TECNO-LOGICA
Revista do depto. de Química e Física, do depto. de Engenharia, Arquitetura e Ciências Agrárias e do Mestrado em Tecnologia Ambiental
http://online.unisc.br/seer/index.php/tecnologica

MOBILITY OF MERCURY OF THE DENTAL AMALGAM IN REDUCTION PROCESS IN THE SEDIMENTS: FACTORIAL DESIGN ANALISYS

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Recebido em 08 de julho de 2008.
Aceito em 05 de setembro de 2008.

ABSTRACT

The dental wastewater can contribute to the total daily mercury load on environment. Factorial design of experiments is useful to analysis of factors that influence in this mobility. The aim of the present study was to design experiments to examine the effects of operational variables – temperature, pH and contact time - which may affect the mobility of mercury in form of dental amalgam residue in reduction process in the sediments of the Pirapó River. Based on the factorial design of experiments and the analysis of variance, the temperature was the most significant factor in this process, followed by the pH and contact time. The parameters affecting the mobility of total mercury showed that when the temperature and contact time increases and pH decreases there is an important increase of mercury concentration in process. For the tested conditions, the high total mercury concentration was obtained using the temperature = 35°C, pH = 4.0 and contact time = 10 days.

Keywords: Factorial design. Mercury. Dental amalgam. Sediments.

1 Introduction

Mercury is one the most hazardous environmental pollutants [1-2-3-4]. Dental amalgam consists of about 50% metallic mercury [1-5-6-7]. Its release into traditional waste streams, such as the municipal solid waste stream or the sewer system, and its potential point source discharge into the environment is becoming a major concern. Studies have found that the dental wastewater stream can contribute from 10 to 70% of the total daily mercury load on wastewater treatment facilities [1-8].

In the biogeochemical cycle of mercury, these species may interchange in atmospheric, aquatic and terrestrial environments [2]. Several principally different processes and environmental variables (temperature, pH and chemical composition) affecting the solubility, mobility and chemical form influence metal ions in the aquatic and the geological environmental [9-10].

The methylation of inorganic mercury occurs by abiotic and biotic processes [3-11]. Abiotic methylation of mercury by methylcobalamin, methyltin compounds, and/or natural organic matter is very likely. Among these three compounds (or classes of compounds) natural organic matter is the most likely methylating agent [12-13].

Natural organic matter, such as humic and fulvic acids, contain a larger number of functional moieties such as carboxylic, phenolic and alcoholic groups that interact with surface groups as well as ion in solution. Most active groups, in this respect, are titrable and will at the natural pH range associate with dissolved metal ions through inner- as well as outer-sphere complexation [9].

When mercury was methylated, it is accumulated in food chains, particularly in the aquatic milieu where a high degree of biomagnification occurs. The food chain seems to be the predominant route of human exposure to organic mercury compounds [13-14-15]. Methyl mercury compounds are considerably more toxic than elemental mercury and its inorganic salts [2-14-15-16].

The aim of the present study was to design experiments to examine the effects of operational variables, which may affect the mobility of mercury as dental amalgam residue in reduction process in the sediments of the Pirapó River. That is, the significance of the effect of four main experimental variables, temperature, pH and contact time, which has been selected as a representative parameter of mobility of mercury.

2 Materials and Methods

2.1 Dental amalgam residue

Dental amalgam residues used in this study were obtained in odontologic clinical of State University Maringá.

This residue is an interaction of mercury (50-52%), silver (20-34%), tin (8-15%) and cupper (1-15%) [17].

2.2 Sediments of the Pirapó River

Sediment of the Pirapó river in the Maringá City, Northwestern Paraná State, Brazil, presents pH: 5.8, Total Organic Carbon (TOC): 3.1% and was not detected presence of mercury in samples.

2.3 Experimental design

The variables and their levels selected for the study of mercury mobility were: temperature [T] (10 and 35^{o}C); pH (4.0 and 10.0); and contact time [CT] (5 and 10 days).

The response variable in this study was the concentration of total mercury (T-Hg). In order to determine the effect of the operating variables on the concentration of mercury compound of the reduction process in the sediments of the Pirapó River a set of designed experiments was performed. Table 1 shows the independent factors - x_i, (X_1, X_2 and X_3), levels and experimental design in terms of coded and uncoded variables.

