Ultrasonic-Assisted Extraction and Swarm Intelligence for Calculating Optimum Values of Obtaining Boric Acid from Tincal Mineral

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Keywords: optimization; central composite design; ultrasound assisted extraction; swarm intelligence; artificial intelligence; boric acid; tincal

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1. Introduction

Boron minerals are found as borate salts in nature. Boron minerals have been used as ores in different industries, especially with the help of refinement processes and production of pure chemicals. Since there is an increased use of boron minerals in nuclear technology, fuels of rocket motors, hydrogen energy storage technologies, production of glass, refractory materials, high-strength steels, high-temperature resistant polymers, detergents, ceramics, and catalysts, the production of boron compounds has gained higher importance [1–3]. It has been known that Turkey, USA, and Russia are three countries having the most important levels of boron minerals. Approximately 72% of the world's boron reserves belong to Turkey, with boron reserves of 851 million tons (as B_2O_3), amking Turkey the world's major supplier [2,3].

Boric acid is typically found as a constituent of naturally occurring minerals, such as tincal ($Na_2B_4O_7{\cdot}10H_2O$), colemanite ($Ca_2B_6O_{11}{\cdot}5H_2O$), and ulexite ($NaCaB_5O_9{\cdot}8H_2O$). In the western part of Turkey, the most of the boron ore reserves are found, and the main boron mineral is found as tincal ores, which naturally exist in Eskisehir City. Others are mainly located in Bigadic-Balıkesir, Emet-Kütahya, and Kestelek-Bursa as colemanite, and Bigadic-Balıkesir and Kestelek-Bursa as ulexite [4–6].

The tincal crystal system has a monoclinic density of 1.715 g/cm^3. Its aggregates have white and colorless crystalline states [7]. In the literature, the extraction of boric acid from tincals has been accomplished using mostly different organic acid solutions. Researchers have used hydrochloric acid [8], sulfur dioxide saturated water [9], and chlorine saturated water [10], ammonium chloride [11], phosphoric acid [12], oxalic acid [13], and sulfuric acid [14] to obtain boric acid from minerals. The boric acid extraction methods from tincal include electrolysis condcuted at 80 °C with aqueous solution of sulfuric acid [15,16], and boric acid separation using sodium sulphate solution in cold crystallization [17]. When it is being processed by the thermal method it ends up with a 20–29% of boric acid content, whereas when it is subjected to enrichment processes boric acid content could be icnreased to 32% [18]. However, in Turkey, sulfuric acid is the solvent that is generally used to produce boric acid from tincal [19]. Unfortunately, these methods involve long and tedious steps requiring large quantities of toxic solvents, which have costly disposing procedures after extraction, longer extraction times, and complex manipulation, etc.

The ultrasonic-assisted technique is known as an original synthesis method in materials chemistry. This process is known to include an ultrasonic-assisted usage which allows the dispersion of solids into solvents [20,21]. By this method, the size of solid materials is dramatically reduced, and hence, the surface area of the material expands. Therefore, the mass transport is improved, its solubility is enhanced, and the reaction time is reduced [20,21]. Ultrasonic-assisted frequency intensity and extraction time have been found as important factors for the product yield. In addition, sample size, solvent type, and extraction temperature have been considered as other significant factors affecting the extraction performance [21]. On the other hand, ultrasonic-assisted extraction (UAE) is known as an environmentally-friendly process, and also has reproducible procedures which are easy to manipulate, and requires short extraction times, low temperature, and low solvent consumption. It uses high-frequency sound waves to create mechanical energy (pressure in general; as created by cavitation bubbles) resulting in a better interaction surface between the liquid and solid components, which allows the release of phenolics to the extraction solvent [20,22–24]. Moreover, the advantages of sonochemistry have been rarely implemented in many other fields.

The objective of this study is to focus on boric acid extraction from tincal in order to determine the optimum conditions thanks to the combination of several techniques. To the best of our knowledge, utilizing ultrasonic irradiation to straightly for obtaining boric acid from tincal using pure water has not been reported. This is the first remarkable contribution to the literature by the research aimed in this study. In an experimental study, conventional one-factor-at-a-time methodologies determine the response and importance of the experimental factors one by one and, furthermore, those methods are not able to predict the synergistic and antagonistic effects of many factors on a response variable [24]. Response surface methodology (RSM) is a very efficient statistical method to determine the effect of each factor individually, and able to analyze the synergistic and antagonistic relationships between those experimental factors. In addition, it is very advantageous as it allows a reduced number of experiments and derives an adequate and reliable model equation for a study. Hence, it makes the study more economic, and requires less time and labor. In the literature, to model and optimize the processes, the RSM has been successfully employed in various processes, such as biological and chemical processes [25,26]. In addition to the explained approaches, there is also artificial intelligence in the literature to be employed successfully for optimization tasks. Therefore, in this study the central composite design (CCD), which is one of the RSMs, was chosen to determine the optimum conditions for boric acid extraction from the tincal ore through the UAE process for the first time and also five artificial intelligence-based swarm intelligence techniques, including particle swarm optimization (PSO), cuckoo search (CS), genetic algorithms (GA), differential evolution (DE), and the vortex optimization algorithm (VOA), were used within the optimization process. In the CCD, solvent/solid ratio, pH, extraction time, and temperature were selected as independent experimental variables, and the boric acid extraction yield was the response. A combination of the UAE, CCD, and swarm intelligence techniques for extraction of boric acid from tincal (using pure water) points to a novel solution approach for the extraction research in the associated literature. The combination of the related techniques is another contribution of this study.

Considering the research conducted, the remaining content is organized as follows: the next section is devoted to the materials and the methods used along the study. In detail, components associated with the extraction problem and all methods-techniques employed for the related solution approach are explained generally. After that section, the third section focuses on the obtained results supported with also discussion and, finally, the content is ended with conclusions and plans regarding future works.

2. Materials and Methods

This section is devoted to background regarding essential materials and methods employed along the study. As it was mentioned before, the solution approach designed in this study is a combination of different methods-techniques to ensure optimum boric acid extraction from tincal. Figure 1 briefly represents the general scheme of the solution approach.

Figure 1. General scheme of the solution approach in this study. UAE: ultrasonic-assisted extraction; CCD: central composite design; RMS: Response surface methodology.

Materials considered within the research and the methodologies followed in this manner are explained briefly as follows:

2.1. Materials and Chemical Analysis

Tincal ore was obtained from Kirka town of Eskisehir City (in Turkey) (30′32″ E, 39′46″ N). After the tincal ore was crushed and ground, the particles were sieved and separated based on their size. Two-hundred mesh (0.075 mm)-sized tincal powder was used in all experiments (the entire experimental work after that stage were condcuted at Usak University in Usak, Turkey). Analytical grade HCl (37%; v/v) and NaOH (98%) (Merck, Darmstadt, Germany) were used. For each assay, freshly prepared 0.15 M NaOH (for conductometric assay), and 2.5 M NaOH and 2.5 M HCl solutions (for pH adjustments) were used. A Bandelin ultrasonic HD 3200 (Berlin, Germany) with probe model KE 76 was used to produce ultrasonic irradiation.

