Chemosphere 167 (2017) 322–329

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Aplication of the statistical experimental design to optimize mine-impacted water (MIW) remediation using shrimp-shell

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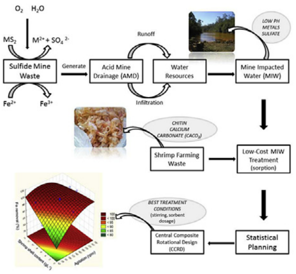
HIGHLIGHTS

- A low-cost treatment for Mine Impacted Water (MIW) remediation is proposed.
- MIW is an environmental pollutant of major concern throughout the world.
- A waste material (shrimp-shell) was use as a biopolymer for MIW remediation.
- Central composite design was used to optimize of the remediation treatment.
- Shrimp-shell has effective performance in pH raising and removing heavy metals.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 May 2016
Received in revised form
20 September 2016
Accepted 21 September 2016
Available online 11 October 2016

Handling Editor: T Cutright

Keywords:
Sorption
Chitin
Metal ions
Statistics
Acid mine drainage
Remediation

ABSTRACT

Mine-impacted water (MIW) is one of the most serious mining problems and has a high negative impact on water resources and aquatic life. The main characteristics of MIW are a low pH (between 2 and 4) and high concentrations of SO_4^{2-} and metal ions (Cd, Cu, Ni, Pb, Zn, Fe, Al, Cr, Mn, Mg, etc.), many of which are toxic to ecosystems and human life. Shrimp shell was selected as a MIW treatment agent because it is a low-cost metal-sorbent biopolymer with a high chitin content and contains calcium carbonate, an acid-neutralizing agent. To determine the best metal-removal conditions, a statistical study using statistical planning was carried out. Thus, the objective of this work was to identify the degree of influence and dependence of the shrimp-shell content for the removal of Fe, Al, Mn, Co, and Ni from MIW. In this study, a central composite rotational experimental design (CCRD) with a quadruplicate at the midpoint (2^2) was used to evaluate the joint influence of two formulation variables—agitation and the shrimp-shell content. The statistical results showed the significant influence ($p < 0.05$) of the agitation variable for Fe and Ni removal (linear and quadratic form, respectively) and of the shrimp-shell content variable for Mn (linear form), Al and Co (linear and quadratic form) removal. Analysis of variance (ANOVA) for Al, Co, and Ni removal showed that the model is valid at the 95% confidence interval and that no adjustment needed within the ranges evaluated of agitation (0–251.5 rpm) and shrimp-shell content (1.2–12.8 g L^{-1}). The

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Abbreviation: MIW, Mine-Impacted Water; CCRD, Central composite rotational experimental design; ANOVA, Analysis of variance; ICP-MS, Inductively coupled plasma mass spectrometry; VIS, Visible; AMD, Acid mine drainage.

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http://dx.doi.org/10.1016/j.chemosphere.2016.09.094

model required adjustments to the 90% and 75% confidence interval for Fe and Mn removal, respectively. In terms of efficiency in removing pollutants, it was possible to determine the best experimental values of the variables considered as 188 rpm and 9.36 g L^{-1} of shrimp-shells.

1. Introduction

The study and description of coal-mining processes have been an object of attention of the scientific community and other institutions both because of the scope, as well as the magnitude, of the impacts caused. Among the environmental impacts, surface water and groundwater pollution in the regions near the mines where the mineral is exploited are highlighted (Ortiz and Teixeira, 2002). In 1999, Nordstrom & Alpers described the pyrite (FeS_2) oxidation process as the main source of acidic water or “acid mineral drainage” (hereafter referred to as “AMD”), which is characterized by a pH between 2 and 4, large amounts of suspended solids and a high content of sulphate and dissolved metals (Fe, Al, Mn, Zn, Cu, Pb, etc.) (Morin and Hutt, 2001; Nordstrom and Alpers, 1999; Mills, 1995). Once in the aquatic environment, these metals can be captured by living organisms, mainly in the form of free cations, directly through the cell surface or through membranes in plants and bacteria (bioaccumulation) or can be transferred organically via the food chain (biomagnification) (Hodson, 1988) causing substantial toxicity (Cronin et al., 1980; WHO, 1998; Nascimento et al., 2002; Corain, 1996; Zatta et al., 1998; Klein, 2005; Meyer–Baron, 2007; Lima and Pedrozo, 2004; Pereira, 2010). Streams contaminated with mining waste acids are environmentally complex systems requiring chemical treatment processes for physical and biological remediation (Daubert and Brennan, 2007).

The conventional treatment of these effluents, and/or the watercourses affected by them, consists of adding alkaline substances (typically lime) to neutralize the acidity and allow the formation of metallic-hydroxide precipitates (Robinson-Lora and Brennan, 2009). However, even though such treatments are simple, effective, and widely used, they are costly because of the requirement of a large amount of reagents, high volume of toxic sludge, and energy (Younger, 1997). In light of this situation, passive treatment methods can be considered to be a good alternative based on the positive proven results for pH neutralization and elimination of dissolved metals, low energy requirements and limited maintenance. (López Pamo, 2002). Among these passive treatments are those based on the use of biosorbents.