Table 1- Experimental design for mobility of T-Hg in reduction process in the sediments of the Pirapó River

Expt º.	Variable No Codified			Variable Codified		
	T (^{o}C)	pH	CT (days)	X_1	X_2	X_3
1	10	4,0	5	-1	-1	-1
2	10	4,0	10	-1	-1	+1
3	10	10,0	5	-1	+1	-1
4	10	10,0	10	-1	+1	+1
5	35	4,0	5	+1	-1	-1
6	35	4,0	10	+1	-1	+1
7	35	10,0	5	+1	+1	-1
8	35	10,0	10	+1	+1	+1

A two-level-four-factor factorial design was employed in this study, requiring 8 tests, performed in duplicate.

2.4 Experimental procedure

Experiments were carried out in 250 mL erlenmeyers with a solution volume of 50 g of the sediments and 1 g of dental amalgam residue. The pH was adjusted to the desired value (4.0 and 10.0) using hydrochloric acid (HCl) and sodium hydroxide (NaOH).

Erlenmeyers were incubated in desired temperature (10 and 35^{o}C), below constant agitation (150 rpm) into shaker (Marioni MA 830). Samples removed at predetermined intervals (5 and 10 days) in factorial design analysis.

Subsequently to digestion with oxidant mixture – water, hydrochloric acid and nitric acid (3:2:1) in "cold finger" reactor, samples were separated by vacuum filtration through a cellulose porous material, with a 0.45 μm pore diameter

Mercury was analyzed by cold vapor atomic absorption spectrometry (Varian SpectrAA – 10 plus with steam generation). Total mercury (T-Hg) was determined by oxidizing all forms of Hg with bromine chloride solution (1 mL of HCl 50% + 1 mL of KB_2O_3 1.5%), before reduction with $SnCl_2$ [13,18].

3 Results and discussion

Table 2 shows the experimental results of reduction process as an average of the duplicate experiments, which results at each operation condition are shown in Table 1.

A statistical analysis software package (SAS Institute, Inc., Cary, N.C. – version 6.12) was used to analyze the results.

The analysis of variance for main effects and interactions indicates that the main effects of the variables X_1 (temperature), X_2 (pH) and X_3 (Contact Time) and their interaction ($X_1 \cdot X_2$ and $X_1 \cdot X_2 \cdot X_3$) affect significantly (P-value<α=0.05) the mobility of total mercury in reduction process, with a confidence level of 95%.

Table 2 - Results of T-Hg mobility in reduction process in the sediments Pirapó river

Expt nº.	T (^{o}C)	pH	TC (dia)	HgT (mg/Kg TOC*)
1	10	4,0	5	135,67
2	10	4,0	10	146,33
3	10	10,0	5	138,00
4	10	10,0	10	129,00
5	35	4,0	5	210,67
6	35	4,0	10	216,67
7	35	10,0	5	177,67
8	35	10,0	10	189,33

* TOC: Total Organic Carbon

In the factorial design of experiments, it is useful to consider the factor response relationship in terms of a mathematical model such as a response function. Considering the effecting factors and interactions, it is possible to fit an adequately regression model to the data by using a linear parameter model (Equation 1) as described by Myers and Montgomery (1995) and obtain a first order polynomial equation, so that the response at intermediate factor levels can be predicted.

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_1.X_2 + \beta_5 X_1.X_3 + \beta_6 X_2.X_3 + \beta_7 X_1.X_2 X_3 + \varepsilon \quad (1)$$

where y is the total mercury concentration, β's are the main and interaction coefficients, X_1, X_2 and X_3 are the coded variables according to Table 1.

The analysis of variance to concentration of total mercury (Table 3) indicates that the statistical model can be satisfactorily used ($R^2 = 0.9932$, P-value<α)

Table 3- Analysis of variance

Source of variation	Degree of freedom	Sum of square	Mean square	*F*-value	*P > F*
$X_1 = T$	1	22570.6	22570.6	746.1	<0.0001
$X_2 = pH$	1	2128.6	2128.1	70.3	<0.0001
$X_3 = CT$	1	140.1	140.1	4.6	0.0470
$X_1.X_2$	1	770.6	770.6	25.4	0.0001
$X_1.X_3$	1	96.0	96.0	3.1	0.0938
$X_2.X_3$	1	73.5	73.5	2.4	0.1386
$X_1.X_2.X_3$	1	240.6	240.6	7.9	0.0123
Error	16	484.0	30.2		
Corrected total	23	26503.8			

The estimated main effects of the four factors and their interaction of the total mercury concentration are summarized in Table 4.

