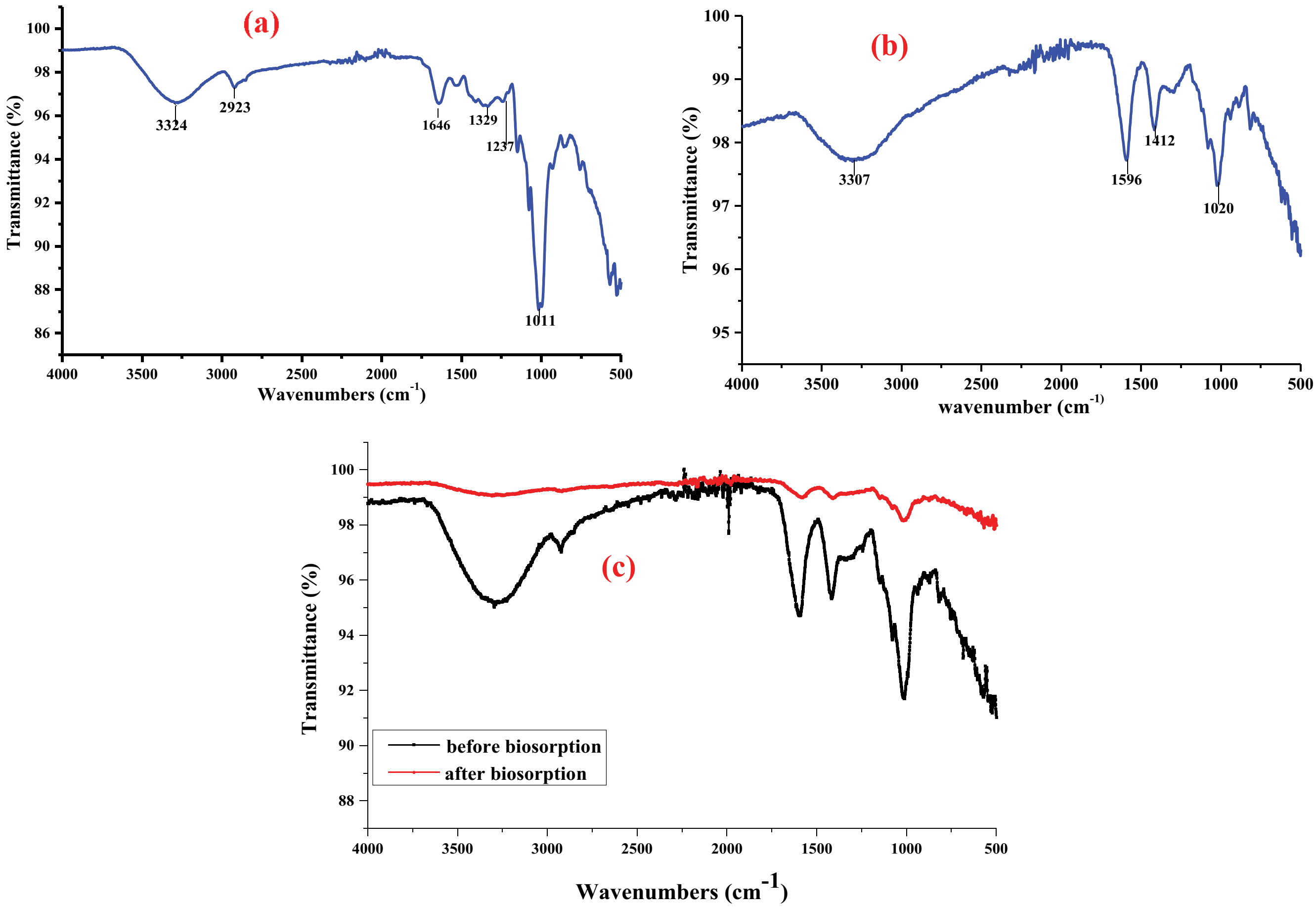

Fig. 9. The ATR spectra of raw ZMS biomass (a), Na-alginate beads (b), and ZMS/Na-alginate before and after adsorption (c).

