Electroflocculation as a tool for teaching design of experiments

Eletrofoculação como ferramenta para o ensino de delineamentos experimentais

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Abstract

This work aimed at presenting the electroflocculation treatment of water as well as the statistical tool called Design of Experiments to evaluate factor effects on methyl orange percent removal from aqueous solution. Two factors, reaction time and amount of support electrolyte, were evaluated at two levels: 5 and 10 minutes, and 0.585 g and 2.930 g of NaCl salt, respectively. The results showed that main and interaction effects were statistically significant at 95% level. The average removal of methyl orange from aqueous solution reached 99.83 % as the reaction time and the amount of NaCl salt factors were fixed at high levels – 10 minutes and 2.930 g, respectively. The interaction plot showed that reaction time effect depends on the level fixed for the amount of salt factor. The reaction time effect is greater when the other factor is at low level.

Keywords: electroflocculation, experimental design, chemometrics.

Resumo

O presente estudo teve como objetivo apresentar o tratamento de eletrofloculação da água, bem como a ferramenta estatística denominada delineamento experimental para avaliar o efeito dos fatores na remoção de percentual de alaranjado de metila de soluções aquosas. Dois fatores, tempo reacional e quantidade de eletrólito de suporte, foram avaliados em dois níveis: 5 e 10 minutos, e 0,585 g e 2,930 g de sal NaCl, respectivamente. Os resultados mostraram que os efeitos principal e de interação apresentaram um nivel de significância estatística de 95%. A porcentagem de remoção média do alaranjado de metila das soluções aquosas foi 99,83 %, quando os fatores tempo reacional e quantidade de NaCl foram fixados nos maiores níveis (10 minutos e 2,930 g, respectivamente). A curva de interação mostra que o efeito do tempo reacional depende do nível da quantidade de NaCl fixada. O efeito do tempo reacional será maior quanto menor for o fator quantidade de NaCl.

Palavras-chave: eletroflocução, delineamento experimental, quimiometria.

INTRODUCTION

This educational work has two goals. One is to present the eletroflocculation treatment of waste water and the other is to show the application of the statistical tool, design of experiments, to evaluate quantitatively two factors that affect the performance of that process in removing dye compounds from aqueous solution.

The conventional treatment methods for removal of organic matters from waste waters employ biodegradation, but it takes longer time and is not efficient as the effluent contains great amount of toxic organic contaminants such as azo dyes. The electrochemical process might be a better alternative since it is faster and not sensitive to toxic organics because it doesn't rely on microorganism activity.

The electrolytic cell is composed of two active electrodes (cathode and anode), generally made of aluminum or iron, a source of continuous current and the electrolytic recipient where resides the problem solution. A support electrolyte must be added in order to increase the amount of current in the system. Iron and aluminum are usually the chosen metals because they are abundant and produce trivalent cations (M^{3+}) which hydrolyze and transform into insoluble hydroxides that form colloidal particles responsible for the adsorption of the dye molecules or other small particles, forming agglomerates that settle down.

The organic dyes are removed from the aqueous medium in the eletroflocculation process not only by adsorption onto colloidal particles as previously mentioned. Metal atoms, dye and water molecules undergo oxidation at the anode. Due to water oxidation, oxygen gas is released from it. At the cathode the metal cations, which were generated at the anode, are reduced as well as water molecules and that's why hydrogen gas is also released from this electrode.

Neto et al., (2011) have recently presented an educational paper suggesting an experiment about electroflocculation for undergraduate students. In their work besides a good explanation of the mechanism by which an organic contaminant is removed and broken down by that process, they also showed the influence of three parameters that affects orange II dye removal efficiency: type of active electrode, current density and temperature. They concluded that the electroflocculation system produces better dye removal results when aluminum active electrode, high temperature and high current density are employed.

In this study we chose to work with methyl orange compound (MO), which is similar to the azo dye orange II as the target molecule to be removed from the aqueous solution. Since the previous work also mentioned that aluminum is better than iron, we decided to select aluminum as the active electrode and two factors or parameters were quantitatively evaluated: reaction time and amount of NaCl salt added as support electrolyte.