Crystalline structures of tincal were determined by an XRD (X-Ray Diffraction) technique (Thermo Fisher Scientific Inc., Waltham, MA, USA). The X-ray analysis was carried out at an ambient temperature by a Philips analytical X'Pert Pro diffractometer using CuKα radiation (λ = 0.15418 nm). Operating parameters were 40 mA and 45 kV with a step size of 0.02° and at a speed of 1°/min. Phase identification of solids was performed by the inorganic crystal structure database. For thermal analysis of tincal samples, a TG-DTA (Thermo-Gravimetric/Differential Thermal Analysis) instrument (Perkin Elmer, Wellesley, MA, USA) was employed. Twenty milligrams of tincal was weighed, and heated from 20 °C to 500 °C under N_2 gas at a heating rate of 5 °C/min. At the end of the heating step, a weight loss of nearly 50% was measured. In addition, attenuated total reflectance of FTIR (Fourier-Transform Infrared) spectroscopy (Shimadzu Corp., Kyoto, Japan) was also used to identify the chemical bonds in the tincal samples.

2.2. Experimental Design for Ultrasound-Assisted Extraction (UAE)

All designed experiments require that a certain number of combinations of factor and levels be tested to observe the results of those test conditions. In order to enhance the yield of boric acid extraction from tincal through the UAE process, optimum conditions were determined using CCD within the Design Expert software (version 8.0.7.1, Stat-Ease Inc., Minneapolis, MN, USA). The CCD approach relies on the assignment of factors in specific determine those test combinations. For the design, solvent/solid ratio (X_1), pH (X_2), extraction time (X_3), and temperature (X_4) were utilized where X represents for an independent variable (Table 1). The CCD contained a total of 30 experiments. To detect the effect of these four variables responsible for the yield of boric acid extraction, each variable was considered at five different levels in the CCD lowest, low, center, high and highest coded as −2, −1, 0, +1, and +2, respectively (Table 1). The full experimental design was shown in Table 2. The yield of UAE was considered to be the experimental response.

For each CCD experiment, 1 g of tincal powder was placed in a 50 mL Erlenmeyer flask containing different volumes of 2.5 M HCl (15–35 mL) as presented in Table 2. For each experiment, pH was adjusted (Mettler Toledo Seven Easy) to its specific value given in the design table of this study (Table 2). Each Erlenmeyer flask was placed into an ultrasound bath (Table 2).

Table 1. Coded levels (at five levels of lowest, low, center, high and highest coded as −2, −1, 0, +1, and +2, respectively) of independent variables used in the central composite design (CCD).

Indep. Variables	Symbol	Levels				
		Lowest	**Low**	**Center**	**High**	**Highest**
		−2	**−1**	**0**	**+1**	**+2**
Solvent/solid ratio (mL/g)	X_1	15	20	25	30	35
pH	X_2	1	2	3	5	7
Extraction time (min)	X_3	30	40	50	60	70
Extraction temperature (°C)	X_4	30	50	70	90	100

Table 2. Central composite design (CCD) used in this study and yield results by considering different solvent/solid ratio, pH, extraction time, and extraction temperature.

Run	Solvent/Solid Ratio (mL/g)	pH	Extraction Time (min)	Extraction Temperature (°C)	Yield (%)
1	30	5	40	50	40
2	20	5	40	90	54.5
3	20	2	40	90	66.45
4	25	3	50	70	30
5	30	5	60	50	51.25
6	25	3	50	70	30.5
7	25	3	50	30	26.25
8	25	3	50	100	79.25
9	25	3	50	70	29.5
10	30	5	60	90	82.75
11	25	3	50	70	29.75
12	30	5	40	90	49.75
13	20	5	50	50	39.375
14	20	5	60	90	36.375
15	25	3	70	70	43.125
16	30	2	40	50	28.25
17	15	3	50	70	55
18	25	3	50	70	30.75
19	20	2	40	50	53.125
20	25	3	50	70	30
21	20	5	40	50	50
22	25	7	50	70	62.75
23	20	2	60	50	50.25
24	25	3	30	70	34.875
25	30	2	40	90	63.75

Table 2. *Cont.*

Run	Solvent/Solid Ratio (mL/g)	pH	Extraction Time (min)	Extraction Temperature (°C)	Yield (%)
26	30	2	60	50	32.5
27	30	2	60	90	82.5
28	25	7	50	70	50.35
29	35	3	50	70	42.5
30	20	2	60	90	58.75

After the extraction processes were done at the specified conditions (Table 2), each reaction mixture was filtered through Whatman filter paper (0.45 µm). In the filtrates, boric acid was determined by the conductometric method [27], and the boric acid extraction yield (%) was calculated by using Equation (1):

$$\text{Boric acid extraction yield } (\%) = \frac{C}{C_0} \times 100 \quad (1)$$

where C is the amount of extracted boric acid after the time (specified in Table 2) passed, and C_0 is the amount of boric acid in the tincal ore. The yield results were shown in Table 2.

2.3. Data Analysis

In this study, Design Expert software was also used for the regression and graphical analyses. The quadratic model for predicting the optimum conditions was expressed below in Equation (2) and Equation (3):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{\substack{i=1 \\ i<j}}^{k-1} \sum_{j=2}^{k} \beta_{ij} X_i X_j \quad (2)$$

$$\begin{aligned} Y = {} & \beta_0 + \beta_1X_1 + \beta_2X_2 + \beta_3X_3 + \beta_4X_4 + \beta_{11}X_{12} + \beta_{22}X_{22} + \beta_{33}X_{32} + \beta_{44}X_{42} + \beta_{12}X_1X_2 \\ & + \beta_{13}X_1X_3 + \beta_{14}X_1X_4 + \beta_{23}X_2X_3 + \beta_{24}X_2X_4 + \beta_{34}X_3X_4 \end{aligned} \quad (3)$$

Here, $X_1, X_2, \ldots, X_k$ are the independent variables indicate the response Y. β_0, β_j (i = 1, 2, ... , k), β_{ii} (i = 1,2, ... , k) and β_{ij} (i = 1, 2, ... , k; j = 1, 2, ... , k) are the offset term, linear coefficient, quadratic coefficient, and interaction coefficient, respectively, and k is the quantity of each variable. Here, Equation (3) is the obtained result from Equation (2). These equations have been taken through some regression process to obtain further equations. $p = 0.05$ was taken into consideration in the variance analysis (ANOVA). The quality of the model was presented by the coefficient of determination (R^2).