Biosorbents are naturally occurring substances that are abundant, renewable, non-toxic, and low-cost (Velazquez, 2006). Among the existing natural polymers, chitin, which is available in large quantities from fishery processes, stands out (Spinelli, 2001). Chitin is a white, hard and crystalline nitrogen polysaccharide. It was first isolated in 1811 by Braconnot from higher fungi and has been called “*fungina*”(Branconnot, 1811). Chemically, it is a high-weight molecular polymer comprising units of N-acetyl-2-amino-2-deoxy-D-glucose joined together by glycosidic linkages β (1 → 4) forming a linear chain with some deacetylated monomer units (Fig. 1).

Chitin is widely distributed in nature and, behind cellulose (raw basis for paper), is the second most-abundant polysaccharide. Its main source is the exoskeletons of many crustaceans and mollusks, insect wings of arthropods, cell walls of fungi cell, among others (Dutta et al., 2002). Chitin is an excellent metal-ion adsorbent, especially under strongly acidic conditions and is able to remove elements, such as aluminum, arsenic, chromium, copper, iron, manganese, nickel and zinc, from aqueous solution (Mcafee et al., 2001; Franco, 2004; Vijayaraghavan, 2005). It has been successfully used in the treatment of well water (Lobo-Recio and Tarpani, 2014; Tarpani, 2012), textile effluents (Simionato, 2006), mining effluents (Daubert et al., 2007; Robinson-Lora and Brennan, 2009; Gamage and Shahidi, 2007) and various areas of the food, pharmaceutical and cosmetics industries (Gildberg and Stenberg, 2001; Peter, 1995).

Hydric resources of the South region of Brazil are strongly impacted by coal mine impacted water (MIW). Most of the rivers of the coal basin of the Santa Catarina State are contaminated by acid mine drainage (AMD) and then no use can be given to its water. The research work of our group has the final objective of transforming coal MIW to water adequate for non potable reuse, viewing the preservation of the limited water sources of high quality of the region for potable use. Thus, in this work, shrimp shell was selected for use as the MIW treatment agent due to its low cost (it is a very abundant reject in the Santa Catarina State) and high content of chitin and calcium carbonate, an acid neutralizing agent. Preliminary studies demonstrated that shrimp shell is a better MIW treatment agent than processed chitin (Núñez-Gómez et al., 2016). High metal removal percentages, as well as high increases in the river water pH value, were obtained in different treatment experimental conditions of ratio shrimp-shell content/water volume, contact time and stirring rate. Sulphate and other anions, as expected, were not removed.

In this context, as an alternative optimization strategy to the trial and error method to find the optimal parameters of MIW remediation by chitin, a factorial design was used because it is more efficient in regard to optimizations involving different variables and their interactions. This strategy allows variables or factors to be analyzed simultaneously at different levels by minimizing the number of treatments that need to be performed simultaneously in one experiment. In addition to allowing each factor's effect on the response variable (or dependent variable) to be visualized, the factorial design also allows the synergistic interaction effect of these factors on the response variable to be viewed (Brito et al., 2002; Kaps and Lamberson, 2004; Toledo, 2007). According to Myers and Montgomery (1995), compared to full-factorial designs, the central composite rotational design (CCRD) is superior due to the smaller number of combinations of factor levels, which promotes the effectiveness of the design.

Thus, the main objective of this work was the use of the experimental design to identify the best conditions for mine-impacted water (MIW) remediation with shrimp shells due to the decrease in the number of experiments and statistical treatment results. To this end, an outline of Central Composition Rotational Design (CCRD) consisting of a 2^k factor, an axial portion (in the $+\alpha$ and $-\alpha$ levels) and central points that improve the estimates of the quadratic and allow additional degrees of freedom was developed. In addition, the central points give extra information about the center of the experimental region, where the best response values are often located (Mateus et al., 2001). The results were then analyzed by plotting the response surface using contour graphics, which allowed the visualization of the points in which the combination of variables led to a better response (Rodrigues and Iemma, 2005; Gong and Chen, 1997).

2. Material and methods

2.1. Chitin

Shrimp-shells (without the head) were washed with water meticulously to eliminate the remains of organic matter and other coarse materials; subsequently the shells were dried in an oven for 72 h at 100 °C for the first 48 h and at 50 °C for the last 24 h. After this process, the shrimp-shells were pulverized in a blender and sieved to promote greater homogeneity and contact surface. To prevent moisture absorption, they were kept in a glass desiccator until use (Núñez-Gómez, 2014; Núñez-Gómez et al., 2016). Shrimp-shell was characterized for inductively coupled plasma-mass spectrometry (ICP-MS) in a Perkin Elmer, Nexlon 300D apparatus (Table 1).

