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A NEW APPROACH TO THE DESALINATION PROCESS OF ARCHAEOLOGICAL POTTERIES

Somayeh Noghani¹, Mohammad C. Amiri² and Mohammadamin Emami¹

¹*Faculty of Conservation, Art University of Isfahan, P.O. Box: 1744, Isfahan, Iran*

²*Department of Chemical Engineering, Isfahan University of Technology, Isfahan, Iran*

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Corresponding author: Dr. Mohammad Amiri (amir33@cc.iut.ac.ir)

ABSTRACT

As salt crystallization is one of the most serious damages in historical porous materials (e.g. potteries, bricks, etc.), desalination is highly important process in conservation. Since this process is irreversible, and object has direct vicinity with water, preventing the misrepresentation of valuable archaeological and archaeometrical data of historic object will be substantial. On the other hand, a considerable amount of water is used in this process because of a huge number of excavated potteries in archaeological sites, therefore, controlling the amount of rinse water consumption is extremely desirable. As this process is a multivariable system, a new approach based on a mathematical design of experiment, response surface methodology (RSM), was used as an aid in determining the significance of the various parameters and optimization of this process. The input (independent) variables in the experimental design were immersing time, agitation rate, firing temperature (as void fraction indicator), type and concentration of surfactant. For each variable, five levels were selected in a batchwise pilot tests. Electrical conductivity (EC) and Ca^{2+} concentration of rinse solutions were measured as responses of experiments. It was found that the most effective parameters in the immersing desalination process are: firing temperature of specimen, immersing time, and agitation rate. The experimental results revealed that desalination process in optimized conditions results in speed up the operation time up to less than 8% and saving up to 50% water consumption compared to conventional method at the same desalination achievement. The accuracy of the modeling was validated with triplicate experiments. It was found that the average Ca^{2+} concentration and EC value in rinse solution fit approximately 90% with RSM predicted data.

KEYWORDS: Desalination, optimization, rinse water, agitation, response surface methodology (RSM), archaeological potteries

1. INTRODUCTION

Extracted historical objects from open or underground archeological sites most often contain various salts and deterioration of archaeological porous materials due to salt crystallization is a well-known phenomenon (Jang *et al.*, 2013; Montana *et al.*, 2014; O'Brien, 1990; Römich, 2006). Soluble salts in pottery exert destructive forces through crystallization that can lead to the physical disruption of the ceramic body and therefore complete fracturing of object, as well as efflorescence can be so dense as to completely obscure an object and cause loss of archaeological information (Paterakis and Steiger, 2015).

Desalting or desalination process of archaeological porous material refers to the removal of salts from contaminated objects (Franzen *et al.*, 2013). Therefore, desalination process is one of the most important and critical step for safe conservation of contaminated archaeological ceramics. Since potteries are one of the most abundant and important remains in archaeological sites (Palanivel & Kumar, 2011), desalination of these objects needs a considerable amount of water and time. In addition, the long duration of water in contact with object may damage the historical artefact.

Moreover, this treatment usually focuses on the removal of the soluble salts to prevent future deterior-

ation especially where storage conditions have introduced salts (White *et al.*, 2010).

Two classical desalination methods are: a) total immersion of object in the water bath and b) using poultice treatment (often for immovable objects) (Buys & Oakley, 1999). In spite of scientific researches about salt removal by poultice in desalination of historical stones and masonries (Bourges & Verges-Belmin, 2008; Hees *et al.*, 2006; Lubelli & van Hees, 2010; Pel *et al.*, 2010; Sawdy *et al.*, 2008), only few studies have been done on effectual desalination of excavated archaeological potteries (Jang *et al.*, 2013; Koob & Ng, 2000; Montana *et al.*, 2014; Unruh, 2001).

In several previous studies, some of parameters that effect on desalination efficiency are mentioned such as porosity, salt solubility and ion-specific behavior in the extremely complex desalination environment, and wash characteristics (a single longer bath or multiple baths with drying periods) (White *et al.*, 2010). The immersing system desalination depends on various parameters that can be categorized in three different issues: properties of porous object, immersing system and soluble salts (Fig. 1). As features of the object and salts cannot be changed, therefore, modifications in immersing system can enhance efficiency of desalination.

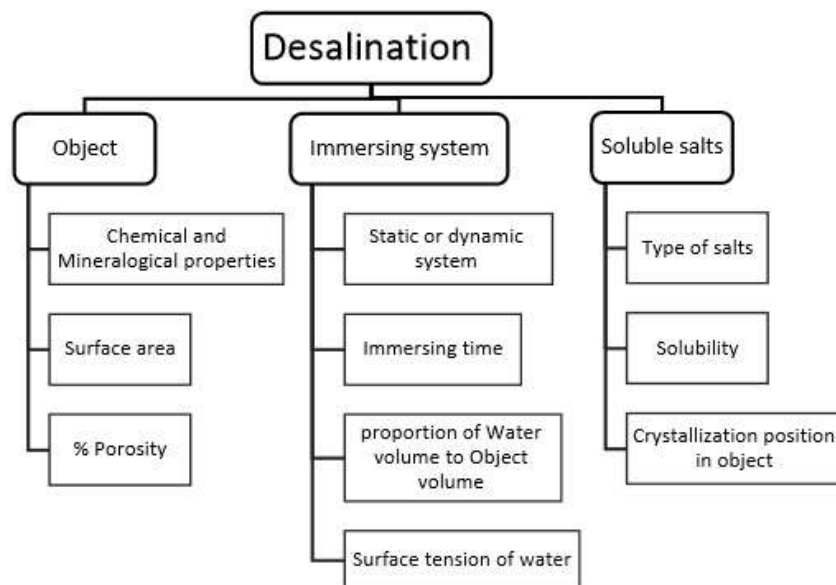


Figure 1. Some effective parameters in immersing desalination process of potteries.