Instead of one-at-a-time approach in which the analyst fixes one factor at one level whilst vary the levels of the other factor, in this study we set up a factorial design. By this approach each factor level is combined with the levels of the other factor. If k factors are combined in two levels, 2^k different experimental conditions or treatments will be generated. Since two factors were studied at two levels, the number of different experiments were $2^2 = 4$. In order to assess the statistical significance of the factor effects the error must be estimated that is why in this work one replicate for each experiment were also performed generating a total of 8 experiments.

Guedes et al., (2013) reasoned about the lack of educational work on chemometrics and described a simple experiment to evaluate the influence of three factors - cooling temperature, dissolution temperature and gelatin to water ratio (m/m) - on setting-time of comercial gelatins.

Krawczyk, Slupska and Baj, (2015), presented an educational article which studied the influence of three factors - hemin, NaOH and urea hydrogen peroxide concentrations – on the light emission length (seconds) of luminol during its oxidation. The statistical analysis involved the calculated effects (mains effects and interactions), an ANOVA table and the predicted values. Ligouri (2017) described a tasting experiment to teach statistical experiment designs. The author studied the effect of two factors, lemon juice and baking powder amount (grams) on the taste of lemon cakes. The author built up a mathematical model, plotted the three dimensional graph of the factors against the response variables (fluffiness, lemon taste and overall rating) and constructed the contour plots. After, s/he validated the model comparing some experimental results to predicted values.

Both works in the previous paragraph are excellent, but the first one uses some expensive chemicals, such as luminol, and the second is very time consuming as it takes long to make the cakes and to collect the variable response which is based on sensory panels (it requires lots of people to taste the cakes and grade them). The experiment we suggest uses cheaper chemicals and it only takes about 3 hours or less if all the materials and reagents are previously arranged by the laboratory technician.

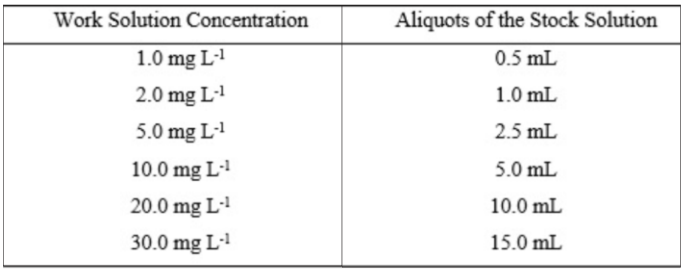
MATERIALS AND METHODS

Aluminum wires that might be bought from an electrotechnical store; 12 V continuous current source; 500 mL volumetric bottle for MO stock solution; 50 mL volumetric bottles for work problem solutions; 5 mL micropipette; 50 mL beakers as the electrolytic cell recipient; 250 mL Erlenmeyers to collect the filtrates; Filtration funnel; Qualitative filter paper; Methyl Orange ($C_{14}H_{14}N_3NaO_3S$ Dinâmica); NaCl salt (Sigma-Aldrich 99-100,5%); Spatula; Glass rod; Spectrophotometer UV-Vis model NOVA 6100 UV; a wood disk with two holes distant from each other by 2 cm (this is the electrode support in the electrolytic cell) acquired from the carpentry sector of the Institute Federal of Mato Grosso.

Calibration of the spectrophotometer UV-Vis

1) 500mL of stock solution of MO (methyl orange) 100 mg L^{-1} were prepared using distilled water as solvent.
2) The six work solutions were prepared in 50 mL volumetric bottles from stock solution. The concentration of each work solution was 1.0 mg L^{-1}, 2.0 mg L^{-1}, 5.0 mg L^{-1}, 10.0 mg L^{-1}, 20.0 mg L^{-1} and 30.0 mg L^{-1}. See Table 1.
3) The spectrophotometer was calibrated using the previous work solutions and the absorbance readings were performed at 464 nm wavelength.