2.2. Impacted water sampling points

The samples for the tests were obtained from the Sangão River at its passage through the city of Criciuma/SC in the Araranguá River Basin (River Region 10: “Extreme South of Santa Catarina”), located within the Carboniferous Santa Catarina Region in the southern Santa Catarina State, Brazil.

The samples were collected at points of easy access in 5-L polypropylene bottles (non-sterile) with no headspace, carried and maintained at a constant temperature of 4 °C, and characterized on the same day of collection for determination of the pH (pH meter ThermoFisher, Scientiphic Orion 3Stars) and metal and metalloid species (ICP-MS, Perkin Elmer, Nexlon 300D). Anions were measured at room temperature using Ion chromatograph, Dionex ICS - 1000 (Table 2).

2.3. Factorial experimental planning

Based on the preliminary results of the comparative tests (Núñez-Gómez, 2014), CCRD was performed for two variables in quadruplicate at the midpoint (2^2), with agitation and shrimp-shell content as the independent variables and the final concentration of the metal species Al, Fe, Mn, Co, and Ni as dependent variables (responses). The contact time was not considered to be an independent variable because the ideal time was identified experimentally in kinetic experiments and was subsequently performed with the ideal amount of shrimp shell, and the ideal agitation speed determined in this factorial experimental planning (unpublished data).

The factor scores (+1 and −1) that indicate the minimum and maximum level for each test of the variables, the central point (0) and the axial points (+1.414 and −1.414), calculated by Equation (1), where α is the axial distance from the point and n is the number of independent variables ($n = 2$), were used in the experiment. The variable levels were defined based on the results of the comparative preliminary tests, as shown in Table 3 (Núñez-Gómez et al., 2016). Thus, twelve experiments were performed following the matrix presented in Table 4.

$$\alpha = \left(2^n\right)^{1/4} \tag{1}$$

The experiments were performed in an orbital shaker thermostatic bath (Dubnoff 252). In the cases in which a more precise agitation was necessary (48.5 and 251.5 rpm), a magnetic agitator (Dist mark) was used. In all cases, 100 mL of liquid samples were placed in non-sterile polypropylene flasks with a 250 mL total capacity and were capped with plastic wrap to prevent the entry of environmental dirt and/or water from the thermostatic bath.

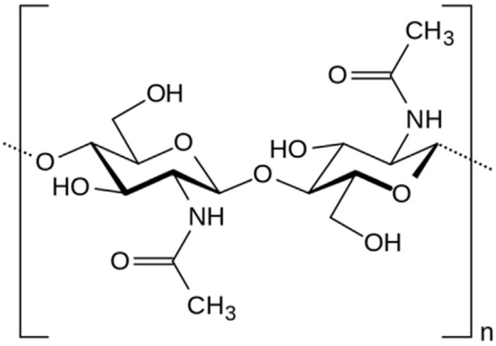

Fig. 1. Structure of the chitin molecule.

All experiments were performed with a 48 h contact time water/biosorbent and a controlled temperature (22 °C ± 1). For sample filtration, cellulose acetate membranes with a 0.45-μm porosity were used. To monitor the possible changes in the intrinsic conditions, a blank was tested (no biosorbent liquid sample).

The final concentration of the metal species was monitored by VIS spectrometry (DR/4000U) using HACH® colorimetric kits. The pH (pH meter ThermoFisher, Scientiphic 3 Stars Orion) was also monitored throughout the process.

Subsequently, the experimental results were subjected to statistical analysis by STATISTICA® 7 StatSoft software, using analysis of variance (ANOVA) to estimate the statistical parameters and to evaluate the prediction, or lack thereof, from the mathematical model.

3. Results and discussion

3.1. Factorial design for water remediation impacted with AMD with shrimp shells in nature

Several of the tested conditions showed the total removal (100%) of species and, except for Mn, other metal species showed a high-removal percentage (>80%), confirming the validation of the factorial design for the MIW remediation through treatment with shrimp shells (Table 4).

3.2. Statistical analysis for Al, Fe, Mn, Co, and Ni removal

For the calculated effects to be statistically significant, the p-value should be less than 0.05 at a significance level of 95%. Using this estimate, it was found that the variables that were tested, when considered individually, had different behaviors for each species. For example, while the removal of Fe and Mn were single variables with significant influence ($p < 0.05$), the removal of Al and Ni showed two significant variables, and only Co showed three significant variables, one of which was the interaction between stirring and the biosorbent content, both of which were in linear form (Table 5). To facilitate viewing, the significant variables ($p < 0.05$) are italicised in the table in which the estimated effects are shown.

Using the significant variables, analysis of variance, ANOVA, was performed, and it was found that for the removal of Al, Co, and Ni (Table 6), $F_{calculated} > F_{tabulated}$. Therefore ANOVA regarding the removal of these species showed that the model is valid at the 95% confidence interval; no adjustment is needed within the range evaluated, resulting in an excellent reproduction of experimental samples.

For the removal of Fe and Mn (Table 6), the model required

Table 1
Characterization of Shrimp-shell used in the tests.