2.4. Artificial Intelligence-Based Swarm Intelligence Techniques for Optimization

Artificial Intelligence is known today as one of the most effective and popular research fields because of its great multidisciplinary scope to deal with advanced problems. In terms of optimization, artificial intelligence-based approaches, methods, and techniques have proved their success according to traditional methods, which are not too effective on especially more complex and advanced optimization problems. As a result of many inspirations from the nature, Artificial intelligence has found its ways to develop intelligent optimization algorithms and in this context, a subfield called swarm intelligence has appeared in the associated scientific literature [28–30]. Nowadays, there are many different swarm intelligence techniques to be employed for continuous, constrained, and even dynamic optimization problems [31–33]. In this study, five of them were chosen to be applied on the optimization process taken into consideration. In this way, it was aimed to prove effectiveness of intelligent solutions in the objective problem and the effectiveness of artificial intelligence in any future problems of physicochemistry. In this study, five different techniques: particle swarm optimization (PSO), cuckoo search (CS), genetic algorithms (GA), differential evolution (DE), and the vortex optimization algorithm (VOA) were included in the optimization process.

- **Particle Swarm Optimization:** As introduced by Kennedy and his friends [34,35], the particle swarm optimization (PSO) algorithm is a simple and easy-to-design optimization algorithm, which inspires from social behaviors, shown by bird flock or fish school. In the PSO process, a swarm of particles (candidate solutions) are located in the solution space and then the optimum value(s) are tried to be found by the swarm by following a mechanism, like searching for food source in the nature. PSO is an important intelligent optimization since it employs simple, but effective, mathematical calculations to simulate swarm behaviors for solving optimization problems. In detail, the following points are essential for the default PSO algorithmic flow [34,35]:

    - All particles have position (variable value) and velocity parameters, which are changed iteratively during the solution process.
    - Velocity is a parameter determining the next movement-direction of a particle.
    - For each particle, movements are affected by its own best known position as well as the best known position (global optimum) within the swarm.
    - As general, particle movements affect the solution flow of the whole swarm and the searching mechanism is run until a stopping criterion (like objective optimum value(s) or total iteration number, total particle numbers, etc.) is met.

    Figure 2 shows the typical algorithmic flow in the PSO technique.

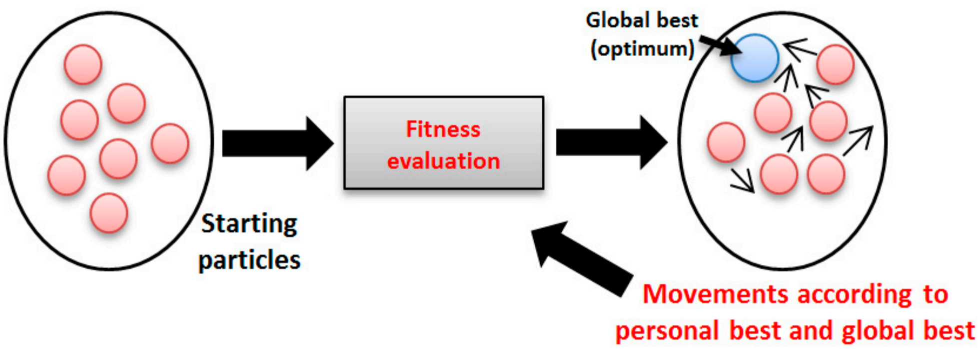

Figure 2. Typical algorithmic flow in the particle swarm optimization technique.

- **Cuckoo Search:** Cuckoo search (CS) is a popular and simple structured intelligent optimization algorithm as developed by Yang and Deb [36]. Briefly, CS tries to simulate the obligate brood parasitism of some cuckoo species as such species lay the eggs in the nests of other host birds and, in this sense, some of the host birds can engage in conflicts with the intruding cuckoos [37]. As a natural reaction, sometimes a host bird throws such cuckoo eggs out of nests or forms a new nest in a different place after leaving the nest including foreign eggs [36]. In order to simulate an optimization approach in this algorithm, the following mechanisms are employed in an algorithmic manner [36,37]:

    - Eggs in the nests are for potential solutions and a cuckoo egg is associated with a new solution.
    - In the algorithm, each nest has one egg free space or multiple eggs free space according to the considered problem details.
    - The main objective here is to use new solutions (if they are better) to replace worse solutions taking place in the nests.

- ○ Along the solution process, a cuckoo lays one egg at a time and locates an egg in a nest randomly determined.
- ○ The nests with good eggs (good solutions) are kept for next generations through the algorithmic process.
- ○ In terms of random solution chances, a cuckoo egg can be detected by a host bird according to a calculated probability.
- ○ Algorithmic solution steps are run according to some stopping criteria, like objective optimum value(s) or total iteration number, total particle numbers, etc.

The general solution flow of the CS is given in Figure 3.

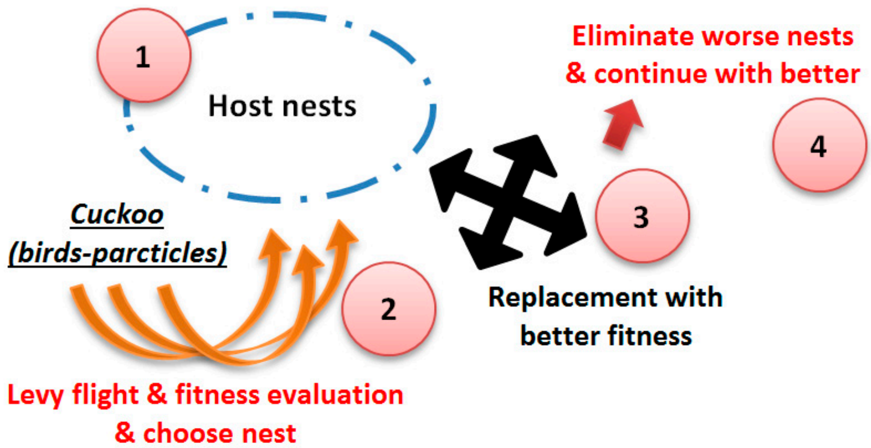

Figure 3. General solution flow of the cuckoo search algorithm.

- **Genetic Algorithms:** As a long-used, popular intelligent algorithm, genetic algorithms (GA) is widely used in optimization problems. As inspired from well-known mechanisms of evolution theory, GA tries to use the objective of naturally selected, good populations for reaching to desired optimum results in the considered problems. At this point, particles in a typical GA are coded (i.e., with binary codes) as in the form of chromosome and during the algorithmic solution process, genes of each particle's chromosome are taken into some evolution-based updates, like cross-over and mutation [38,39]. In the roots of the algorithm, it is aimed to consider well-produced generations according to their parents to deal with the objective problem better and, in this way, run a natural selection process to obtain the desired results quickly. Some essential points for a default GA can be expressed as follows [38–40]:

  - ○ Particles (individuals) having better solutions are taken into the cross-over process according to some pre-determined rules, in order to produce new generations.
  - ○ Some members of each new generation are taken into also mutation process to run a chance approach for getting potentially better particles.
  - ○ There are different types of mechanisms to determine which particles will receive cross-over and mutation operations with which parameter/probability values.
  - ○ Algorithmic solution steps are run according to some stopping criteria like objective optimum value(s) or total iteration number, total particle numbers, etc.

