Effective desorption of metals from loaded biomass using response surface methodology based on Box-Behnken design

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Abstract

Desorption of metal is an important step of bioremediation as it allows to maximize the benefit (recovery of value) of the process and regenerate the biosorbent. To broadly investigate the tendency of desorption, two metals, lead and nickel were selected for the adsorption process, because Bacillaceae bacteria exhibit different affinity for each of these metal ions and possibly different mechanism of adsorption. In this study the response surface methodology (RSM) and the Box-Behnken design were applied to investigate the effect of the interaction of parameters susceptible to influence metal desorption process. The experiment was based on the four-variable-three-level design of the parameters such as adsorption time, pH of desorbing solution, speed during desorption and volume of desorbing solution. Metal removal process was designed such as to enhance desorption and regeneration of biosorbent. The active groups involved in the uptake of metal ions were identified using Fourier Transform Infrared Spectroscopy (FT-IR). The results show that all the four variables influence metal's desorption from biomass,and experimental design allows to observe optimum interaction level of parameters suitable for desorption process leading to effective recovery and regeneration of biosorbent. The desorption process was also found to be dependent on the type of mechanism involved during biosorption and the active groups on the cell surface interacting with the metal.Desorption of metal from biomass is very important for its recovery, as well as regeneration of biosorbent necessary for undiminished uptake in the next cycle of metal removal.

Keywords: desorption; biomass regeneration; Bacillaceae bacteria; response surface methodology; Box-Behnken design

Introduction

Identified a few decades ago as a valuable alternative to conventional methods, biosorption has become very popular for the remediation of heavy metal pollution of industrial effluents. Several biosorbents have the potential for metal uptake, but the use of microorganisms has often resulted in better removal of metal ions. The process of bioremediation of heavy metal pollution can only be complete if it leads to recovery of solute and regeneration of biosorbents; in this way minimizing the cost of the process as the supply of biosorbent will be reduced and recovered metal can be exploited.To effectively reverse the process of metal loading on biomass and regenerate the biosorbent, a suitable eluant which is cheap, less aggressive to the biomass structure and effective should be selected. Various chemical agents have shown good performance when used for desorption of metal (Kuyucak and Volesky, 1989; Yang, 1999; Davis et al., 2000), however, mineral acids such as HCl, H_2SO_4 and HNO_3 are often used for desorption of metals from biomass. Acidic desorption of metal mainly occurs as a result of dissolution and competition between metals and protons for the binding sites on the biomass surface (Crist et al., 1990; Brooks, 1991; Aldor et al., 1995). The solid to liquid ratio of the mass of biosorbent to the volume of eluant and the pH are parameters generally consideredto study metals desorption. However parameters such as the mechanism of adsorption of metal may influence the success of desorption as the later process attempts to reverse the first.

In this study key parameters that can influence desorption of nickel and lead from Bacillaceae bacterium were investigated using the Box-Behnken design (Box and Behnken, 1960) to determine optimum conditions, and improve the understanding of metal adsorption behaviour, further addressed by identification of the active groups on the biomass surface involved in the adsorption process.

Methodology

Biomass loading experiment

Bacillaceae bacterium biomass and metallurgical solution were prepared as described in previous work (Fosso-Kankeu et al., 2011). The biomass (0.3 g) and metallurgical solutions (50 mg/L) were mixed in 100 ml final volume. The mixture was shaken (160 rpm)in an incubator at 37°C.

Desorption experiment

After adsorption of nickel and lead by Bacillaceae bacteria, loaded biomass was pelleted by centrifugation for 10 minutes at a speed of 8000 rpm; the pellet was washed with sterile distilled water to remove loose metal ions and suspended in the various eluants, that were either distilled water (neutral pH) or H_2SO_4 (pH 5 and 3) for design purposes these values were considered in an acidity scale: -1, 2 and 4 respectively. The mixture was shaken (80, 140 and 200 rpm) for an hour in an incubator at 37°C.

Response surface methodology (RSM)

RSM is an optimisation, development and improvement technique for processes based on the use of factorial designs. For optimum desorption of nickel and lead from loaded biomass, the Box-Behnken experimental design,an RSM, was applied. Four independent variables, adsorption time (A), acidity scale (B), shaking speed (C) and eluant volume (C)with significant influence on the process were considered and examined at three different levels, low (-1), basal (0) and high (1). The ranges and specific level of independent variables are indicated in Table 1 below:

Table 1 *Range and level of independent variables*

Independent variables	Factor	Level and ranges		
		-1	**0**	**1**
Adsorption time (min)	A	20	60	180
Acidity scale	B	-1	2	4
Eluant volume (ml)	C	30	50	80
Shaking speed (rpm)	D	80	140	200

The response was measured for all the possible combinations of the level chosen of the variables and represented the percentage of metal desorbed. The number of experiments was calculated according to the following equation:

$$N= k^2 + k + cp \qquad (1)$$

Where k is the factor number and cp is the replicate number of central point.

