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Araştırma Makalesi

Synthesis of AuPdNi Powders Using an Environmentally Friendly Ultrasound Assisted Extraction for Obtaining Boric Acid from Colemanite: Optimization by Response Surface Methodology

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ABSTRACT

In this study, simple ultrasonic assisted extraction was proposed as the environmental method at all stages of catalyst synthesis.A homogeneous catalyst was synthesized from high grade monodisperse gold-palladium-nickel nanoparticles using ultrasonic assisted extraction method (UAE) instead of conventional methods to obtain boric acid from colemanite.The most important advantage of this method is that AuPdNi nanoparticles can be easily separated and used repeatedly for further studies. Because of this feature, increasing amount of boric acid obtained from colemanite using AuPdNi nanocatalyst was investigated.For the test parameters, solvent/solids ratio, pH, extraction time and extraction temperature were used for extraction. Responsive Surface Methodology (RSM) method was used to determine optimum conditions. In this study, it was determined that presence of AuPdNinanocatalyst significantly increased boric acid activity. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analyses were performed for the characterization of nanomaterials. According to the results of the RSM test program, boric acid yield was found to be 95.73% with the aid of AuPdNi nanocatalyst.

Keywords: *Colemanite, Ultrasound-assistedextraction, Central composite design, Optimization, AuPdNi nanocatalyst*

Çevre Dostu Ultrasonik Destekli Ekstraksiyon Kullanılarak AuPdNi Tozlarının Sentezi ve Kolemanit'ten Borik Asit Elde Edilmesi: Tepki Yüzey Metodolojisi ile Optimizasyonu

ÖZET

Bu çalışmada, katalizör sentezinin tüm aşamalarında çevresel yöntem olarak basit ultrasonik destekli ekstraksiyon önerildi.Kolemanitten borik asit elde etmek için geleneksel yöntemler yerine ultrasonik destekli ekstraksiyon yöntemi (UAE) kullanılarak, yüksek dereceli monodispers altın-paladyum-nikel nanoparçacıklarından homojen bir katalizör sentezlendi. Bu yöntemin en önemli avantajı, AuPdNi nanopartiküllerinin kolayca ayrılabilmesi ve ileriki çalışmalar için tekrar tekrar kullanılmasıdır. Bu özellik nedeniyle AuPdNi nanokatalizörü kullanılarak kolemanitten borik asit elde etme miktarının artması incelenmiştir. Ekstraksiyon için çözücü/katı madde oranı, pH, ekstraksiyon süresi ve ekstraksiyon sıcaklığı kullanılmıştır. Optimum koşulları belirlemek için Duyarlı Yüzey Metodolojisi (RSM) yöntemi kullanılmıştır. Çalışmada, AuPdNi nanokatalizör varlığının borik asit aktivitesini anlamlı şekilde arttırdığı tespit edildi.

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Nanomalzemelerin karakterizasyonu için transmisyon elektron mikroskopisi (TEM), X-ışını kırınımı (XRD) ve Fourier dönüşümü kızılötesi spektroskopisi (FTIR) analizleri yapıldı. RSM test programının sonuçlarına göre, AuPdNi nanokatalizör yardımı ile borik asit verimi % 95.73 olarak bulundu.

Anahtar Kelimeler: *Kolemanit, Ultrason destekli ekstraksiyon, Merkezi kompozit tasarım, Optimizasyon, AuPdNi nanokatalizör*

I. INTRODUCTION

Boron is one of the most used elements in the world because of its superior properties. Boron minerals and products have a wide usage area and these fields are increasing. The use of boron minerals and products that are used commercially in a wide and diverse field is increasing. Nearly 10% of the produced boron minerals are consumed directly as minerals, while the remainder is used to obtain boron products. The use of boron minerals and products that are used commercially in a wide and diverse field is increasing. Boron minerals and productsused in many industries such asglass, ceramics, cleaning and bleaching, anti-fire, agriculture, nuclear applications, textile and metallurgy. It produces naturally different boron minerals such as boric acid (H_3BO_3), colemanite (calcium borate), kernite (sodium borates), tincal, charcoal (magnesium borate) andulexite (sodium calcium borate) [1]. Turkey in terms of boric acid, colemanite, which has large reserves of production at low cost. Bigadic located in Balıkesir, has the largest colemanite deposits [2,3]. Commercially, colemanite ($2CaO.3B_2O_3.5H_2O$) is an important boron mineral in boric acid production. Boric acid is used as a starting material for the production of many boron compounds in trade.