Figure 4 provides a brief scheme explaining the solution flow in the GA.

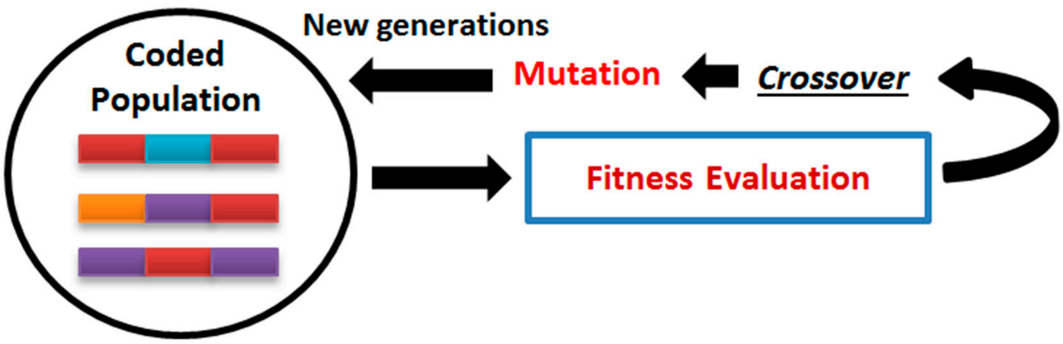

Figure 4. Solution flow in the genetic algorithms.

- **Differential Evolution:** The differential evolution (DE) algorithm is another intelligent optimization technique, which inspires from mechanisms of the evolution theory, like GA. As developed by Storn and Price, DE employs particles in the form of parameter vectors and run mutation and cross-over processes over them to obtain new generations for better optimum values [41]. In the context of mutation, new parameter vectors are created by summing a weighted difference calculated between two vectors (particles) with a third vector. On the other hand, the cross-over is conducted by mixing mutated vectors' parameters with some other determined vectors, which are called trial vectors. After that process, if a trial vector (particle) has a better fitness value-result, then it is replaced with the associated vector [41,42]. As it can be understood, default DE uses real numbers rather than specific codes used generally in a typical GA.

  The general algorithmic flow of the DE is provided in Figure 5 as follows:

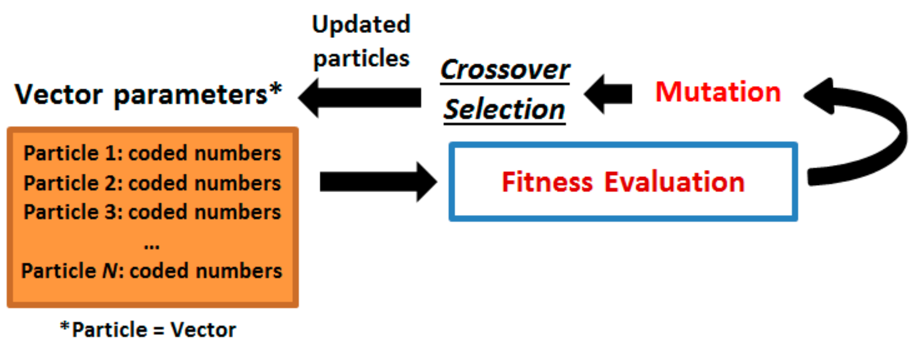

Figure 5. Algorithmic flow of the differential evolution algorithm.

- **Vortex Optimization Algorithm:** The vortex optimization algorithm (VOA) is a recent intelligent optimization algorithm, which was developed by Kose and Arslan [43,44], inspired from vortices in the nature. In the algorithm, particles go through two roles of being a vortex or a normal particle. In detail, a selection process has also been employed to benefit from an evolutionary mechanism for keeping particles with better solutions alive in the solution process. That mechanism can be explained briefly as follows: After fitness calculation, a certain number of 'non-vortex' particles (defined with e: elimination rate) whose fitness are worse than average fitness value are removed from the search space and new particles with the same number of eliminated particles are randomly placed in the search space, just before the next iteration. The algorithm also uses an in-system optimization approach to improve the quality of optimization in especially larger problems. The in-system optimization has been done when the total number of particles located out of a certain 'flow-circle' (fc: defined with a radius) are above 60% of all particles. The process has been done by normalizing—adjusting variables of 'vortex' particles (having better fitness value than the average) to the variables of the current global optimum particle (vortex). Details regarding the algorithm were shaped in time with the performed alternative works [43].

Figure 6 shows the default solution flow idea under the early VOA [44].

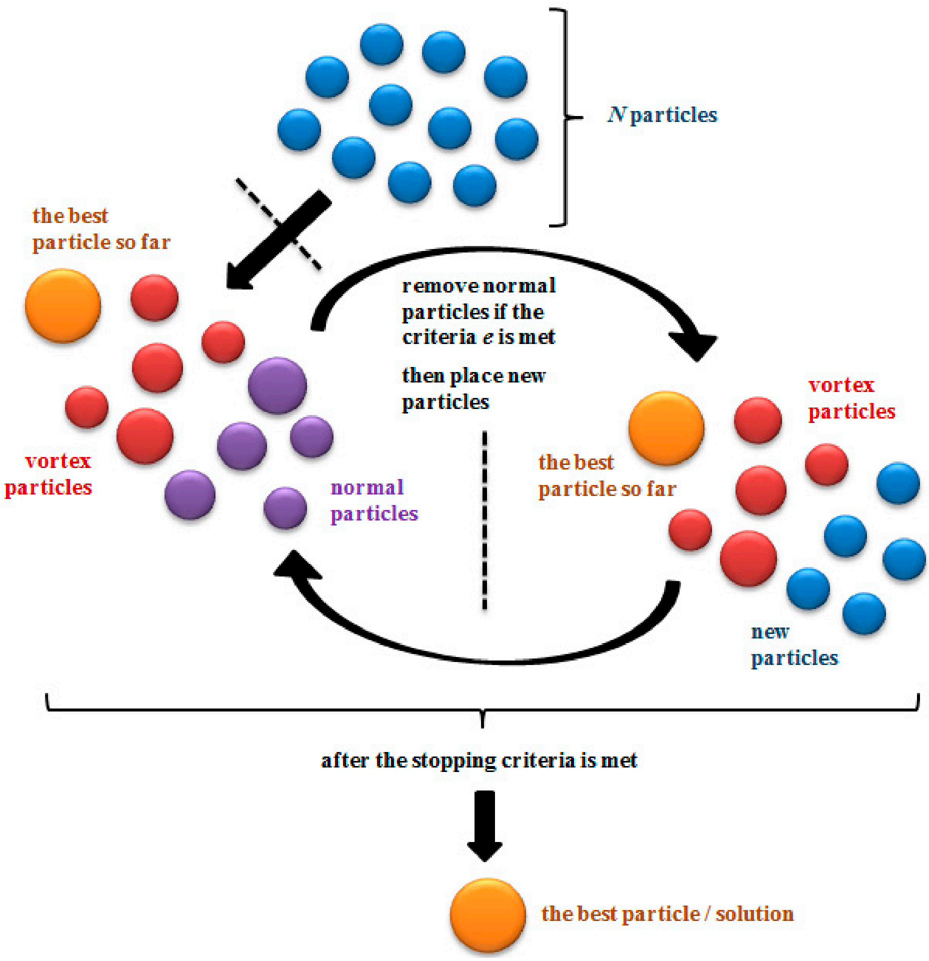

Figure 6. Default solution flow idea under the early vortex optimization algorithm [44].