Parameter	ppm
Na	853.44
Mg	3857.83
Al	6.80
K	1674.28
Ca	44611.42
Cr	0.55
Fe	43.12
Mn	100.86
Zn	22.32
Sr	1219.25
Ba	232.97
Ni	0.31

Table 2
Initial characterization of MIW used in the tests.

Variable	Unit	Value
pH	–	3.04
Arsenic	mg·L^{-1}	0.002
Aluminium	mg·L^{-1}	35.92
Cadmium	mg·L^{-1}	0.001
Lead	mg·L^{-1}	0.002
Cobalt	mg·L^{-1}	0.078
Copper	mg·L^{-1}	0.013
Iron	mg·L^{-1}	56.30
Manganese	mg·L^{-1}	2.72
Nickel	mg·L^{-1}	0.117
Sulphate	mg·L^{-1}	617.26
Chloride	mg·L^{-1}	13.91
Phosphate	mg·L^{-1}	0.281

Table 3
Levels of variables used for CCRD.

Variable	(−1.414)	(−1)	0	(+1)	(+1414)
Shrimp-shell content (g L^{-1})	1.2	4	7	10	12.8
Agitation (rpm)	48.5	0	50	250	251.5

adjustments. Thus, to confirm $F_{calculated} > F_{tabulated}$, the confidence intervals were 90% for the removal of Fe and 75% for the Mn.

The coefficient of determination (R^2) provides a variance proportion measure that is explained by the regression equation in relation to the response variations. (Saramago and Silva, 2005).

The obtained R^2 values were close to 0.8 for Al removal (0.8221), Co (0.8488), and Ni (0.8168), indicating that the model can explain approximately 80% of the variation in these final concentrations of metals. For Fe (0.7588) and Mn (0.6926), a considerably lower R^2 was obtained, which is in agreement with the above results for the validation of the ANOVA model for Fe and Mn. These values may be considered unsatisfactory for obtaining a valid and useful model for predictive purposes.

The linear coefficients, quadratic coefficients and their interactions are part of the template used to compose the response surface defining the most appropriate conditions to maximize the efficient removal of the studied metals. The graphical representation employs impact color differentiation and/or synergies of the independent variables in the dependent variables evaluated. These types of graphics can be displayed in 2D (response surface) and 3D (contour curve) to facilitate the visualization and assist in locating an optimal point.

Thus, it is observed that the removal of Al (Fig. 2) was greater using shrimp-shell contents between 7 and 12 gL^{-1} and agitation ranges from 40 to 60 rpm and 240–260 rpm. On the other hand, it was minimal (<44%) with low shrimp-shell contents, regardless of the agitation, confirming the relationship and dependence of the shrimp-shell content as a significant variable of the process.

The removal of Fe (Fig. 3), by contrast, had a higher response when a high agitation rate was applied, showing a high removal central band (between 95% and 100%), with agitations between 160 rpm and 260 rpm, irrespective of the shrimp-shell content, in accordance with the factorial design. Nevertheless, regarding Fig. 3, shrimp-shell contents higher than 12 gL^{-1} allow an iron removal of very near to 100%.

In contrast, the removal of Mn (Fig. 4) provided the best results (>80%) when using a higher shrimp-shell content, with a transverse downward region to a minimum content of 6 g L^{-1} of shrimp shell independent of the applied agitation. Removal is not significant below this minimum content.

Similarly, the removal of Co (Fig. 5) was high (<92%–100%) in the lateral points of the central range, i.e., in the region with low agitation and high shrimp-shell content and the region with high agitations and low shrimp-shell levels, confirming the significant interaction between the two variables as described above.

Finally, for the removal of Ni (Fig. 6), we can observe a central point of high removal (>80%) with a biosorbent concentration between 8 g L^{-1} and 13 g L^{-1} and agitations in the range of 140–180 rpm. There is also a minimum clearance region (>46% - <6%) with less than 6 g L^{-1} of shrimp shells from 140 rpm.

Based on the results for each of the monitored metal species, it was possible to statistically determine the optimal cutoff values of

Table 4
Factorial design (2^2) results for MIW remediation by treatment with shrimp shells in nature.

	Independent variables		Dependent variables (% removal)					
	X_1[a]	X_2[b]	pH	Al	Fe	Mn	Co	Ni
Experiment 1	−1	−1	6.1	100.00	87.23	6.67	54.55	72.07
Experiment 2	1	−1	7.31	98.93	99.79	46.67	100.00	80.45
Experiment 3	−1	1	6.9	96.00	95.96	66.67	100.00	38.55
Experiment 4	1	1	7.15	98.67	99.36	33.33	100.00	72.07
Experiment 5	0	0	7.18	92.00	99.36	33.33	90.91	84.36
Experiment 6	0	0	7.28	92.00	99.57	33.33	90.91	84.92
Experiment 7	0	0	7.56	93.33	99.79	60.00	90.91	82.68
Experiment 8	0	0	7.57	94.67	99.57	73.33	100.00	83.80
Experiment 9	−1.4142	0	3.79	29.33	97.45	−20.00	63.64	59.22
Experiment 10	0	−1.4142	7.29	100.00	87.02	33.33	100.00	55.31
Experiment 11	1.4142	0	7.21	93.33	99.79	86.67	81.82	81.56
Experiment 12	0	1.4142	7.46	100.00	99.79	66.67	100.00	60.89

[a] Shrimp shell content.
[b] Agitation.