A total of 29 combinations were then designed based on the Box-Behnken design model and their observations were fitted to the following second order polynomial model:

$$Y= b_{0}+ b_1A + b_2B + b_3C + b_4D + b_{11}A^2 + b_{22}B^2 + b_{33}C^2 + b_{44}D^2 + b_{12}AB + b_{13}AC + b_{14}AD + b_{23}BC + b_{24}BD + b_{34}CD \qquad (2)$$

where Y is the percentage of metal desorbed, b_o is the offset term, b_x is the first-order main effect, b_{xx} is the second-order main effect and b_{xy} is the interaction effect.

Fourier Transform Infrared Spectroscopy (FT-IR) analysis.

The nature of the binding sites as well as their contribution to metal adsorption (estimated by changes in vibration frequency in the functional groups of unexposed and metal-loaded biosorbents) was evaluated using the (FT-IR).

The experimental design for metal desorption involved dryingbiomass samples at 80°C for 24 h in an oven. The dried samples were then ground in a mortar to obtain the pellets. Spectra were recorded within the wavenumber range of 400-4000 cm^{-1} with a Nicolet iS10 spectrometer (Thermo Fisher Scientific, SA).

Results and discussion

Optimization of desorption process

The response surface methodology (RSM) allows evaluation of the effects of combined action of factors, so that the optimum conditions for effective response can be determined. Experimental design set up with one (Box-Behnken design) of such methods allowed to obtain the responses in Table 2 below.

Table 2 *Box-Behnken design of coded values and experimental results of Ni^{2+} and Pb^{2+} desorption (%) from loaded biomass of Bacillaceae bacterium*

Standard order	Coded values Adsorption time	Acidity scale	Eluant volume	Shaking speed	Response (% desorption) Ni^{2+}	Pb^{2+}
1	-1	-1	0	0	26.95	14.82
2	1	-1	0	0	14.92	7.86
3	-1	1	0	0	12.38	15.61
4	1	1	0	0	13.33	4.64
5	0	0	-1	-1	13.42	6.74
6	0	0	1	-1	17.74	3.57
7	0	0	-1	1	31.38	19.89
8	0	0	1	1	44.01	6.32
9	-1	0	-1	0	12.03	18.58
10	1	0	-1	0	25.94	9.09
11	-1	0	1	0	18.54	11.09
12	1	0	1	0	21.59	2.90
13	0	-1	0	-1	7.36	8.50
14	0	1	0	-1	8.96	6.19
15	0	-1	0	1	23.07	16.03
16	0	1	0	1	20.50	7.88
17	-1	0	0	-1	22.23	6.66
18	1	0	0	-1	22.31	6.40
19	-1	0	0	1	55.72	21.28
20	1	0	0	1	43.25	17.32
21	0	-1	-1	0	6.11	12.71
22	0	1	-1	0	17.82	14.12
23	0	-1	1	0	51.95	4.21
24	0	1	1	0	13.19	4.48
25	0	0	0	0	27.95	4.61
26	0	0	0	0	25.62	3.17
27	0	0	0	0	22.78	3.56
28	0	0	0	0	28.28	4.30
29	0	0	0	0	23.95	4.49

Determination of relationship between variables and responses

Parameters confirming the suitability of the model were calculated using ANOVA (Table 3), and the P value (0.0186) of the model indicated that proper fitting to the experiment conducted. The correlation coefficient (R^2) obtained were 0.723 and 0.762 for desorption of nickel and lead respectively. This showed that there was better response between prediction and experimental data for lead desorption than for nickel.

The optimum conditions for each metal's desorption was determined by solving the regression equation using the Reliasoft DOE++ software.