Table 1
Preparation of the work solutions



Work Solution Concentration	Aliquots of the Stock Solution
1.0 mg L^{-1}	0.5 mL
2.0 mg L^{-1}	1.0 mL
5.0 mg L^{-1}	2.5 mL
10.0 mg L^{-1}	5.0 mL
20.0 mg L^{-1}	10.0 mL
30.0 mg L^{-1}	15.0 mL

Electroflocculation experiment

1) The MO concentration used in the electroflocculation experiment is 30.0 mg L^{-1} which is the upper limit of the calibration curve.
2) The amount of b_1 grams of NaCl salt (0.585 or 2.930 grams) were weighed in each beaker according to the experiment identification in Table 2.
3) 50 mL of 30.0 mg L^{-1} MO solution were added to each 50 mL beaker.
4) The aluminum electrodes were inserted into the wood disk support.
5) The mixture was mixed with a glass rod for 40 seconds to dissolve the salt.
6) The electrode set was fit over the 50 mL beaker containing MO solution and the 12V source turned on.
7) The process took b_2 minutes according to the experiment identification in Table 2.
8) The power source was turned off and the

treated solution left for 10 minutes in a water bath to cool down.

9) The mixture was then filtrated and the absorbance reading at 464 nm was performed for each final filtrate.
10) The percent removal of MO from the aqueous solution, which is the response variable, were calculated according to the following equation 1.

$$R = \left(\frac{C_{filtrate} - 30}{30}\right)100 \tag{01}$$

R - MO removal %.

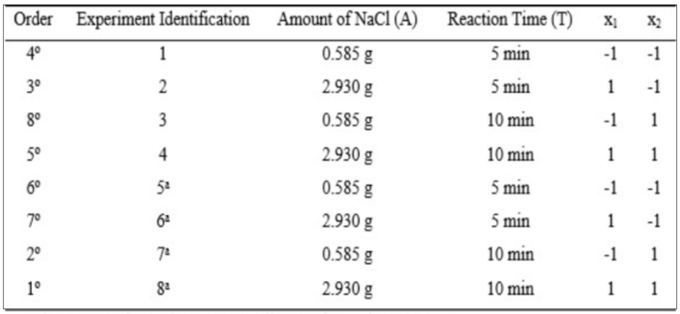
$C_{filtrate}$- final concentration of MO (mg L^{-1}) in the filtrate.

The 2^2 Factorial Design

In the electroflocculation process we aimed at evaluating two factors, reaction time and amount of NaCl at two levels: reaction time from 5 to 10 minutes and amount of salt from 0.585 to 2.930 grams (which correspond to salt molar concentrations of 0.2 and 1.0 mol L^{-1}, respectively). The combination of each factor level with one another produces 4 different experiments. Those would be enough to evaluate the main factor and interaction effects, but to statistically verify the significance of them we must perform replicates so that we can compare the effect values to the standard deviation (MONTGOMERY, 2005; BRUNS, SCARMINIO and NETO, 2007; HUNTER, HUNTER and BOX, 1978). In Table 2 the 2^2 factorial design is presented with 8 experiments in which each of the original four combinations are replicated.

Table 2

Design of a 2^2 factorial experiment with replicates



Order	Experiment Identification	Amount of NaCl (A)	Reaction Time (T)	x_1	x_2
4º	1	0.585 g	5 min	-1	-1
3º	2	2.930 g	5 min	1	-1
8º	3	0.585 g	10 min	-1	1
5º	4	2.930 g	10 min	1	1
6º	5[a]	0.585 g	5 min	-1	-1
7º	6[a]	2.930 g	5 min	1	-1
2º	7[a]	0.585 g	10 min	-1	1
1º	8[a]	2.930 g	10 min	1	1

a: these array of experiments are replicates of experiments 1 to 4.