Table 5
Estimated effects for metals removal variables.

	Coefficient	Effect	Standard error	t(2)	p-value
Fe					
Agitation (L)	Q_1	*7.0143*	*2.583*	*2.714*	*0.034*
Agitation (Q)	Q_{12}	−8.883	3.730	−2.382	0.054
Shrimp-shell content (L)	Q_2	3.566	1.876	1.900	0.106
Shrimp-shell content (Q)	Q_{22}	−0.210	1.432	−0.147	0.887
Agitation *Vs.* Shrimp shell content	$Q_1 vs Q_2$	−4.574	3.180	−1.438	0.200
Mn					
Agitation (L)	Q_1	26.565	18.306	1.451	0.197
Agitation (Q)	Q_{12}	−9.895	26.428	−0.374	0.720
Shrimp-shell content (L)	Q_2	*37.092*	*13.297*	*2.789*	*0.031*
Shrimp-shell content (Q)	Q_{22}	−9.868	10.084	0.979	0.365
Agitation *Vs.* Shrimp-shell content	Q_1 vs Q_2	−36.667	22.534	−1.627	0.154
Al					
Agitation (L)	Q_1	−1.407	9.084	−0.155	0.882
Agitation (Q)	Q_{12}	23.275	13.114	1.774	0.126
Shrimp-shell content (L)	Q_2	*21.838*	*6.598*	*3.309*	*0.016*
Shrimp-shell content (Q)	Q_{22}	*−15.976*	*5.003*	*−3.192*	*0.018*
Agitation *Vs.* Shrimp-shell content	Q_1 vs Q_2	1.866	11.182	0.167	0.872
Ni					
Agitation (L)	Q_1	−11.954	6.975	−1.713	0.137
Agitation (Q)	Q_{12}	*−35.696*	*10.069*	*−3.545*	*0.012*
Shrimp-shell content (L)	Q_2	*14.822*	*5.066*	*2.925*	*0.026*
Shrimp-shell content (Q)	Q_{22}	−5.828	3.842	−1.517	0.180
Agitation *Vs.* Shrimp-shell content	Q_1 vs Q_2	12.569	8.585	1.464	0.193
Co					
Agitation(L)	Q_1	14.999	6.596	2.273	0.063
Agitation(Q)	Q_{12}	5.417	9.522	0.568	0.590
Shrimp-shell content (L)	Q_2	*14.038*	*4.791*	*2.929*	*0.026*
Shrimp-shell content (Q)	Q_{22}	*−11.689*	*3.633*	*−3.216*	*0.018*
Agitation Vs. Shrimp-shell content	Q_1 vs Q_2	*−22.727*	*8.119*	*−2.798*	*0.031*

L: Linear; Q: Quadratic; *p-value* significant at $p < 0.05$.

Table 6
Analysis of variance for the Al removal variable for the 2^2 factorial design.

Variation source	SS	d.f.	MS	F.		*p*
				Cal	Tab[a]	
Aluminum Removal						
Regression	3467.417	5	693.4834	5.546	4.39	<0.05
Sediments	750.248	6	125.0413			
Total	4217.665	11				
Cobalt Removal						
Regression	2221.489	5	444.2978	6.738	4.39	<0.05
Sediments	395.591	6	65.9318			
Total	2617.080	11				
Nickel Removal						
Regression	1972.304	5	394.4608	5.35	4.39	<0.05
Sediments	442.311	6	73.7185			
Total	2414.615	11				
Iron Removal						
Regression	190.9875	5	38.1975	3.77	3.11	<0.10
Sediments	60.6952	6	10.1158			
Total	251.6825	11				
Manganese Removal						
Regression	6864.305	5	1372.861	2.70	1.79	<0.25
Sediments	3046.806	6	507.801			
Total	9911.111	11				

SS: sum of square; d.f.: degree of freedom; MS: mean of square; F: Fisher's ratio; *p*: probability.
[a] Tabulated values (Box et al., 1978).

the maximum efficiency independently of the removal process (Table 7). The need, in general, for a high shrimp-shell content (>7 g L^{-1}) and agitations at the 150–205 rpm range for the high removal of metals was confirmed. This indicates that future experiments will achieve better results under these conditions.

In the case of Fe removal, it was not possible to statistically determine the optimal biosorbent level; for computational purposes, this value is below the extrapolated experimental minimum tested, possibly because of the influence of the pH on the Fe removal process from the sample. This variable was not considered in the test.

Through these data, the significant effect of the shrimp-shell content on the metal's removal process is evident, possibly because both the metal species sorption on the chitin biosorbent, as well as the shell, influence the liquid sample pH increase, enhancing the removal of species via precipitation as hydroxides.