From theoretical point of view, desalination is a mass transfer phenomenon and it is occurred due to molecular diffusion and/or convection flow (Pel *et al.*, 2010). Molecular diffusion has significant role in desalination by immersing system (Sawdy *et al.*, 2008) and concentration gradient is driving force.

Convection flow is dominate occurrence in poultice method and can be produced by both pressure gradient and also surface tension gradient.

As can be seen in Fig. 2, because of differences in concentration between two points, A (region of high concentration) and B (region of low concentration),

mass (or salts ions in desalination system) transfers over time and with decreasing of concentration gradient, mass transfer rate is reduced (Eq. 1), where ∇C is concentration gradient and $C_{A1} > C_{A2}$; c is concentration and x is distance between points A and B.

$$\nabla C = \frac{C_{A1} - C_{A2}}{x_2 - x_1} \quad (1)$$

According to Fick's first law, the diffusion flux of mass transfer is amount of substance per unit area per unit time (Eq. 2) (unit: $\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$), where J is diffusion flux, and D is diffusion coefficient or diffusivity.

$$J = -D \frac{dC}{dx} = -D \nabla C \quad (2)$$

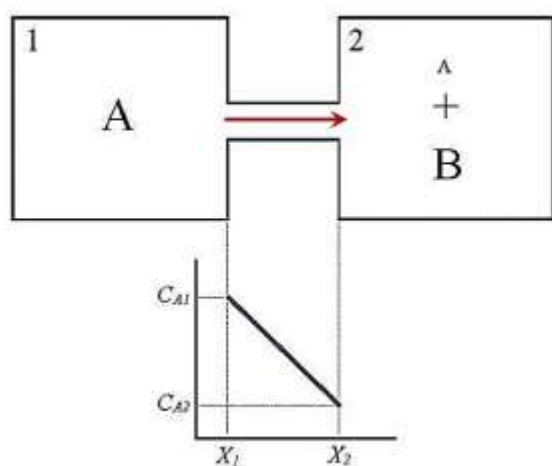


Figure 2. Schematic design of one dimensional mass transfer through concentration gradient in molecular diffusion.

Salt removal rate can also be enhanced by increasing in diffusivity or molecular diffusion coefficient as it depends on temperature and concentration. Since molecular diffusion is a slow and time-dependent phenomenon, optimization of desalination can be improved by:

1. Providing better access of water to salts; Salt dissolution can be facilitated through increase in access of water molecules to soluble salts. One way for increasing water access to soluble salts can be decreasing of water surface tension by using surfactant agents.
2. Establishing concentration gradient between ions in texture of object and immersing water. It seems that the main cause of deficiency in current desalination in immersing system is due to a stagnant liquid layer near the interface of the solid object and the water, known as concentration boundary layer

(CBL) (Amiri et al., 2015). CBL decreases the mass transfer as it decrease the driving force in molecular diffusion process (about enrichment and leaching of cations and on surface saturation layer of water in obsidian medium, in Liritzis et al., 2004; Liritzis, 2006).

The purpose of this study is to investigate the effective parameters on desalination process according to improving ions diffusion to immersing bath and providing optimal conditions to reduce both contact time between pottery and water and also the amount of wastewater.

2. MATERIALS AND METHODS

In order to investigation on understanding of significant parameters in efficiency of desalination, in this study four steps were considered:

1. Design of experiments
2. Making specimens
3. Accelerated saturation process of specimens
4. Desalination process according to RSM design

All properties and reagents are tabulated in Table 1.

Table 1: Properties of materials and instruments in this research.

Materials and Instruments	Properties
Distilled water	$EC \leq 5.0 \mu\text{S} \cdot \text{cm}^{-1}$
CaCl_2 (anhydrous)	MW=110.984; Art. 2385, Merck
CaCO_3 (for AAS std.)	MW= 100.09 g/mol; A700966, Merck
X-ray Fluorescence (XRF)	Analyzer, Bruker, S4 PI-ONEER, Germany
Atomic Absorption Spectroscopy (AAS)	PERKIN-ELMER, 2380, USA
Ca^{2+} measurement through AAS	According to ASTM D511 - 14
EC meter	inoLab 740, WTW, Germany
EC measurement	According to ISO 7888:1985
Mercury Immersion Porosimetry (MIP)	Micromeritics Autopore IV
Magnetic Stirrer	IKA, RH basic 2, Germany
Oven	OGAWA SEIKI Co. Ltd., Model: EE2-145, Japan
Ceramic Kiln	Metallurg Company, Isfahan, Iran

2.1. Experimental Design

Response Surface Methodology (RSM) was used for design of experiments. The aim of the RSM is the construction of reliable response surfaces character-

ized by high adherence to the experimental data describing the reality being studied (Cassettari et al., 2013). The main advantages of RSM are: predictive accuracy, recognition of variables interaction, optimization of process, reducing the required experimental runs and thus reducing the cost and time of experiments, and graphically presentation of response (Cassettari et al., 2013; Khuri & Mukhopadhyay, 2010).