Table 3 *Analysis of variance (ANOVA) of the model*

Source	DF		Mean squares		P value	
	Ni^{2+}	Pb^{2+}	Ni^{2+}	Pb^{2+}	Ni^{2+}	Pb^{2+}
Model	14	14	227.01	51.71	0.042	0.019
Residual	14	14	87.14	16.15		
Lack of fit	10	10	108.83	22.46	0.13	0.001
Pure error	4	4	32.91	0.36		

This allowed the coefficient estimates and the P values to be obtained, which informed about the significance of factors or interactions. The data from the regression analysis were fitted to the second-order polynomial equation as follows:

$$Y_{Ni} = 26.67 + 3.08A + 1.72B - 0.4C + 11.9D - 5.27A^2 - 3.8B^2 + 3.36C^2 + 0.57D^2 + 3.5AB - 4.37AC + 5.64AD + 16.75BC - 0.69BD + 2.5CD \quad (3)$$

$$Y_{Pb^{2+}} = 0.24 - 2.75A - 2.45B - 3.3C - 3.9D + 7.6A^2 + 3.03B^2 + 3.8C^2 + 3.1D^2 + 0.19AB + 0.0004AC + 5.01AD - 1.69BC - 2.02CD \quad (4)$$

The results (Table 4) showed that for nickel desorption the shaking speed and interaction between the acidic condition (B) and volume of eluant (C) were significant. All the factors were significant for lead desorption. Quadratic effects as well as interaction of adsorption time (A) and shaking speed (D) were found to be combinations suitable for lead desorption. Previous works (Kuyucak and Volesky, 1989; Goto et al., 1993; Holan et al., 1993; Davis et al., 2000) have also reported parameters such as pH, shaking speed and eluant are significant for metal desorption from loaded biomass.

Table 4 *Regression analysis of Ni^{2+} and Pb^{2+} desorption*

Source	Coefficient		T value		P value	
	Ni^{2+}	Pb^{2+}	Ni^{2+}	Pb^{2+}	Ni^{2+}	Pb^{2+}
A	3.0772	-2.7459	1.0936	-2.267	0.2926	0.0398
B	1.7161	-2.4462	0.5508	-1.8239	0.5905	0.0896
C	-0.3974	-3.2852	-0.1276	-2.4495	0.9003	0.0281
D	11.9083	3.9039	3.7259	2.8376	0.0023	0.0132
AB	3.4816	0.1882	0.8156	0.1024	0.4284	0.9199
AC	-4.3707	0.0004	-1.0238	0.0002	0.3233	0.9998
AD	5.6382	5.0068	1.3036	2.6892	0.2134	0.0176
BC	16.7541	-1.6854	3.6816	-0.8604	0.0025	0.4041
BD	-0.6871	-1.56	-0.1491	-0.7863	0.8836	0.4448
CD	2.4986	-2.0227	0.5421	-1.0196	0.5963	0.3252
AA	-5.276	7.5811	-1.0133	3.3825	0.3281	0.0045
BB	-3.7636	3.0259	-0.9751	1.8213	0.3461	0.09
CC	3.3607	3.7935	0.8707	2.2833	0.3986	0.0385
DD	0.5692	3.1385	0.1552	1.9885	0.8789	0.0667

To determine the trend of metal desorption from loaded biomass of Bacillaceae bacterium, following the interaction of factors (adsorption time, acidity scale, eluant volume and shaking speed), response surface plots were used. Figures 1-4 below, show significant interactions leading to maximum desorption under the conditions used in this study.

It can be observed in figures 1 and 2 that optimum desorption of nickel required high volume (C=80 mL) of eluant, very acidic (B=pH 3) eluant and high shaking speed (D=200 rpm), but in different coupled interactions (BC and CD).These results confirmed the findings by Crist and colleagues (1990; 1991 and 1992), who suggested that acidity plays a major role in desorption processes as protons insolution tend to compete for binding sites on the loaded biomass. However, as observed in figures 3 and 4, optimum desorption of lead required different conditions; In this case, adsorption time (20 or 180 min depending of the interaction), eluant volume (C=80 mL) and shaking speed (D=200 mL) were the conditions suitable for desorption of lead from loaded biomass.