3. Results and Discussion

Results regarding the objective application processes and detailed findings in this context are provided within this section.

3.1. Characterization of Tincal

Figure 7 shows the pattern of solid phase tincal that was obtained from the separation process (the 0.075 mm (200-mesh) fraction). According to the XRD analysis results, the highest peak indicated tincal.

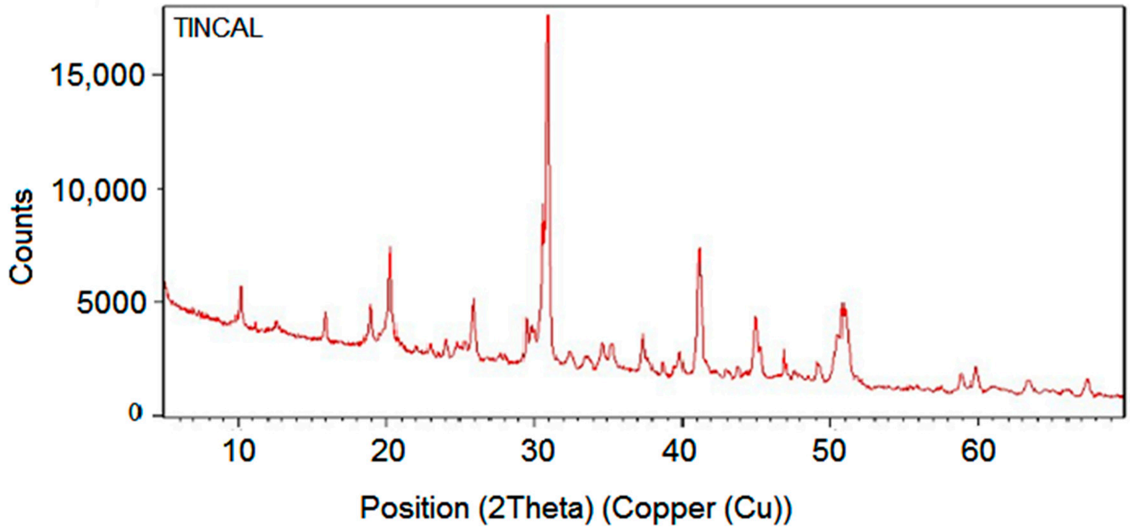

Figure 7. The XRD pattern analysis of solid phase tincal that was obtained from the separation process (the 0.075 mm (200-mesh) fraction) (the highest peak indicates tincal).

Figure 8 shows the FTIR spectrum of solid phase tincal which exhibited the infrared absorption bands. This FTIR analysis was made to illuminate the chemical structure of tincals used in the present study. The bands at 728 cm^{-1} and 880 cm^{-1} indicated the characteristic peaks of tincal. When the FTIR spectrum is examined in detail, the decreasing peaks shown with red lines correspond to B_2O_3 content due to Tinkal removal. On the other hand, B_2O_3 content is high in the peaks shown with blue lines, which also supports the presence of OH peaks. Vibration bands belonging to the 728–880 cm^{-1} titanium range Na–O are supported with peaks.

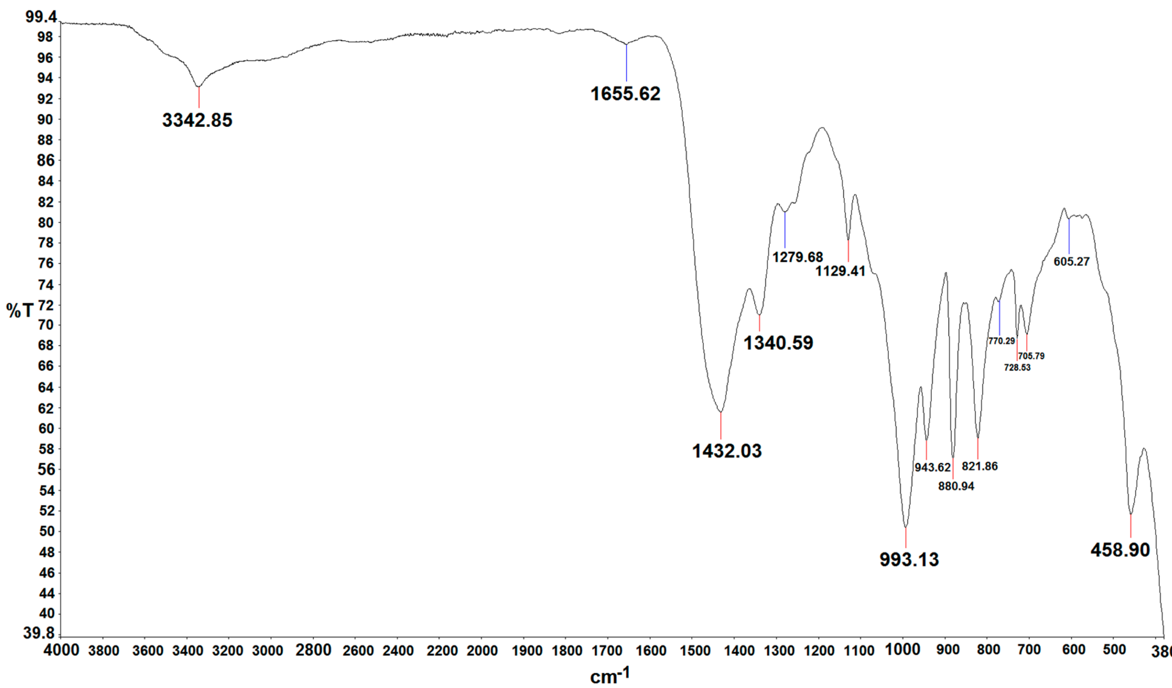

Figure 8. FTIR (Fourier Transform Infrared) spectra (made to illuminate the chemical structure of tincals) of solid phase tincal exhibited the infrared absorption bands (the bands at 728 cm^{-1} and 880 cm^{-1} show the characteristic peaks of tincal).

Thermal dehydration of tincal was also investigated with the thermal analysis technique using a Perkin Elmer TG-DTA instrument (Wellesley, MA, USA). Its results are given in Figure 9, which shows the standard tincal curves. In detail, analysis and the obtained curve here shows the mass change as a function of the temperature as related with also heat flow. The green line (TG: thermogravimetric rate) represents the mass while the blue line is for differential thermal analysis (DTA), which shows the change in the heat flow against the temperature.