RSM is collection of statistical and mathematical techniques that is for modeling and analysis of problems in which a response of interest is influenced by several variables and uses quantitative data from appropriate experiments to determine regression model equations and operating conditions (Lee et al., 2006). This method is used for fitting a model and helps to optimize the effective variables with a minimum number of experiments, as well as to analyze the interaction among the variables (Cassettari et al., 2013; Montgomery, 2009). Analysis of variance (ANOVA) for the model is also carried out to establish its statistical significance.

Fitting a second-order model is common in RSM and there are several second-order model designs in the literature which include Central Composite designs (CCD), Box-Benken designs (BBD), etc. (Chigbu et al., 2009). In this research, CCD is selected for five independent variables, each at five levels to fit second order polynomial model.

The empirical model for predicting optimal conditions can be expressed according to Eq. (3):

$$Y = a_0 + \sum_{i=1}^k a_i X_i + \sum_{i=1}^k a_{ii} X_i^2 + \sum_{i=1}^k \sum_{j=1}^k a_{ij} X_i X_j \quad (3)$$

where Y is the predicted response, and X is the coded form of operating parameters, respectively. The term a_0 is coefficient of the equation, a_i are the coefficient of the linear terms, a_{ii} are the coefficient of the quadratic terms, a_{ij} are the coefficient of the interaction terms and k is the number of independent variables (Montgomery, 2009; Myers et al., 2009).

The above model was used in the present work and tested with ANOVA.

The ANOVA result was used for graphical analyses of the data to obtain the interaction between the responses and the variables. Three-dimensional plots are obtained based on the effect of the five factors and their levels (Hedayati & Ghoreishi, 2015).

Minitab software (version 16) is used for the statistical DOE and data analysis. The total number of experimental runs in the constituted CCD was 52 runs.

In this study, five operating variables were chosen according to important parameters in desalination based on mass transfer phenomena and pilot tests, as follows: 1- firing temperature of sample, 2- immersing time, 3- type of surfactants, 4- concentration of surfactants and 5- agitation rate in immersing system. Each levels of variables have coded values. This experiments are planned according to the full factorial design with all parts of the factors. As mentioned before, each parameter has five levels that coded from -2 (minimum) to +2 (maximum) and un-coded value (or actual amount) of each level are calculated according to Eq. 4, 5 and 6. Real value of variables in low and high levels are selected and calculated according to pilot tests. The coded and un-coded levels of independent variables can be found in Table 2. It should be mentioned that, different levels of qualitative parameters (like type of surfactant in this experimental work) are refers by their coded values (-2, -1, 0, +1, +2) in RSM design.

$$\begin{aligned} \text{center point of each parameter} \\ = \frac{\text{max. level} + \text{min. level}}{2} \quad (4) \end{aligned}$$

$$(\text{coded value} - 1) = \frac{(\alpha - 1)\text{max.} + (\alpha + 1)\text{min.}}{2\alpha} \quad (5)$$

$$(\text{coded value} + 1) = \frac{(\alpha - 1)\text{min.} + (\alpha + 1)\text{max.}}{2\alpha} \quad (6)$$

The coefficient of "a" is calculated through $\sqrt[4]{2^k}$ that k is the number of variables.

Table 2: Coded and un-coded levels of independent variables used in the RSM design.

Parameters	Mathematical code	-2	-1	0	+1	+2
Firing temperature (°C)	X ₁	850	900	950	1000	1050
Immersing time (h)	X ₂	2	3:44	5:00	6:16	8:00
Surfactant type*	X ₃	PEG 200	COE 36	LAE 7	Triton X-100	SDS
Surfactant concentration (ppm)	X ₄	500	1225	1750	2275	3000
Agitation rate** (rpm)	X ₅	1 (77)	2 (389)	3 (804)	4 (1160)	5 (1572)

** Agitation rate is equivalent to rate step of magnetic stirrer.

* ** Coded values were used for RSM design.

2.2. Samples preparation

Since excavated archaeological ceramics are experienced different burial conditions and uncontrolled variables such as types of soluble salts, contact time with aggressive solutions, different structural characterization of objects, etc., therefore experimental specimens were made to control effective parameters on desalination process.

Experimental ceramics were prepared in an industrial workshop in Isfahan, Iran. The specimens were cubic with dimensions 5×5×1 cm (1 cm height).

Before firing, samples were placed in an oven at 50°C for 24h after drying in room temperature for 7 days. Firing was performed in an electronic-ceramic kiln at oxidizing atmosphere. Soaking time in maximum temperature for all samples was 1 h and then specimens stay in kiln for 24 h. The heating and cooling rate in all cases were 5°C.min⁻¹. Specimens are classified in five groups. The firing temperature of each group and color of samples are tabulated in table 3. Chemical composition of specimens according to XRF analysis (Analyzer, Bruker, S4 PIONEER, Germany) are presented in Table 4.