The two last columns presented the variables in the coded form:

$$x_{coded} = \frac{b_{natural} - \left(\frac{b_{high} + b_{low}}{2}\right)}{\left(\frac{b_{high} - b_{low}}{2}\right)} \tag{02}$$

In which $b_{natural}$ is the natural variable value, b_{high} and b_{low} are its natural values at high and low levels. For example for the amount of salt factor (x_2) the coded value are calculated by equation 3.

$$x_2 = \frac{b_2 - \left(\frac{10 + 5}{2}\right)}{\left(\frac{10 - 5}{2}\right)} \tag{03}$$

In which b_2 is the reaction time values.

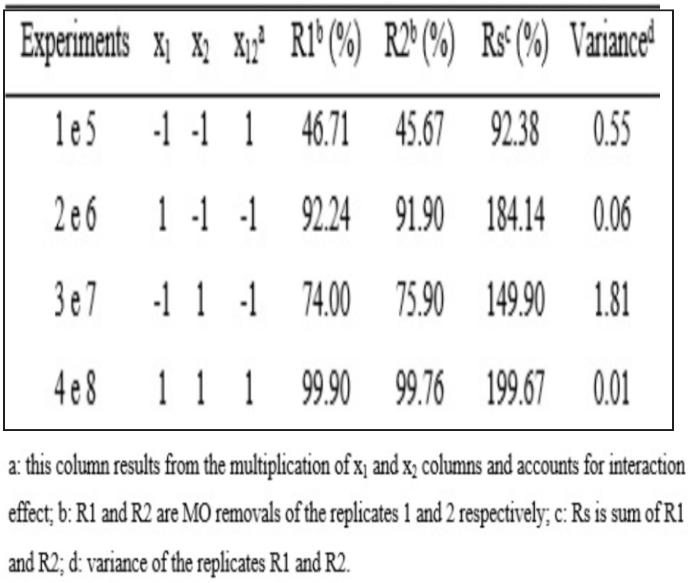
In order to prevent the cofounding of the nuisance factors (uncontrollable and unknown influences) with the effects, the randomization of the experiments must be done before performing them (BRUNS, SCARMINIO and NETO, 2007; HUNTER, HUNTER and BOX, 1978). The first column in Table 2 shows the order in which the experiments were carried out.

RESULTS AND DISCUSSION

Table 3 shows the MO percent removal for each experiment. When we look at this table it seems no meaningful information can be extracted from it. But in Figure 1 the data were arranged in such a way that we can see the factor effects. The square corners represent each of the four original experiments. The left signal in the corner represents the level of x_1 (amount of salt) and the right one, the level of x_2 (reaction time). For instance, the corner " - - " is the experiment performed at lower amount of salt

(0.585 g) during less time (5 minutes). The corner "+ -" represents the experiment performed at higher amount of salt (2.93 g) during less time (5 minutes) and so on.

Table 3
MO percentage removal from the problem solution



Experiments	x_1	x_2	x_{12}[a]	R1[b] (%)	R2[b] (%)	Rs[c] (%)	Variance[d]
1 e 5	-1	-1	1	46.71	45.67	92.38	0.55
2 e 6	1	-1	-1	92.24	91.90	184.14	0.06
3 e 7	-1	1	-1	74.00	75.90	149.90	1.81
4 e 8	1	1	1	99.90	99.76	199.67	0.01

a: this column results from the multiplication of x_1 and x_2 columns and accounts for interaction effect; b: R1 and R2 are MO removals of the replicates 1 and 2 respectively; c: Rs is sum of R1 and R2; d: variance of the replicates R1 and R2.