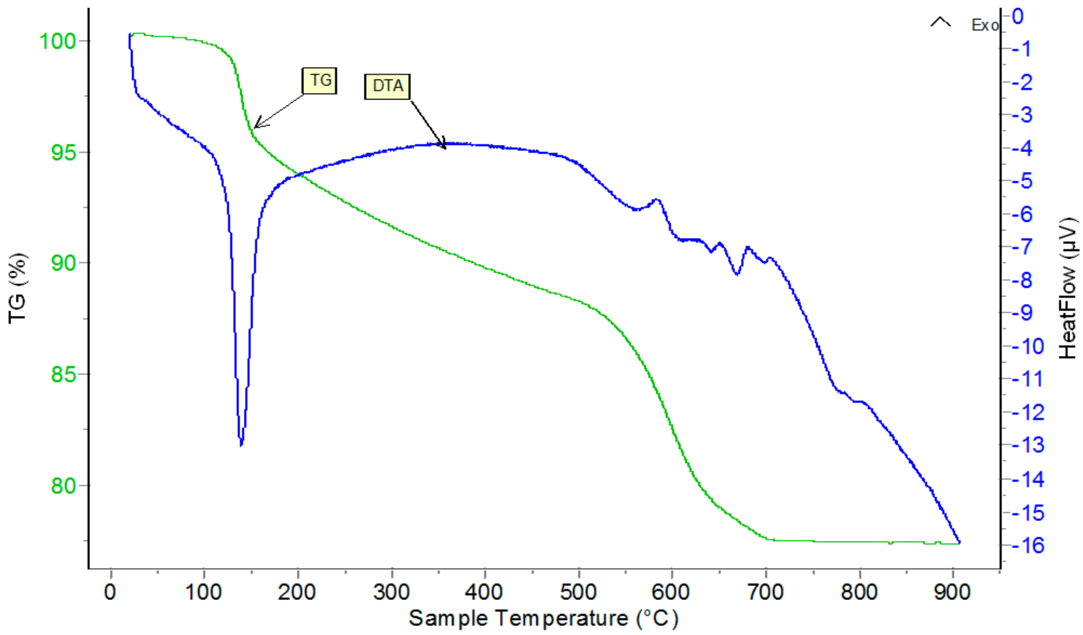

Figure 9. Thermal dehydration of tincal with thermal analysis with TG (green) and DTA (blue) curves regarding standard tincal.

3.2. Optimization Analysis of the Central Composite Design

In this study, we investigated the effect of ultrasound irradiation on the model to straightly for obtaining boric acid from tincal using pure water. Firstly, the effect of different solvent/solid ratio (15–35 mL/g), pH (1–7), extraction time (30–70 min), and extraction temperature (30–100 °C) on the yield of boric acid extraction by CCD were studied. These variables were defined as X_1, X_2, X_3, and X_4, respectively. For the optimization, boric acid extraction yield was considered as dependent variable (or response) of the study. The design table and the yield results are given in Table 2.

The outcome of the regression analysis of the CCD was presented in Table 3. Here, R^2 indicates how the dependent variable is explained well by the independent variables while adjusted R^2 is for a similar explanation rate as adjusted for the number of independent variables that time. Finally, predicted R^2 indicates predictive quality level of the model against new observations and prediction error sum of squares (PRESS) shows the model competency by considering the sum of the squared differences between the experimental response and the predicted response by the regression model. Joglekar and May were proposed that for a significant model, R^2 values should be at least 0.80 [45]. In our study, the R^2 values of the response were greater than 0.80. For instance, in our study, R^2 was 0.9001 indicating that our statistical model is able to explain 90.01% of the variability in the response. In addition, 'adjusted R^2' and the 'predicted R^2' values were found as 0.8101 and 0.8079, respectively. However, high R^2 and predicted R^2 values confirm the high significance of our model. Additionally, it can be seen that the predicted and adjusted R^2 values are slightly smaller than the R^2 value. In relation to this, it was declared that this is an acceptable situation if there are many terms in a design, which is the case of our study [25].

Table 3. Results of the regression analysis considering statistical indicators.

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	14.04	0.3667	0.2611	0.0332	7217.32	
2FI	12.35	0.6324	0.4281	−0.0465	7812.20	
Quad.	7.30	0.9001	0.8101	0.8079	5316.28	Suggest.
Cubic	3.47	0.9887	0.9549	-	+	Alias.

Table 4 provides the information for coefficients of boric acid extraction yield obtained by the ANOVA. The model F-value of 9.01 and its *p*-value (<0.0001) reports that model is very significant. Here, *p*-values less than 0.0500 and *p*-values less than 0.0100 indicate the highly significant and significant model terms, respectively, and therefore, X_4, X_1X_3, X_1X_4, X_2X_4, X_{12}, X_{22}, and X_{42} were found as the significant terms for the response.

Table 4. Second-order model constants and regression equation coefficients for the CCD.

Variable	Sum of Square	df	Mean Square	F-Value	*p*-Value	
Model	6714.29	14	479.95	9.01	<0.0001	Very significant
X_1	0.47	1	0.47	8.802×10^{-3}	0.9266	
X_2	232.16	1	232.16	4.36	0.0556	
X_3	24.28	1	24.28	0.46	0.5107	
X_4	545.01	1	545.01	10.23	0.0064	
X_1X_2	211.76	1	211.76	3.97	0.0661	
X_1X_3	709.89	1	709.89	13.32	0.0026	
X_1X_4	684.06	1	684.06	12.84	0.0030	
X_2X_3	4.21	1	4.21	0.079	0.7826	
X_2X_4	403.36	1	403.36	7.57	0.0156	
X_3X_4	35.78	1	35.78	0.67	0.4263	
${X_1}^2$	678.86	1	678.86	12.74	0.0031	
${X_2}^2$	635.82	1	635.82	11.93	0.0039	
${X_3}^2$	204.15	1	204.15	3.83	0.0705	
${X_4}^2$	1194.79	1	1194.79	22.42	0.0003	
Residual	745.97	14	53.28			
Lack of Fit	668.01	8	83.50	6.43	0.0179	Highly significant
Pure error	77.96	6	12.09			
Cor. Total	7949.77	29				
Adeq. Precision	11.610					

X_1 = solvent/solid ratio, X_2 = pH, X_3 = extraction time, X_4 = extraction temperature, df = degrees of freedom. $p < 0.0100$ is significant, $0.0100 \leq p < 0.0500$ is highly significant, $p \geq 0.0500$ is not significant. Cor. Total of all information corrected for the mean.