Table 3: Introduction of samples and firing temperature of each group.

	Group A	Group B	Group C	Group D	Group E
Firing Temperature (°C)	850	900	950	1000	1050
Code of Color*	5YR 6/6	5YR 7/6	7.5YR 7/4	7.5YR 7/3	2.5Y 7/4

* According to Munsell Soil Color Chart (2000)

Table 4: Chemical composition of samples were presented in oxides.

Sample Number	SiO ₂ (%wt)	Al ₂ O ₃ (%wt)	Fe ₂ O ₃ (%wt)	CaO (%wt)	Na ₂ O (%wt)	K ₂ O (%wt)
A-2	51.94	14.06	5.64	17.96	0.86	1.86
B-1	52.03	14.36	5.46	18.91	0.96	2.41
C-10	51.86	14.59	5.62	18.21	0.83	2.21
D-12	52.68	14.73	5.65	19.53	0.86	2.27
E-11	52.51	14.16	5.72	19.02	0.75	2.43
	MgO (%wt)	TiO ₂ (%wt)	MnO (ppm)	P ₂ O ₅ (ppm)	S (ppm)	L.O.I (%wt)
A-2	2.51	0.613	740	830	70	4.12
B-1	3.48	0.653	770	820	20	1.27
C-b-10	3.02	0.608	740	870	50	2.49
D-12	3.12	0.616	730	800	60	0.05
E-11	3.56	0.601	740	760	30	0.81

2.3. Saturation process

Accelerated saturation process has been designated to prepare experimental specimens for desalination. Before saturation, all experimental specimens were immersed in distilled water as pretreatment stage for 24 hours in three times to extract all removable cations from samples. Extraction of Na⁺, K⁺ and Ca²⁺ were monitored by Atomic Absorption Spectroscopy (AAS), and sulfate and chloride ions, through qualitative method. After the third washing step, Cl⁻ and (SO₄)²⁻ ions were non-detected. It was found that after three washes, the amount of cations extraction reduced and the minimum removal was belonged to calcium ions. Calcium was selected as the indicator for desalination performance based on a) presence in almost any natural damaging salts, b) minimum leakage from the experimental specimens and c) easily measurement. Ca²⁺ concentration is measured by ASTM method.

Saturation step is done by 0.01 M solution of calcium chloride anhydrous (CaCl₂). No deposition detected after 72 hours.

According to pilot tests, 72 hours continuous saturation was performed for preparing specimens. All samples are saturated in separated containers in 300 ml 0.01 M solution of CaCl₂. For preventing evaporation all containers are covered. After accelerated saturation, specimens are kept to dry in oven for one week in 50°C temperature and then in temperature 100°C to achieve constant weight. For saturation, all samples are placed in different container and the volume of solution was 300 ml.

2.4. Desalination and Monitoring of responses

Desalination process was accomplished on specimens according to experimental design four month later saturation steps. The volume of water bath for all runs was constant (800 ml) and samples were

placed about 4 cm from bottom of the container. For avoiding evaporation, all containers were covered with foil.

The efficiency of desalination process was evaluated by two principal responses Ca^{2+} concentration by atomic absorption spectroscopy (AAS) and electrical conductivity (EC) measurement. It should be noted that $\Delta\text{EC} = \text{EC}_{\text{final}} - \text{EC}_{\text{initial}}$ was used in statistical analysis of responses.

3. RESULTS AND DISCUSSION

3.1. ANOVA analysis of responses

Analysis of variance and regression coefficient of factors, their quadratics and interactions for both responses (Ca^{2+} concentration and ΔEC measured through 52 runs of experiments) are tabulated in table 5 and 6, respectively. Statistically, the parameters with *p-value* less than 0.05 are significant and their regression coefficient is used in the equation mode.

The significance of each coefficient was determined by absolute *t-value* and *p-value* which were listed in the same table. For any of the terms in the model, a large absolute value of *t*, a small *p-value* and large value of *F*, would indicate more significant effects on the corresponding response variables. Model terms with $p < 0.001$, $0.001 \leq p < 0.05$ and $p \geq 0.05$ indicate highly significant, significant and insignificant, respectively (Hedayati & Ghoreishi, 2015). Both responses (extracted Ca^{2+} and ΔEC) are given as a functions of significant parameters in second order model according to regression coefficient of coded values of variable in Eq. 7 and 8, respectively. Results of statistical analysis suggests that these responses are influenced by firing temperature, immersing time, agitation rate, and quadratic of firing temperature and agitation rate.

$$Y = 1.95949 - 0.66149 X_1 + 0.40804 X_2 + 0.29159 X_5 + 0.24965 X_1^2 + 0.12971 X_5^2 \quad (7)$$

$$Y = 21.9661 - 12.1147X_1 + 4.2806X_2 + 2.2897X_5 + 4.6861X_1^2 \quad (8)$$

It should be notified that equations no. 7 and 8 are classified as random equation in modeling of responses and since they are written according to regression coefficient of coded values, are used for studying the pattern of response surface, merely and not for calculation of responses.