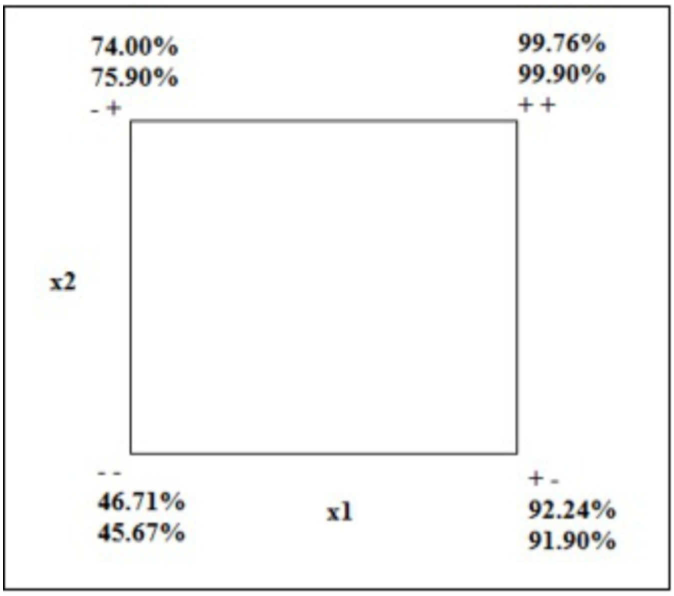


Figure 1. Square representation of the effects

We can clearly see as the amount of salt increased (x_1 ranged from -1 to +1) the process removed greater amount of MO from aqueous solution - the removal percentages ranged from [46.71 and 45.67%] to [92.24 and 91.90%]. As the reaction time increased (x_2 ranged from -1 to +1) the MO removals also increased – the results changed from [46.71 and 45.67%] to [74.00 and 75.90]. And as both factors are changed from -1 to +1, the MO removal increased further from [46.71 and 45.67%] to [99.76 and 99.90%].

Just by inspecting the square in Figure 1, without going into the statistic tests of significance we notice that the two factor effects are impacting, because it is clear that corner-to-corner differences are greater than differences inside each corner, which means the effects have overcome the noise and were visually detected.

Two main effects and one interaction effect might be estimated by a 2^2 factorial experiment design. The main effects were named A and T for amount of NaCl salt and reaction time, respectively. The first order interaction effect was AT. Using the data presented in Table 3 we can easily determine the effects by calculating the contrasts related to each factor. Considering columns, x_1, x_2 and x_{12}, as coefficient vectors, the contrast for each factor is determined using (MONTGOMERY, 2005).

$$contrast = \mathrm{x^tRs} \quad (04)$$

Then the effects might be calculated using equation 5.

$$effect = \frac{2}{n2^k} contrast \quad (05)$$

In which n is the number of replicates and k the number of levels of each factor. In this work n and k equal to 2.

In order to estimate de standard deviation of the effects first we calculated the variance of the replicates for each experimental combination:

$$\mathrm{S_i^2} = \frac{\Sigma(\mathrm{R}-\bar{\mathrm{R}})^2}{\mathrm{n}-1} \quad (06)$$

In which i ranges from 1 to 4 as there were four original designed experiments and is the mean of each array of replicates. The variances were already presented in Table 3. From this table we obtained the pooled standard deviation:

$$S_p = \sqrt{\frac{\sum S_i^2(n-1)}{i(n-1)}} \quad (07)$$

In which n is the number of replicate for each experimental combination.

The standard deviation of the effects was calculated according to the following equation:

$$sd_{effects} = \frac{2S_p}{\sqrt{n2^k}} \quad (08)$$

In which k stands for the number of factors and n for the number of replicates.

As we can notice in Table 4, the main (A and T) and interaction (AT) effects are greater than the effect standard deviation which indicates their significance as they are way higher than the noise ($sd_{effects}$). In order to show their statistical significance a 95% confidence intervals were built for each effect:

$$\underbrace{effect\ value - t_{0.025,df}sd_{effect}}_{\text{Lower limit}} < \mu_{effect} < \underbrace{effect\ value + t_{0.025,df}sd_{effect}}_{\text{Upper Limit}} \quad (09)$$

The subscript 0.025 stands for the probability in the lower and upper tail of the t distribution, and df is the degree of freedom used to calculate the effect standard deviation, which in this case is 4.