Table 4 - Effects for 2^3 factorial design

Effects	Estimated effect ± standard error
Mean	167.9167 ± 1.2299
$X_1 = T$	30.6667 ± 1.2299
$X_2 = pH$	-9.4167 ± 1.2299
$X_3 = CT$	2.4167 ± 1.2299
$X_1.X_2$	- 5.6667 ± 1.2299
$X_1.X_2.X_3$	3.1667 ± 1.2299

The values of these coefficients were incorporated in Equation 2, which takes the following form:

$$\hat{y} = 167.9167 + 30.6667\, x_T - 9.4167\, x_{pH} + 2.41667\, x_{TC} - 5.6667\, x_T.x_{pH} + 3.1667\, x_T.x_{pH}.x_{TC} \quad (2)$$

The effect values presented in Table 4 shows that the temperature [T] is the most important factor in this process, followed by temperature, pH and contact time.

In addition, it can be seen that T and CT have a positive effect, while the pH has a negative effect on the total mercury concentration in reduction process in the range of variation of each variable selected in this present study. The interaction between T and pH has a negative effect and interaction among the three selected parameters have a positive effect on T-Hg concentration. Then, it can be stated by way of statistical analysis that the studied factors were influenced significantly in the total mercury concentration in reduction process in the sediments of the Pirapó River.

Applying the Tukey's test, with a level of significance of 5%, it can be determined the difference between the averages of the two levels of the factors[19]. Means total mercury concentrations for the two levels of the factors are presented in Table 5.

Table 5 - Means of T-Hg concentration in 2^3 factorial design

Levels	Variation		
	T	pH	CT
-1	37.25	77,33	65,50
1	98,58	58,50	70,33

Tukey's test (α = 0,05).

Table 5 shows the significant difference of the total mercury concentration between the two levels of the factors T, pH and CT (around 62, 19 and 5 mg/kg TOC, respectively). An increase on the temperature and contact time and decrease on the pH resulted in an increase in mobility of total mercury in the sediments.

Figure 1, 2 and 3 presents plots of the three main effects in order to assist in the practical interpretation of the experiments. The main effect plots are figures of the marginal response averages at the levels of the three factors.

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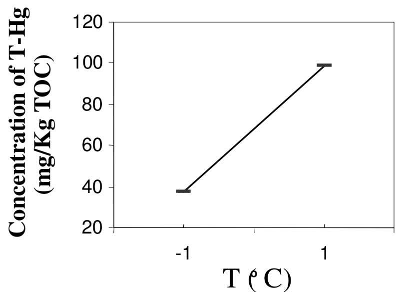

Figure 1 - Main effects plots for T-Hg concentration: T

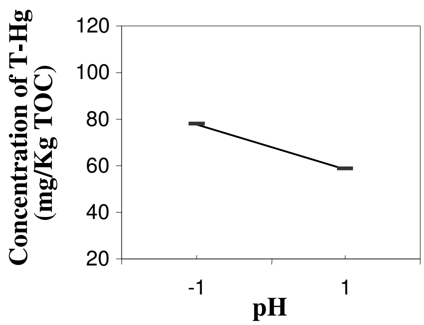

Figure 2 - Main effects plots for T-Hg concentration: pH

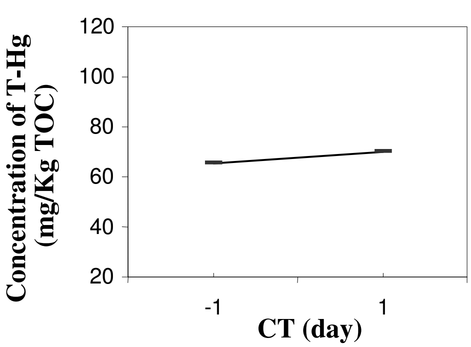

Figure 3 - Main effects plots for T-Hg concentration: CT

Notice that two variables (T and CT) have positive main effects, that is, increasing the variable moves the average deviation from the fill target upward, while one variable (pH) has negative main effect, that is, increasing the variable moves the average deviation from the fill target downward. As can be seen in Figure 1 to 3, a change in the levels of each factor produces a different variation in the mobility. An increase on the temperature from 10 to 35^{o}C resulted in an increase in mobility of total mercury of 62.3% (Figure 1). The same can be observed on the temperature, on which an increase to temperature from 5 to 10 resulted in an increase in mobility of 19% (Figure 2). On the other hand, an increase on the pH from 4.0 to 10.0 decreased the process efficiency in 4.8% (Figure 3).