The results confirm that linear terms of firing temperature, immersing time and agitation rate are highly significant ($p < 0.001$) while surfactant type and concentration are non-significant. The quadratic term of firing temperature is highly significant ($p < 0.001$) while the quadratic term of agitation rate is significant ($0.001 \leq p < 0.05$). Moreover, all linear interactions between different variables are non-significant. Fitted model is proved via the analysis of variance (ANOVA) as shown in Tables 5 and 6. The calculated coefficient of determination (R^2) and adjusted coefficient of determination (Adj. R^2) are 87.85% and 80.01%, for Ca^{2+} concentration and 91.0% and 85.20% for ΔEC in the rinse solution, respectively. These values approve that the model sufficiently characterized the experimental data and 90% of the variations could be approximately covered by the fitted model.

Furthermore, table 5 and 6 shows that firing temperature of specimen (X_1) has a negative linear effect on ion extraction in desalination process. This is due to decreasing of porosity by increasing of firing temperature. MIP analysis indicates this idea. As it is illustrated in figure 3, the result of experiments show that the highest amount of ion extraction ($70.1 \mu\text{S}\cdot\text{cm}^{-1}$) belongs to the highest percentage of open porosity (40.0%) in 850°C of specimen's firing temperature.

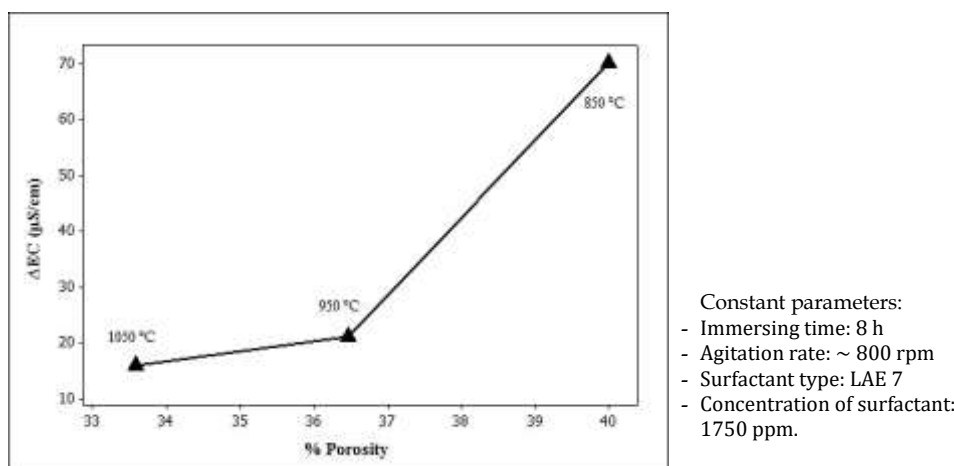


Figure 3. Increasing of ΔEC by increasing % porosity of specimens.

Since quadratic term of firing temperature has significant effect on response models, it reveals that

ion extraction does not have liner function with this parameters.

Table 5: The results of regression coefficient and analysis of variance for Ca²⁺ concentration in rinse solution.

Regression coefficient				Analysis of variance (ANOVA)			
Variables	T	p-value	Regression coefficient (coded values)	DF	F	p-value	
Linear terms				Regression	20	11.20	0.000
α_0	15.406	0.000	1.95949	Linear terms	5	37.11	0.000
X_1	-	0.000	-0.66149	X_1	1	115.73	0.000
X_2	6.636	0.000	0.40804	X_2	1	44.04	0.000
X_3	1.733	0.093	0.10659	X_3	1	3.00	0.093
X_4	0.528	0.601	0.03249	X_4	1	0.28	0.601
X_5	4.742	0.000	0.29159	X_5	1	22.49	0.000
Quadratic terms				Quadratic terms		5.96	0.001
X_1^2	4.720	0.000	0.24965	X_1^2	1	22.27	0.000
X_2^2	0.641	0.526	0.03390	X_2^2	1	0.41	0.526
X_3^2	-1.182	0.246	-0.06254	X_3^2	1	1.40	0.246
X_4^2	0.853	0.400	0.04512	X_4^2	1	0.73	0.400
X_5^2	2.452	0.020	0.12971	X_5^2	1	6.01	0.020
Interaction terms				Interaction terms	10	0.87	0.568
$X_1.X_2$	0.727	-0.353	-0.02525	$X_1.X_2$	1	0.12	0.727
$X_1.X_3$	0.140	-1.513	-0.10825	$X_1.X_3$	1	2.29	0.140
$X_1.X_4$	0.642	0.470	0.03362	$X_1.X_4$	1	0.22	0.642
$X_1.X_5$	0.195	-0.324	-0.09469	$X_1.X_5$	1	1.75	0.195
$X_2.X_3$	0.491	0.697	0.04987	$X_2.X_3$	1	0.49	0.491
$X_2.X_4$	0.624	-0.494	-0.03538	$X_2.X_4$	1	0.24	0.624
$X_2.X_5$	0.433	0.794	0.05681	$X_2.X_5$	1	0.03	0.433
$X_3.X_4$	0.950	0.063	0.00450	$X_3.X_4$	1	0.00	0.950
$X_3.X_5$	0.980	1.706	0.12206	$X_3.X_5$	1	2.91	0.980
$X_4.X_5$	0.809	-0.244	-0.01744	$X_4.X_5$	1	0.06	0.809
Coefficient of Determination				Residual Error	31	---	---
S		0.404679		Lack-of-Fit	22	308.46	0.000
R ²		87.85 %		Pure Error	9	---	---
R ² (adj)		80.01 %		Total	51	---	---

*DF: degree of freedom

Table 6: The results of regression coefficient and analysis of variance for ΔEC in rinse solution.