Table 4
The statistical significance of the effects

Factors	Effects	$sd_{effects}$	95% confidence intervals	
			Lower Limit	Upper Limit
A	35,38	0,55	33,85	36.90
T	18,26	0,55	16,73	19.79
AT	-10,50	0,55	-12,02	-8,97

None of the 95% confidence intervals includes the zero value, which shows that all the effects are statistically significant. The statistical analysis might also be performed by analysis of variance (ANOVA), applying an F test to show the significance of each effect. The ANOVA approach will come to the same conclusion. Ferreira and Teófilo, (2006), developed Excel spreadsheets useful to statistical analysis of experimental designs and their work might be a good resource to build ANOVA tables as well as confidence intervals for the effects. The article has an excellent brief explanation about this statistic field as it further covers complete factorial designs, fractional factorial designs, central composite and Doehlert designs, and surface response methodology.

Since the interaction effect AT were found significant we must not analyze the main effects separately because the effect of each factor depends on the level of the other factor. We can notice in Figure 1 that time effect changes according to the amount of salt level. The difference between the average of the - + corner and the average of the - - corner is 74.95 – 46.19 = 28.76%. This is the time effect when the amount of salt is fixed at the lower level, but if the salt amount is at higher level, the time effect, calculated by the difference between the average of + + corner and the average of the + - corner, is 99.83 – 92.07 = 7.76%. Briefly, the T factor doesn't behave the same way at both factor A levels.

The AT interaction might be showed in an interaction plot in which the averages of the replicates are plotted according to Table 5, that's why this plot is also called mean plot.

Table 5
MO Removal Averages

A\T	5min	10min
0,585g	46.19%	74.95%
2,930g	92.07%	99.83%

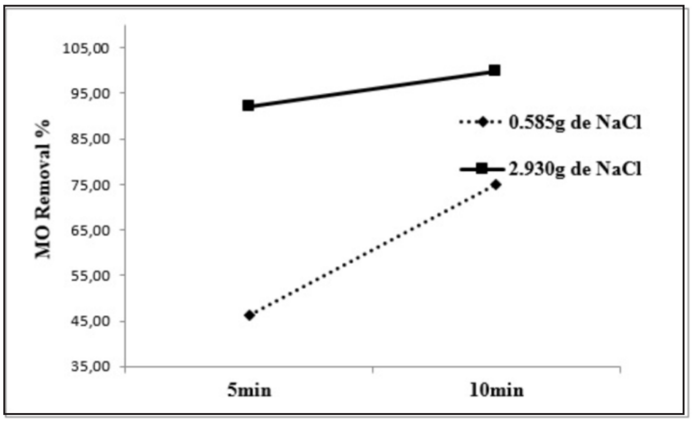


Figure 2. Interaction plot of the MO removal values against each factor

The two lines in Figure 2 show clearly that the increase in MO removal due time change is greater when A factor is fixed at lower level. If no interaction were significant the lines would be parallel to each other.

The NaCl salt in aqueous solution are in the form of Na^+ and Cl^- ions. They increase the electric current going through the system so that oxidation and reduction rates increase, causing the formation of more aluminum hydroxide particles, which adsorbed more MO molecules, besides rising the oxidation rate of these molecules at the anode.

Reaction time had little effect on MO removal at higher concentrations of salt, but greater at lower salt concentrations. This observation is important since the step of support electrolyte addition is one of the drawbacks of the electroflocculation process, since it generates an effluent that will certainly need further treatment steps to remove the salts. So by inspection of Figure 2, it seems possible to decrease the amount of salt and increase the reaction time in order to achieve results as good as the experiment combination + +.

The statistical signicance of the main effects, A and T, as well as the their second order interaction, AT, might be determined through analysis of variance. First we determined the total sum of squares (SSTotal) then the sum of squares of main and interaction effects (SSA, SST and SSAT) and the sum of squares due to error (SSE).

From the sum of squares we calculated the mean squares. By using the F statistic the mean square of each effect was compared to the error mean square to evaluate its significance.