Based on these results, amongst the four variables, individually, extraction temperature (X_4) was the most important for the boric acid extraction, and the least effective term was solid/solvent ratio (X_1). In Table 2, it can be seen that the highest yields were observed when the extraction temperature is equal to or higher than 90 °C (such as in the experiments 8, 10, and 27). The next term that showed less individual effect was found to be extraction time (X_3). However, by analyzing the mutual effects in the RSM, solid/solvent ratio and extraction time together (X_1X_3) showed a great effect on the yield, as well as solid/solvent ratio and extraction temperature together (X_1X_4). In case of pH, only X_2X_4 and X_{22} were found to be significant (Table 4). In addition, in order to confirm that CCD and its outcomes are acceptable and reproducible, 'adequate precision' of the response was determined by ANOVA. In the literature, a ratio greater than 4 is found to be too attractive, and a ratio greater than 4 is generally expected, and a higher value is accepted as the better [46]. Our ratio was 11.610 and indicated that this model is suitable to be used to navigate the design space for this study.

Furthermore, after multiple regression analyses were applied to our results (moving from Equation (2), and Equation (3)), a second-order quadratic model was predicted by Design Expert software (version 8.0.7.1, Stat-Ease Inc., Minneapolis, MN, USA) and described in Equation (4). According to the results of regression analysis of boric acid extraction experiments, the mathematical model obtained presented a function of the independent variables.

$$\begin{aligned} Y = 637.02198 - 23.98246\ X_1 - 23.22722\ X_2 - 6.49975\ X_3 - 3.69762\ X_4 + 0.51572\ X_1X_2 \\ + 0.13322\ X_1X_3 + 0.069186\ X_1X_4 - 0.038608\ X_2X_3 - 0.17424\ X_2X_4 \\ + 0.007476\ X_3X_4 + 0.21589\ X_{12} + 3.20892\ X_{22} + 0.029597\ X_{32} + 0.019882\ X_{42} \end{aligned} \tag{4}$$

In Equation (4), Y represents the boric acid extraction yield, whereas X_1, X_2, X_3, and X_4 are the solvent/solid ratio, pH, extraction time, and extraction temperature, respectively. As it was mentioned earlier, highly significant and significant factors for the model ($p < 0.05$) were X_4, X_1X_3, X_1X_4, X_{12}, X_{22}, X_{42}, and X_2X_4. The rest of the factors were found to be insignificant and. thus, these insignificant regression coefficients were removed from Equation (4) to get a better model equation and it was described as Equation (5) below:

$$\begin{aligned} Y = 637.02198 - 3.69762\ X_4 + 0.13322\ X_1X_3 + 0.069186\ X_1X_4 - 0.17424\ X_2X_4 + \\ 0.21589\ X_{12} + 3.20892\ X_{22} + 0.019882\ X_{42} \end{aligned} \tag{5}$$

As the sum of this equation, a powerful linear relationship was drawn as a parity plot using the observed (actual) and calculated (predicted) values as shown in Figure 10.

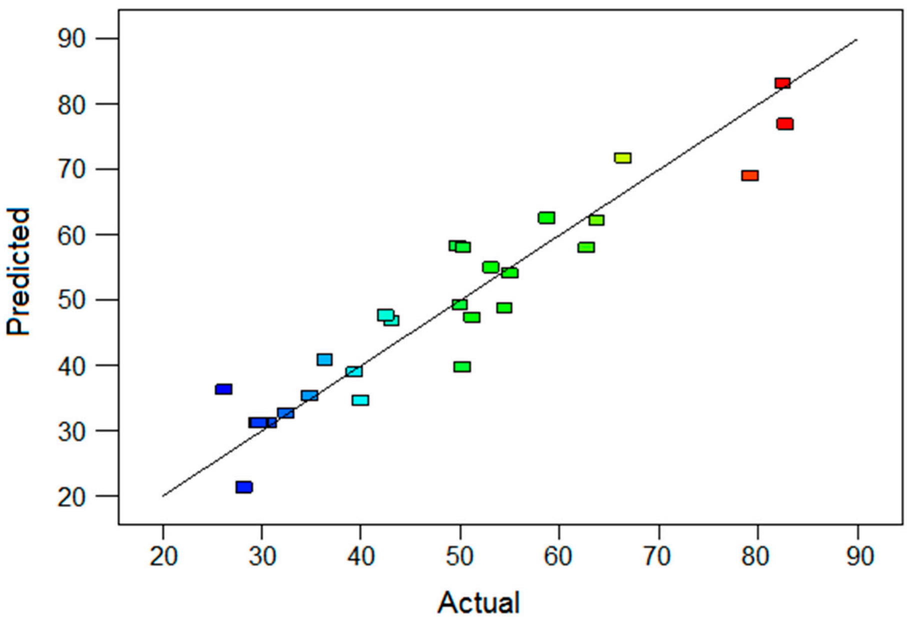

Figure 10. Parity plot of CCD (actual and predicted values for the designed response) pointing to a powerful linear relationship.

The response surface plot having the pH and solvent/solid ratio results (Figure 11A) generated through the Design Expert software shows that when pH and solvent/solid ratio is at their minimum levels and when they are at their maximum levels the boric acid extraction yield was increased. This was represented in red color on the plot (Figure 11A).

In Figure 11B, the response surface plot was drawn to show the effect of solvent/solid ratio and extraction time on the boric acid extraction yield. As seen in Figure 11B, higher solvent/solid ratio and extraction time as well as lower solvent/solid ratio and extraction time showed better boric acid extraction yields.

Amongst the test variables, extraction temperature was found to have the most important effect ($p < 0.01$) on the yield of boric acid extraction. It was found that higher extraction yields can be achieved by employing increasing temperature and increasing solvent/solid ratio (Figure 11C). In previous studies, it was reported that an increased solvent/solid ratio resulted in increased yields to certain levels which is the case of our study [47]. The interaction between extraction temperature and solvent pH principally affected the yield activity that like in our study. Figure 11D shows the effect of extraction time and pH on the yield of boric acid extraction. According to Figure 11D, higher yields can be achieved with increasing extraction time and pH. As shown in Figure 11C,E, the increasing extraction temperature augmented the yield of extraction.