Regression coefficient				Analysis of variance (ANOVA)			
Variables	T	p-value	Regression coefficient (coded value)	DF	F	p-value	
Linear terms				Regression	20	15.68	0.000
α_0	13.088	0.000	21.9661	Linear terms	5	52.39	0.000
X_1	-14.931	0.000	-12.1147	X_1	1	222.93	0.000
X_2	5.276	0.000	4.2806	X_2	1	27.83	0.000
X_3	1.787	0.084	1.4501	X_3	1	3.19	0.084
X_4	0.153	0.879	0.1244	X_4	1	0.02	0.879
X_5	2.822	0.008	2.2897	X_5	1	7.96	0.008
Quadratic terms				Quadratic terms	5	9.22	0.000
X_1^2	6.713	0.000	4.6861	X_1^2	1	45.07	0.000
X_2^2	0.800	0.430	0.5583	X_2^2	1	0.64	0.430
X_3^2	1.066	0.295	0.7440	X_3^2	1	1.14	0.295
X_4^2	0.559	0.580	0.3904	X_4^2	1	0.31	0.580
X_5^2	1.471	0.151	1.0268	X_5^2	1	2.16	0.151
Interaction terms				Interaction terms	10	0.55	0.839

X ₁ .X ₂	0.314	0.755	0.2969	X ₁ .X ₂	1	0.10	0.755
X ₁ .X ₃	-1.453	0.156	-1.3719	X ₁ .X ₃	1	2.11	0.156
X ₁ .X ₄	-0.136	0.893	-0.1281	X ₁ .X ₄	1	0.02	0.893
X ₁ .X ₅	-1.414	0.167	-1.3344	X ₁ .X ₅	1	2.00	0.167
X ₂ .X ₃	-0.288	0.775	-0.2719	X ₂ .X ₃	1	0.08	0.775
X ₂ .X ₄	-0.546	0.589	-0.5156	X ₂ .X ₄	1	0.30	0.589
X ₂ .X ₅	-0.672	0.507	-0.6344	X ₂ .X ₅	1	0.45	0.507
X ₃ .X ₄	-0.566	0.575	-0.5344	X ₃ .X ₄	1	0.32	0.575
X ₃ .X ₅	0.354	0.726	0.3344	X ₃ .X ₅	1	0.13	0.726
X ₄ .X ₅	0.136	0.893	0.1281	X ₄ .X ₅	1	0.02	0.893
<i>Coefficient of Determination</i>				Residual Error	31	---	---
S	5.34001			Lack-of-Fit	22	22.56	0.000
R ²	91.0 %			Pure Error	9	---	---
R ² adj)	85.20 %			Total	51	---	---

3.2. Response surface analysis

Through three-dimensional response surface model, optimum values for achieving the maximum desalination were investigated. In surface plot models, responses are designed by drawing the response (z-axis) versus two independent variables (x and y coordinates) and the other three independent variables were considered constant at zero levels. The effects of firing temperature, immersing time and agitation rate on Ca²⁺ extraction and ΔEC are presented in figures 4 and 5. The maximum extraction occurs in firing temperature 850°C (coded value: -2), at immersing time with coded value +2 (8 h) and agitation rate with coded value +2 (step 5 of magnet stirrer).

As noted before, firing temperature of specimen have significant role in salt removal because its direct effect on percentage of open porosity. Therefore, in the lowest firing temperature, highest amount of salt removal is predictable.

On the other hand, the influence of immersing time on responses indicates the relationship between diffusion time and rate of ions transfer from specimen to rinse water. Diffusion is a time-depending phenomenon and with increasing of time, the transfer rate of mass increase if concentration polarization doesn't occur as a result of accumulating of ions near the surface of object and it causes reduction of concentration gradient. Here, the third effective parameter in desalination fulfils an important role. Indeed, agitation prevents to formation of concentration boundary layer (CBL).