Consequently, and based on individual critical values and percentages for the initial metal concentrations considered in this study, it was possible to determine 9.36 g L^{-1} of shrimp shells and 210 rpm as the best theoretical conditions. The statistical data of Fe (not significant), Co and Ni (very low concentrations) were not considered for calculating the shrimp-shell content.

Nevertheless, the experimental trials with 210 rpm stirring resulted in an increase in the Mn content in the treated water samples, probably due to degradation by the intense mechanical action of the shrimp shell, which also contains manganese in its structural composition. The experimental assays showed 188 rpm as the maximum stirring rate, with no desorption observed.

4. Conclusions

The influence of agitation and shrimp-shell content as independent variables in the removal of each of the monitored metal species and their relationships was identified. For Al and Mn, the significant variable was the biosorbent content; for Fe removal, the significant variable was agitation; and Ni and Co presented two significant variables.

It has been shown that the mathematical CCRD (2^2) model with the quadruplicate at the midpoint for Al, Co, and Ni removal is valid at the 95% confidence interval. In contrast, for Fe and Mn removal,

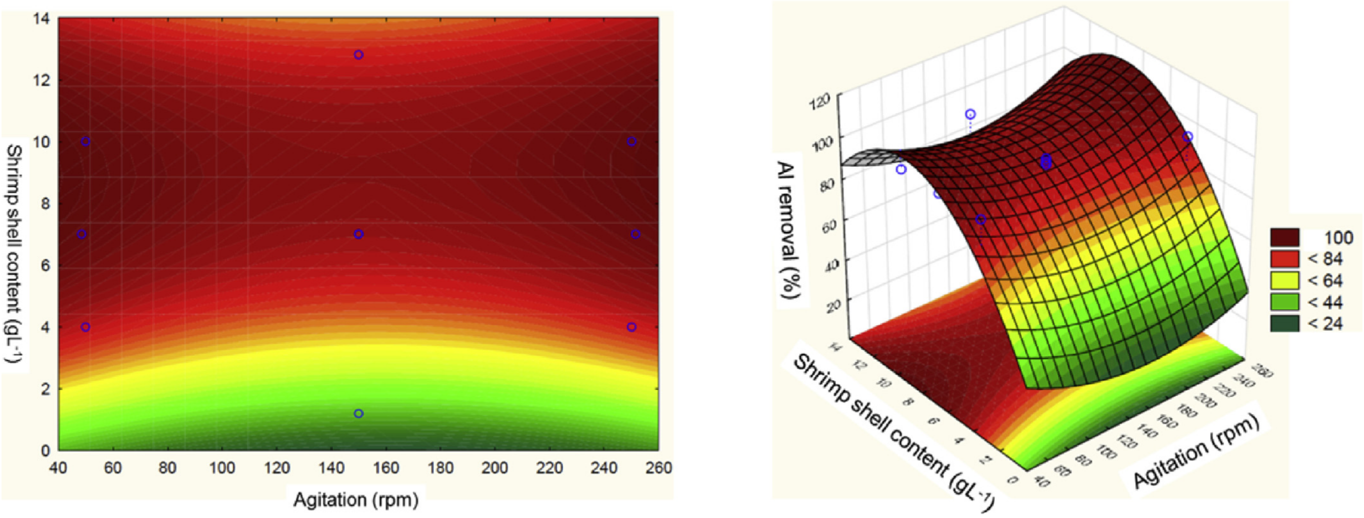

Fig. 2. Response surface (left) and contour curve (right) for Al removal (%).