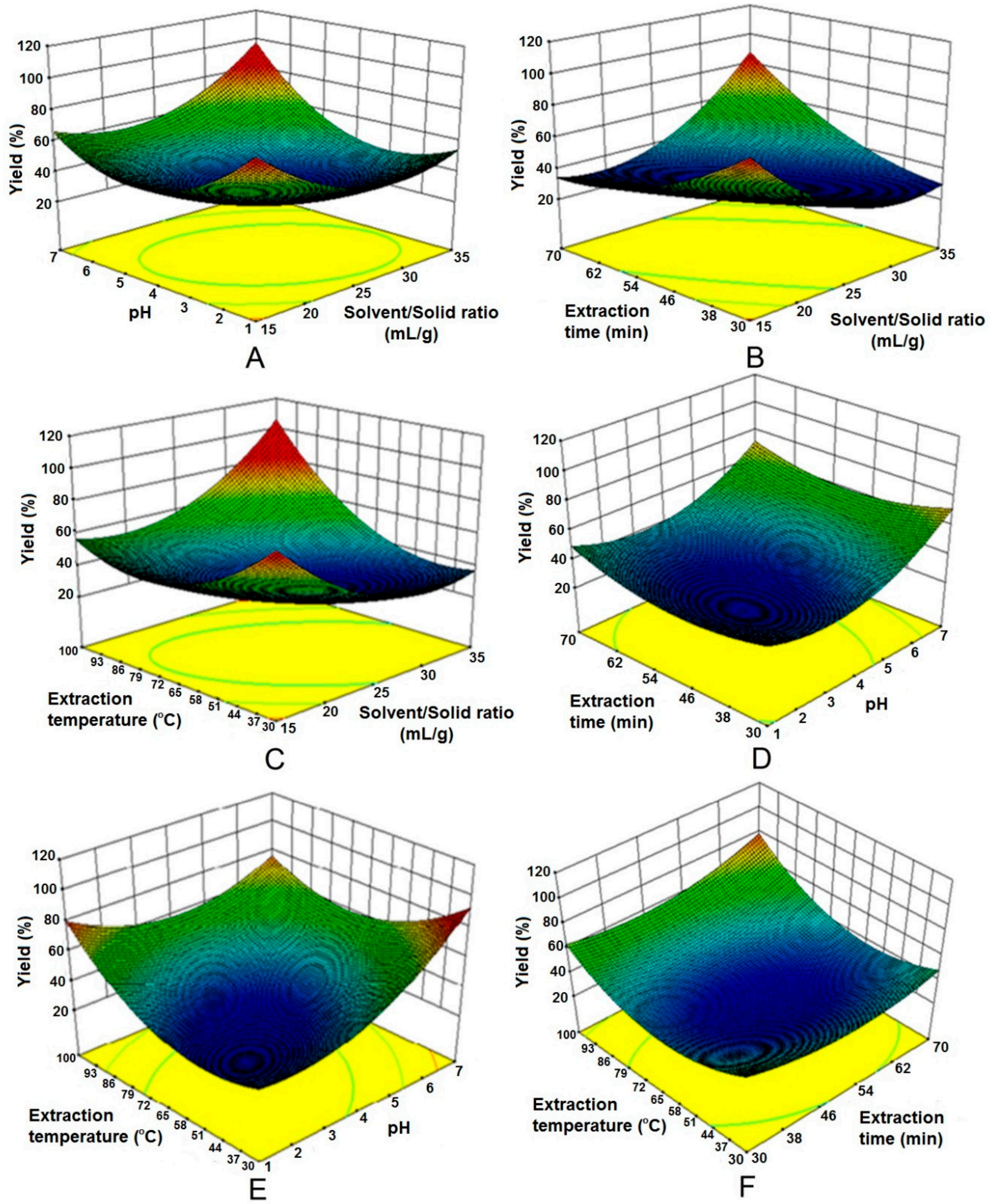

Figure 11. Response surface plot shows the individual and synergistic effects of (**A**) pH and solvent/solid ratio (mL/g); (**B**) extraction time (min) and solvent/solid ratio (mL/g); (**C**) extraction temperature (°C) and solvent/solid ratio (mL/g); (**D**) extraction time (min) and pH; (**E**) extraction temperature (°C) and pH; and (**F**) extraction temperature (°C) and extraction time (min) on the boric acid extraction yield (%).

3.3. Traditional and Intelligent Optimization

During the optimization process of this study, Design Expert software was used as a traditional approach for determining the optimum levels of four factors namely solvent/solid ratio, pH, extraction time, and temperature to obtain a maximum boric acid extraction yield from tincal. A maximum boric acid extraction yield, 88.24%, was predicted by the software under the optimum conditions of 32.72 mL/g, 4.66, 48.61 min, and 98.55 °C for solvent/solid ratio, pH, extraction time, and extraction temperature, respectively. In order to detect whether the predicted optimum conditions are really able to improve the boric acid extraction yield, another set of experiments were run with six replicates, and the yield results were averaged. The result showed that the optimum conditions allowed a higher yield, 88.13% (calculated value). This value was also higher than any CCD condition tested in this study; the highest value was obtained as 82.75% with the CCD. On the other hand, the chosen artificial intelligence-based swarm intelligence techniques were used in the same optimization problem by employing a total of 100 particles in each algorithm technique and running them in ten different 10,000-iteration optimization processes with changing parameters in each. Their yield results were also averaged separately. Table 5 summarizes the optimum conditions of the four test variables and the yields for both traditional and intelligent optimization ways (the best values are provided in bold style).

Table 5. The optimum conditions for the boric acid extraction from tincal (by considering different intelligent optimization algorithms and also Design Expert).

Technique/Method	Solvent/Solid Ratio (mL/g)	pH	Extract. Time (min)	Extract. Temperature (°C)	Yield (%)
PSO	31.64	4.58	47.78	95.79	84.42
CS	**34.15**	**4.70**	**48.93**	**99.67**	**91.56**
GA	31.72	4.64	46.82	96.13	85.08
DE	33.67	4.66	48.86	98.81	89.52
VOA	32.76	4.60	47.68	98.58	87.84
Design Expert	32.72	4.66	48.61	98.55	88.13

4. Conclusions and Future Work

In this study, the UAE process was employed and boric acid extraction yields from tincal ore were investigated by analyzing four different parameters, solvent/solid ratio (15, 20, 25, 30, and 35 mL/g), pH (1, 2, 3, 5, and 7), extraction time (30, 40, 50, 60, and 70 min), and extraction temperature (30 °C, 50 °C, 70 °C, 90 °C, and 100 °C). Optimum conditions to maximize the yield were obtained by employing RSM for the first time, and also five different artificial intelligence techniques, which are also swarm intelligence-based optimization techniques. It is possible to indicate that all the applied alternative optimization methods have provided good yield results and especially the related intelligent optimization algorithms have provided remarkable average performances even under changing parameters in each of ten different runs.

The results demonstrated that higher boric acid extraction yield requires higher extraction temperatures. In case of solvent/solid ratio, pH and extraction time, the higher yield depends on the situation since higher or lower values were both able to augment the yield when there is a synergistic effect of other factors. The aspects distinguish our work from other studies were the usage of UAE, RSM, and also intelligent optimization ways thanks to the swarm intelligence techniques. This study also showed that RSM and artificial intelligence are powerful methods for UAE and can be effectively used for optimization of boric acid extraction from tincal. Since the central composite design method includes both design and factors affecting the variability, the conditions determined in a laboratory environment may be very useful for the production of boric acid at an industrial scale. This process has advantages, which not causes environmental problems. On the other hand, use of artificial intelligence in such optimization processes is another key result to prove the effectiveness of this research field and its future potential in this manner.

Results that have been obtained with this study have encouraged the author(s) to perform further studies. In this context, alternative ways of experiments will be continued to be done in the future. Except from the considered five artificial intelligence techniques here, alternative optimization techniques will also be employed to see if more optimum results can be conducted on producing boric acid from tincal.

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