All sum of squares was determined according to the following equations (MONTGOMERY, 2005):

$$SSTotal = \sum_{1}^{8} (R_i - \overline{OR})^2 \tag{10}$$

$$SSA = \frac{(contrast_A)^2}{n2^k} \tag{11}$$

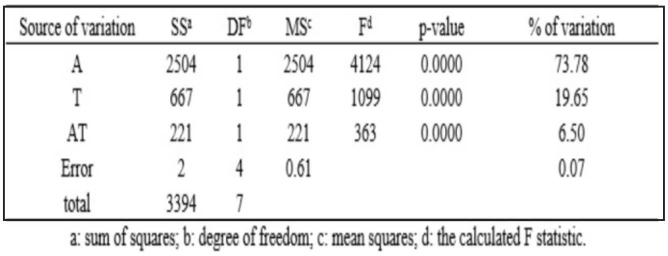
$$SST = \frac{(contrast_T)^2}{n2^k} \tag{12}$$

$$SSAT = \frac{(contrast_{AT})^2}{n2^k} \tag{13}$$

$$SSE = SSTotal - (SSA + SST + SSAT) \tag{14}$$

The term R_i is each of the removal results (%) in Table 3.Or is the overall mean. The contrast terms for each effect are calculated according to equation (4). The total degree of freedom is N-1, whereas N is the total number of results (in this case, 8). So the total degree of freedom is 7. Each effect accounts for one degree of freedom so that the degree of freedom left to error is 7 – 3 = 4. The effect and error means squares were determined by dividing each sum of squares by its correpondent degree of freedom and the ANOVA table constructed.

Table 6
ANOVA table



Source of variation	SS[a]	DF[b]	MS[c]	F[d]	p-value	% of variation
A	2504	1	2504	4124	0.0000	73.78
T	667	1	667	1099	0.0000	19.65
AT	221	1	221	363	0.0000	6.50
Error	2	4	0.61			0.07
total	3394	7				

a: sum of squares; b: degree of freedom; c: mean squares; d: the calculated F statistic.

The ANOVA table shows that the sum of squares associated with the effects are way greater than error sum of squares, which means that each effect accounts for the major variation in the data. For example, the A effect accounts for (2504/3394)*100 = 73.78% of the variation. And all effects account for 99.93% of the variation. The nuisance factors (unkown and uncontrollable factors) account for only 0,07% of the total variation. The p-values for the effects are close to zero. So the analysis of variance showed, as already indicated by the confidence intervals, that all effects are statistically significant and most of the variation are due to factor A effect.

CONCLUSION

The experiments showed that in order to achieve almost 100% MO removal, the amount of salt and the reaction time factors must be fixed at high levels. The interaction plot also demonstrated that time effect depends on the fixed level of the amount of salt factor. In lower level of salt amount, time has a greater effect. So since the addition of salt as support electrolyte is a disadvantage of the electroflocculation process, the amount of NaCl could be reduced and the reaction time further increased to achieve MO removal close to 100%.

The electroflocculation experiment proposed in this work might be used in any course related to analytical chemistry or chemometrics for undergraduate students. It is simple and uses cheap chemicals and materials, which are easily found in any analytical chemistry laboratory. The experiments might be performed in a 3-hour laboratory class if the materials and reagents are previously arranged by the professor or the lab technician. The data might be readily collected and analyzed by the Excel software since the calculations presented here are simple. Lots of scientific works in literature still uses the one-at-a-time approach to evaluate factors that affect a system response, but this approach is usually time consuming and larger number of experiments are required. The factorial design takes a smaller number of experiments and still accounts for interaction effects.

Technical students collaborated to the development of this work, and as they performed the experiments they got overwhelmed by the multitude of chemical reactions taking place: oxygen gas are formed in the anode; hydrogen gas are formed in the cathode; the anode electrode undergoes corrosion; the cathode has its mass increased as the aluminum is reduced; they also saw the aqueous MO solutions losing their color and the formation of insoluble hydroxides which adsorbs MO molecules. All these effects were visually noticed as well as time and amount of salt effects which were further statistically detected.

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