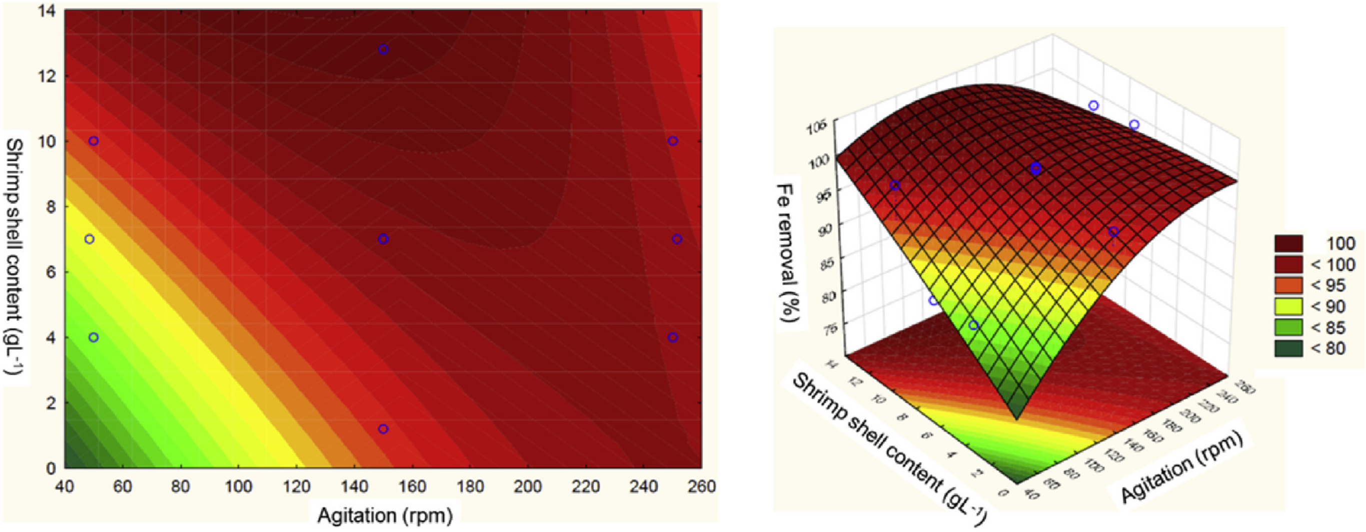

Fig. 3. Response surface (left) and contour curve (right) for Fe removal (%).

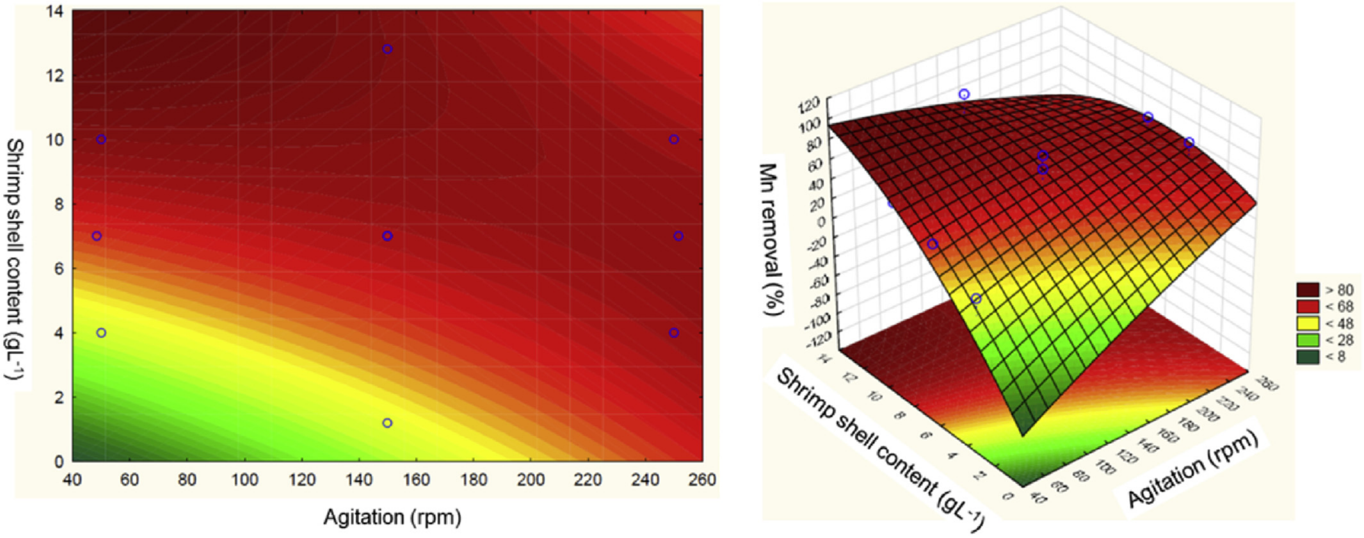

Fig. 4. Response surface (left) and contour curve (right) for Mn removal (%).