As the two-factor interactions among X_1 (T) and X_2 (pH) were also significant, it is necessary to examine the interaction effects, shown in Figure 4.

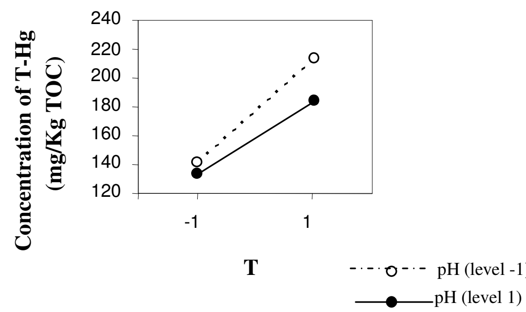

Figure 4 - Two-factor interaction plots for T-Hg concentration: T-pH

The interaction plot is graph of the response averages for the pH at the fixed levels of the T. The T-pH interaction indicates that the T effect is very small when the pH is at the high level and large when the pH is at the low level, with the high T-Hg concentration high temperature and small pH.

The results showed that the mobility of total mercury increased with higher humic acid concentration, temperature and contact time and low pH. The same can be seen in Figure 5 illustrating the surface of response to the significant interaction T-pH. This was also observed by others authors [13,18,20,21,22,23].

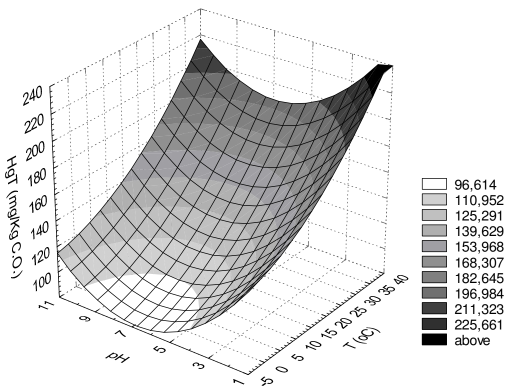

Figure 5 - Surface of response to the significant interaction T-pH for T-Hg concentration

When the dental amalgam residue is discarded in a low pH and high temperature environment, the existing mercury in this residue solubilize easily, reacting and forming inorganic mercury. In contact with the organic matter in the sediment, this compound is methylated and becomes the most toxic compound (methyl-mercury).

4 Conclusions

Based on the factorial design of experiments for total mercury mobility as dental amalgam residue in reduction process in the sediments, they were identified on the mobility of total mercury the effects of three factors: the temperature, the pH and contact time. According to the significance effect obtained in variance analysis, the temperature was the most significant factor in this process, followed by the pH and contact time. The parameters, that affect the mobility of total mercury showed that when the T and CT increases and pH decreases, there is an important increase of total mercury concentration in process

Acknowledgement

The support provided by CNPq and by the State University of Maringá is gratefully acknowledged.

MOBILIDADE DO MERCÚRIO DO AMÁLGAMA ODONTOLÓGICO NO PROCESSO REDUTIVO EM SEDIMENTOS: ANÁLISE FATORIAL EXPERIMENTAL

RESUMO: As águas residuais dentários podem contribuir para a carga diária total de mercúrio no ambiente. Análise fatorial experimental é útil para a análise de fatores que influenciam esta mobilidade. O objetivo do presente estudo foi realizar experimentos para analisar os efeitos das variáveis operacionais - temperatura, pH e tempo de contato - que possam afetar a mobilidade do mercúrio na forma de amálgama odontológica em um processo redutivo nos sedimentos do rio Pirapó. Com base no modelo fatorial de experimentos e na análise de variância, a temperatura foi o fator mais importante neste processo, seguido do pH e do tempo de contato. Os parâmetros afetaram a mobilidade de mercúrio total, mostrando que quando a temperatura e o tempo de contato aumentam e o pH diminui, há um aumento significativo na concentração do mercúrio no processo. Para as condições testadas, o aumento na concentração mercúrio total foi obtida nas condições de operação, temperatura = 35^{o}C, pH = 4,0 e tempo de contato = 10 dias.

Palavras-chave: Análise fatorial. Mercúrio. Amálgama odontológico. Sedimentos.

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