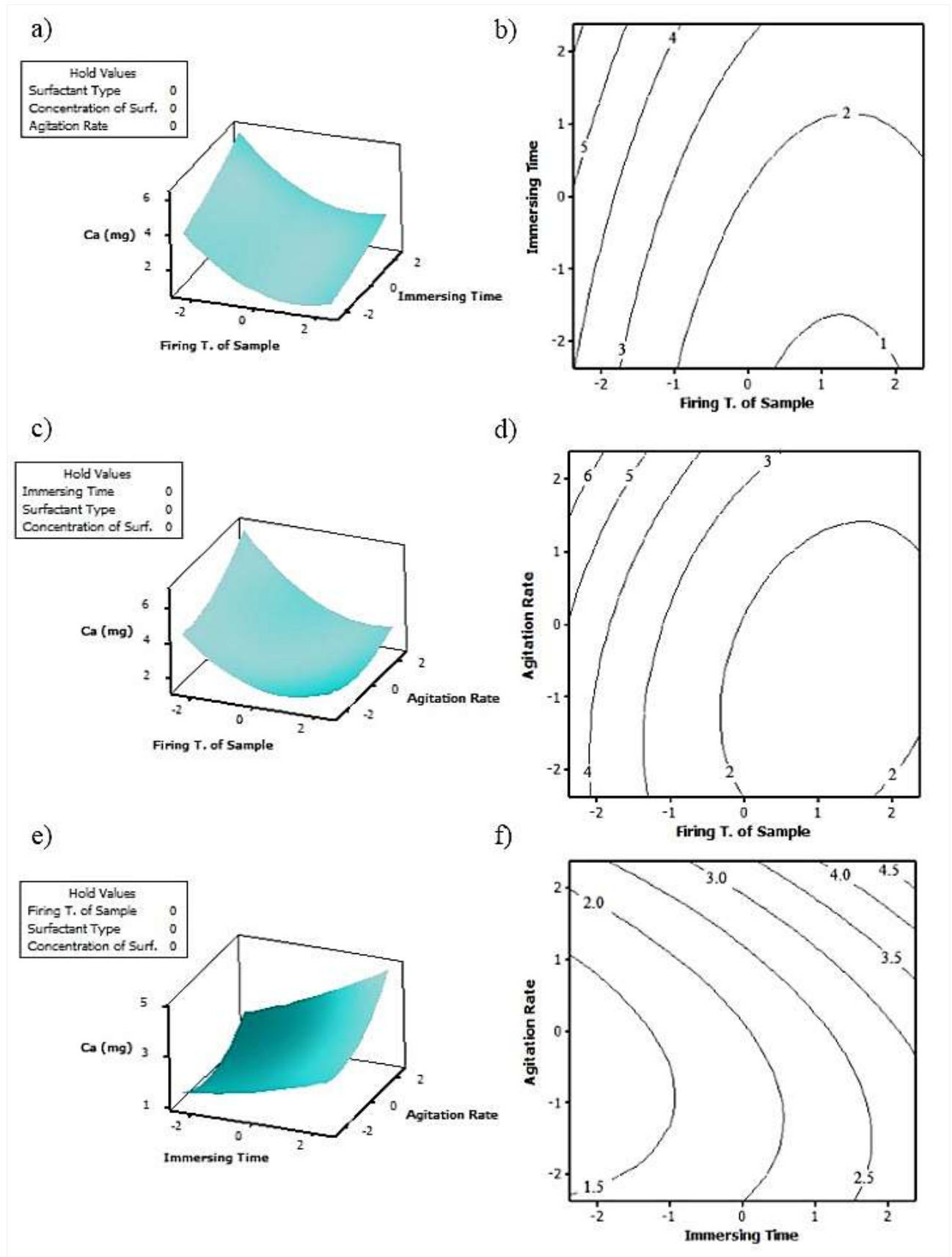


Figure 4. Effect of firing temperature, immersing time and agitation rate on Ca^{2+} concentration in immersing system response surface plot (a, c, e) and contour plot (b, d, f).