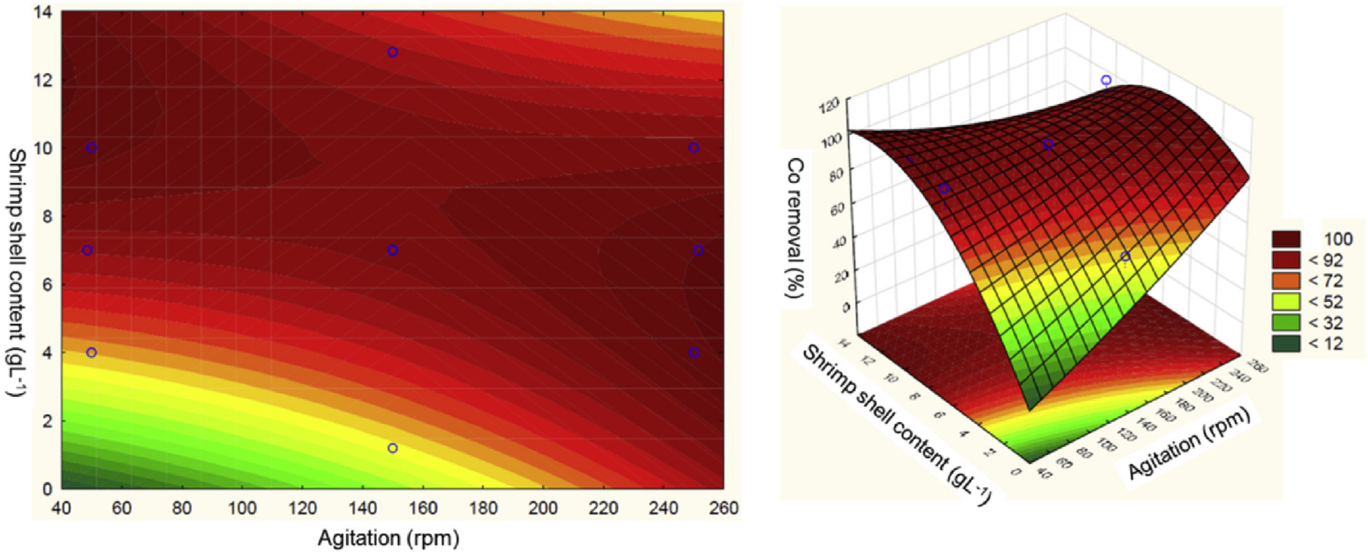

Fig. 5. Response surface (left) and contour curve (right) for Co removal (%).

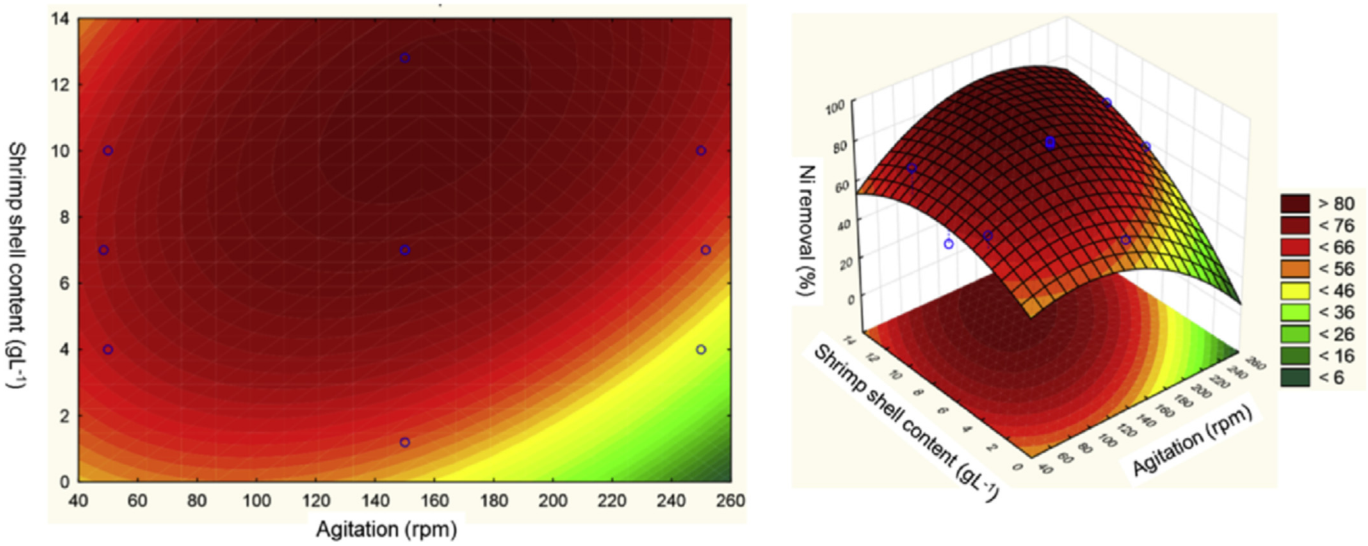

Fig. 6. Response surface (left) and contour curve (right) for Ni removal (%).

the model could only be validated by ANOVA at the 90% and 75% confidence intervals, respectively.

The response surface analysis showed that the optimum range of the parameters identified in this study was 150–250 rpm and 7–11 g of shell L^{-1} for the sample. In this regard, the best statistical conditions for the treatment of Sangão River water were a stirring range of 210 rpm and a shrimp shell content of 9.36 g $\cdot L^{-1}$. However, the structural instability of the shrimp shell was experimentally observed at this stirring rate, resulting in the liberation of compositional and sorbed manganese. The highest observed stirring rate without manganese liberation from the shrimp shells was 188 rpm.

Table 7
Ideal critical values of maximum efficiency in the Al, Fe, Mn, Co, and Ni removal processes.

Metal	Agitation (rpm)	Shrimp-shell content (g L^{-1})
Al	150	9.05
Fe	249	–
Mn	237	7.75
Co	146	8.92
Ni	157	11.04

Thus, 188 rpm and 9.36 g L^{-1} of shrimp shells were determined as the best conditions in terms of efficiency for the removal of the pollutant species for the MIW treated in this study (Table 1). These proportions could be considered for future metal removal experiments in AMD impacted water treatment, allowing for the reduced demand of biosorbent and energy, aiming for a major-scale application.

Acknowledgements

The authors are grateful to the Federal University of Santa Catarina (UFSC) and National Council of Scientific and Technologic Development (CNPq) for the financial and technical support.

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