1,011 and 1,020 cm^{-1}, which could be due to the presence of –CO ring stretching of ether. Therefore, according to this ATR, it is obvious that such two biomaterials (ZMS biomass and Na-alginate) were chosen for this study to produce a biocomposite matrix with functional groups originally. Each of them began to react to obtain ZMS beads; however, in Fig. 9a, the broad –OH band at 1266 cm indicates ZMS biomass reacted truly with Na-alginate, which implies that ZMS biomass particle was immobilized well on Na-alginate (gel polymer). However, the case of Fig. 9c represents the ATR spectra of biocomposite (ZMS/Na-alginate) before and after the removal of Pb(II) ions. By comparing these two curves, it can be remarked that there is a significant change in the intensity of such peaks on biocomposite after the uptake of lead which can be due to reacting and interaction between some of the function groups into surface ZMS beads and the cation of lead during sorption process, as one of them, the hydroxyl bond at 3,307–3,266 cm^{-1} the other one showed a decrease in peak at 1,583 cm^{-1} assigned to the carbonyl group, then also as similarly, the lower peak observed at 1,022 cm^{-1} attributed to –CO groups which indicating the involvement of these group on surface area onto ZMS beads in biosorption procedure to bind lead [16,17,29–39]. From this result of ATR spectrum data, it can be concluded that the functional group –OH, –CO, and –C=O are considered most responsible for the uptake of bivalent lead onto optimized ZMS/Na-alginate biocomposite.

3.10. Reusability of ZMS/Na-alginate biosorbent for uptake Pb(II)

The reusability of biocomposite ZMS/Na-alginate beads was retested and investigated under consecutive cycles of the adsorption-desorption) process. Biosorption procedures were repeated with the same amount of biocomposite beads. The metal uptake onto ZMS/Na-alginate beads was placed with desorbing agent NaOH of 0.1 M solutions at 303 K and stirred for 3 h at 120 rpm. The adsorption-desorption of such biocomposite was checked and repeated five times as a procedure. The lead adsorbed of each step procedure cycle was collected and measured in ASS in the same way in Eq. (1).

The test of regeneration (adsorption–desorption) for an adsorbent is critical to check their ability to utilize on a wide scale, especially in the industrial field of wastewater treatment, as cost-effective. Compared to the results revealed in (Fig. 10), it can be seen that ZMS/Na-alginate presented a good adsorption % for removal lead during 5 consecutive cycles, which is around 97. 11 in the first cycle and 99.05, 98.49, 91.71, 90.024 for other till the fifth cycle respectively and within no complete desorption of Pb(II) was revealed in all five cycles, which may be due to the significant adsorbent-adsorbate interactions [40]. From the analysis of results (Fig. 10), it can be indicated that the synthesized ZMS/Na-alginate beads of biomass (adsorbent) are stable and provide promising regeneration potential for use in removing metal as a lead. Also, the desorbing agent (NaOH) seems efficient for the uptake of Pb(II) ions.

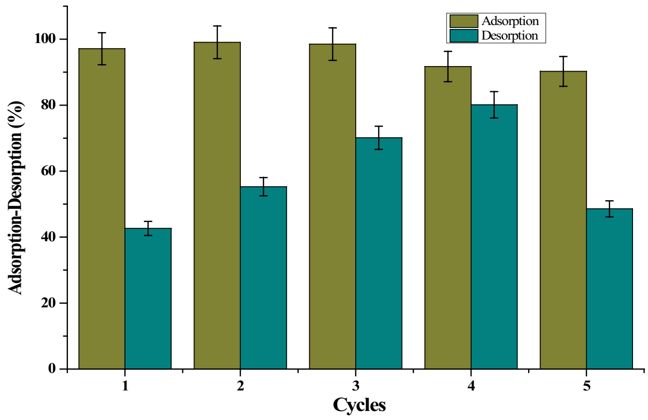

Fig. 10. Adsorption–desorption cycles for Pb(II) removal by ZMS/Na-alginate composite at optimized conditions.

4. Conclusion

This present study reports the application of an approach statistic for optimization lead biosorption onto ZMS/Na-alginate biocomposite beads by screening full factorial design space. The optimized preparation conditions were the Na-alginate concentration (X_1) of 4.5%, ZMS biomass concentration (X_2) of 2.5%, and cross-linker concentration (X_3) of 1.97%. The maximum biosorption was obtained equal to (97.11%) for removing 100 mg/L of lead concentration. The statistic analysis data established that the model gives the goodness of fit within R^2 attain 0.998 value and p-value equal to 0.003. ATR analysis revealed that Pb(II) ions were adsorbed onto ZMS/Na-alginate biocomposite beads from their adsorbed sites surface through carboxyl and hydroxyl as functional groups. This study demonstrates that the determination of optimal preparation condition effect truly in the removal of lead. Also ensure the use of some development on cost-effective bioadsorbents for getting more effective and maximizing their potential of removal in the process of decontaminated water. Furthermore, the regeneration test for biocomposite beads showed considerable stability during 5 consecutive cycles of adsorption-desorption, which could be used for further application in removing the process of inorganic pollutants.

Declarations

Conflict of interest

The authors declare that they have no conflict of interest.

Funding

The author did not receive any fund for this work.

Acknowledgment

A.V. Soldatov would like to thank the Ministry of Science and Higher Education of the Russian Federation for financial support (Agreement № 075-15-2021-1363).

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