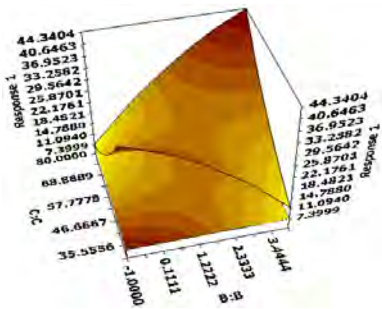

Figure 1 *Surface plot showing the effect of acidity and eluant volume on Ni^{2+}desorption from Bacillaceae bacterium*

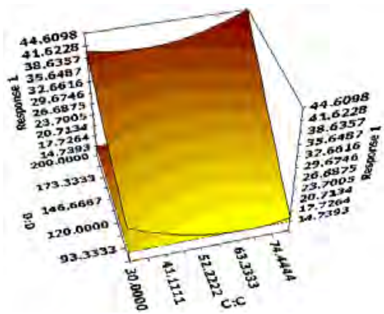

Figure 2 *Surface plot showing the effect of eluant volume and shaking speed on Ni^{2+} desorption from Bacillaceae bacterium*

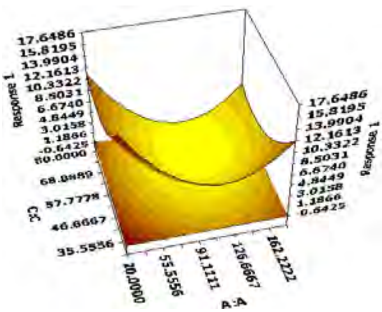

Figure 3 *Surface plot showing the effect of adsorption time and eluant volume on Pb^{2+} desorption from Bacillaceae bacterium*

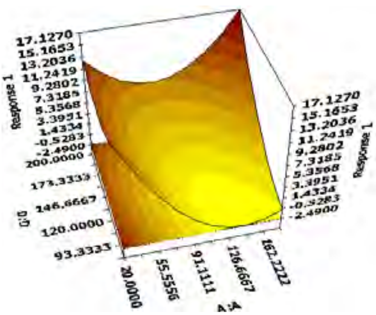

Figure 4 *Surface plot showing the effect of adsorption time and shaking speed on Pb^{2+}desorption from Bacillaceae bacterium*

Active groups involved in metal binding

Infra red spectra of the non-exposed (control) and loaded biomasses are shown in figure5.Reduction of wavelength or disparition of specific peak can be observed in the spectra of loaded biomass corresponding to the attachment of nickel or lead. For these specific binding sites the active groups responsible for binding were identified as –NH, C=O, C-O (acid) and OH (acid and alcohol). Similar active groups were involved in the attachment of lead and nickel to the Bacillaceae bacteria biomass. It is therefore suggested that the strength of the attachment of these metals to the biomass, which affects the efficiency of the desorption process, will mainly depend on the type of bond formed with the active groups and the mechanism of adsorption which can be physical or metabolic (accumulated inside the cell). Desorption could therefore not be a mere reverse of adsorption process, given that after accumulation the sequestered metals cannot be easily recovered, at least not in total.

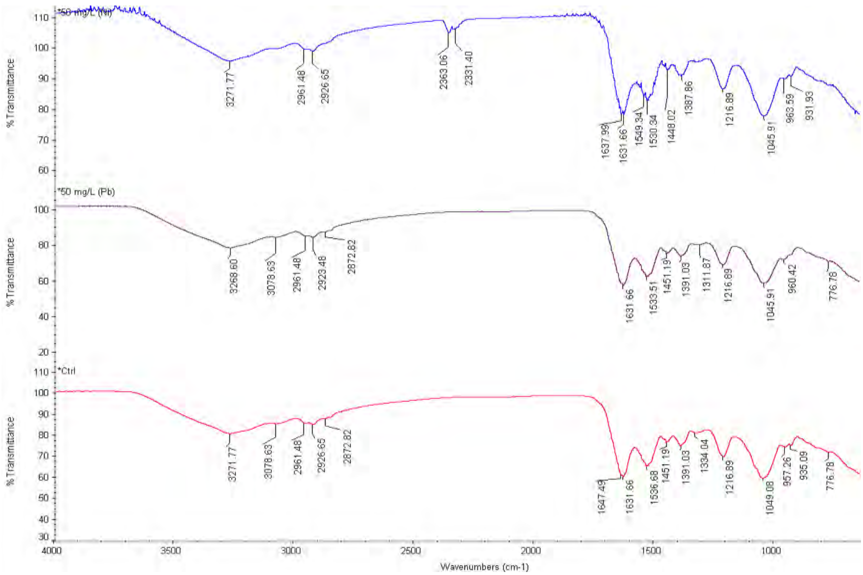

***Figure 5** FT-IR spectra of nickel and lead loaded biomass of Bacillaceae bacterium*

Conclusion

The investigations conducted in this study have shown that the response surface methodology based on Box-Behnken design can allow identification of optimum conditions for metal desorption.Furthermore, observation of the significanceof adsorption time (factor A) on lead desorption indicates thatthe mechanism of metal adsorption can influence its desorption downstream.

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