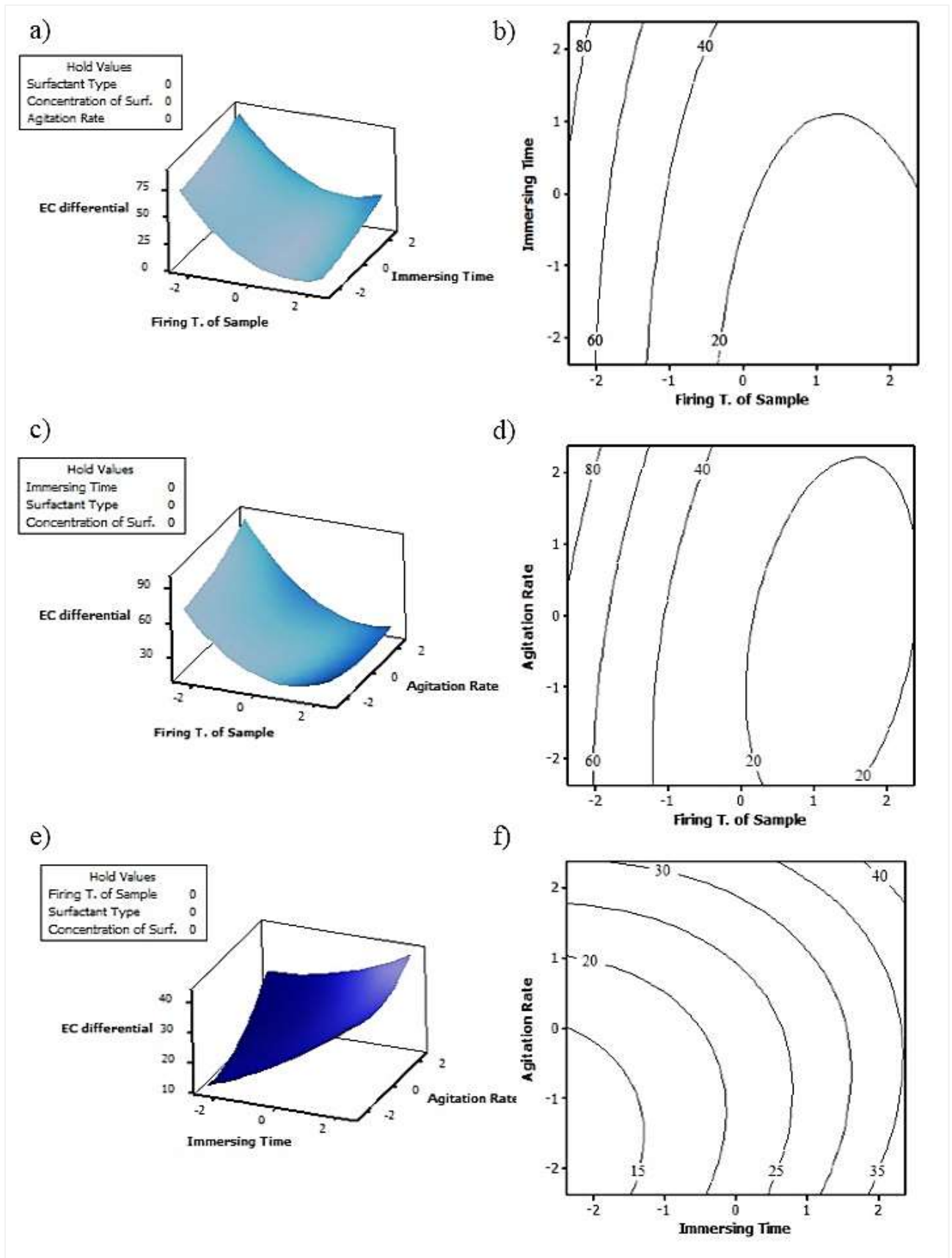


Figure 5. The effect of firing temperature, immersing time and agitation rate on ΔEC in immersing system response surface plot (a, c, e) and contour plot (b, d, f).

3.3. Model optimization

Response optimizer via RSM was carried out and the results are tabulated in Table 7. According to predicted condition via RSM response analysis, the assessment of accuracy of optimization is validated with triplicate experiments on specimens from group A (firing temperature 850°C), in 8 hours of immersing time with step 5 of agitation by stirrer. Results of experiments have approximately 90% goodness of fit with predicted levels.

Table 7: Predicted and experimental data of optimal conditions.

Test No.	Ca ²⁺ extraction (mg)	ΔEC (μS.cm ⁻¹)
1	9.71	128.40
2	8.81	114.44
3	8.85	117.90
Ave.	9.124	120.25
Predicted values by RSM	10.661	126.337
The fitness percentage of experimental data and predicted values	85.58 %	95.18 %

The optimal conditions were carried out in desalination process of studies historical potsherds from

surface surveying gathered from the Haft Tape archaeological site (approx. 1350 B.C.) (Khuzestan Province, Iran). For these certain case, four samples were selected and cut into two pieces in approximately similar weight. Three out of eight samples were chosen randomly to desalinate either conventional and/or optimized method for comparing the needed time for desalination. The last pair of cut sample were examined to compare water consumption in different desalination process. The results of desalination process were tabulated in table 8. The data in 4th run is obtained as following method. Sample 4-1 was desalinated in two stages and final ΔEC was read (24.6 μS.cm⁻¹). Water in immersing bath was renewed every 24 h in sample 4-2 for conventional desalination. It was found that the 4th run conventional desalination was enough to reach the same EC of the second run of optimized process.

The experimental results in table 8 revealed that desalination process in optimized condition can speed up the operation time up to less than 8% and saving up to 50% water consumption compared to conventional method at the same desalination achievement.

Table 8: Final EC measurement in optimized and conventional immersing desalination process.

Samples Number	EC _{final} in 8 h desalination in optimized process	Samples Number	EC _{final} in 8 h desalination in conventional process	EC _{final} in 96 h desalination in conventional process
1-1	103.8	1-2	44.6	104.0
2-1	78.5	2-2	46.8	77.2
3-1	55.8	3-2	27.0	55.2
4-1	1 st run: 70.1 2 nd : 24.6**	4-2*	37.7*	24.8*

* For conventional desalination in this run, immersing bath water was renewed after 24 h.

** Measured EC in optimized method after the second run of desalination.

4. CONCLUSION

A new approach for analyzing desalination process of archaeological potteries based on response surface methodology (RSM) has been employed. RSM can provide reliable information for determining effective parameters in the process, recognition of possible interaction between parameters, and optimization of process. The results of experiments according to RSM design, indicate that desalination of archaeological potteries efficiency can be improved by both facilitating salts dissolution and also by accelerating of salt extraction from object's pores.

RSM analysis demonstrate that higher firing temperature of object results in mass transfer reduction and low efficiency of desalination process. The porosimetry tests support this finding as the porosity of specimens decrease with increasing in firing temperature. On the other hand, immersing time and continuous mechanical agitation of desalination water-bath have positive linear effect on ions extraction. In fact, agitation improves the mass transfer process by minimizing concentration polarization. Finding of this experimental research demonstrates that by using agitation in desalination system, up to 50% water consumption can be reduced compared to the conventional method.

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