Boric acid production from the colemanite ore is produced by conventional methods and about 10% boric acid is produced [2,4,5]. It has been found that some of these methods have causing low yield and product loss [6]. This product has some disadvantages [6,9]. Using low-grade ores and using traditional technologies obtaining metals from industrial wastes is expensive due to their high energy requirement and initial investment cost. Therefore, more economical and environmentally sensitive methods have been developed. Different organic and inorganic acids were studied for the dissolution of boron minerals [4,7,8]. Colemanite; keratite, carbonate minerals and arsenic gangue minerals have been produced at low yields in the recovery and production steps of boric acid [9,10]. This problem has been aimed to be significantly improved by the new ultrasound assisted extraction (UAE) technique. Ultrasonic assisted extraction method (UAE) is used to remove in distinct samples. High extraction temperatures are not required in UAE technique[11,12]. In addition, faster and more efficient extraction is obtained by increasing mass transfer [13] and increases the effect of test parameters on yield [4].

There is a gap in the literatureon boric acid extraction from colemanite using ultrasonically assisted extraction with catalyst support. Experiments have been carried out in previous studies with some reaction parameters such as boric acid extraction, mixing ratios, grain size, solvent ratio, temperature, time, solid content [14,15].

The aim of our study to synthesize catalyst from Au, Pd and Ni powders using ultrasonic supported process. The solvent/solid ratio (mL/g), pH, extraction time (h) and extraction temperature (°C) were used as independent variables to obtain boric acid. In addition, the influence of the ultrasonics on the independent variables was determined. ANOVA analysis was performed using the parameters of the variables in the central composite design (CCD). Optimum conditions yielding the maximum amount of boric acid were determined. Different than the previous studies in the literature, in the study, the removal of boric acid from the colemanite mineral was performed using AuPdNi nanocatalyst with ultrasonic assisted extraction. In our study, the yield value of boric acid was found to be 87.13% without AuPdNi catalyst and 95.37% with catalyst.

II. MATERIALS AND METHOD

A. MATERIALS

The colemanite sample to be used in this study was obtained from the company of Eti Mine Bigadic (Balıkesir-Turkey). First, colemanite minerals were broken into small pieces. The particles were then pulverized into a ball mill and sized at micro level. In this study, colemanite dust of 0.05 mm (50 µm) was used.

B. SYNTHESIS OF AuPdNi NANOPARTICLES USING ULTRASOUND-ASSISTED AND EXTRACTION WITH ULTRASOUND-ASSISTED

AuPdNi nanoparticles were synthesized by solution combustion technique [16]. In the preparation, 0.25 mmol of $RuCl_3$, 0.25 mmol of $PdCl_2$ and 0.25 mmol of $NiCl_2$ were firstly dissolved and stirred separately in deionized water. Oxidizers were used for solution combustion. The aqueous citric acid ($C_2H_8O_7$) solution prepared for the combustion process functions as fuel. It was combined in a porcelain crucible and heated at 120 °C for 4 hours. Reaction process was carefully monitored. In the boiling solvent a foam is formed which shows the complete dehydration of the finely dispersed powder product. This shows that the reaction is complete. It was allowed to cool at room temperature to arrive at equilibrium.

1 g of colemanite and 0.1 g AuPdNi were used to observe the impact of AuPdNi on the colemanite boric acid extraction yield. Each sample was mixed with 2 M HCl at different solvent ratios (15, 20, 25, 30 and 35 mL), pH values (9, 10, 11, 12 and 13), time (1,2,3,4 and 5 hours) (40, 50, 60, 70 and 80 °C.). The traditional one-factor methodology has been used to examine the importance of experimental factors. After certain times each of the samples was filtered with filter paper (0.45 µm). The yield was studied by conducting a filtration test using the conductivity method.

C. STATİSTİCAL ANALYSIS OF CENTRAL COMPOSITE DESIGN WITHOUT AuPdNi CATALYST

One of the most experimental designs used for engineering purposes is a Central Composite Design with four variables and five different levels [17]. In this study, solvent/solid ratio (mL/1 g, X_1), pH (X_2), extraction time (h, X_3) and extraction temperature (◦C, X_4) and values are used in Table 1.

Table 1. *The values of independent variables and observed response*

Run	X_1	X_2	X_3	X_4	Yield (Response) *(%)*
1	25	11	3	60	49.517
2	20	10	4	70	76.791
3	30	10	2	70	59.612
4	30	10	4	70	82.926
5	20	10	4	50	58.37
6	20	10	2	70	59.864
7	25	11	3	60	49.606
8	30	12	4	50	77.124
9	30	12	2	50	46.286
10	30	10	4	50	63.123
11	20	12	4	50	58.765
12	20	12	2	50	49.637
13	30	10	2	50	37.985

Table 1 (continue). *The values of independent variables and observed response*

14	25	11	3	60	49.498
15	20	12	4	70	70.845
16	20	10	2	50	49.762
17	25	11	3	60	49.503
18	30	12	4	70	96.81
19	30	12	2	70	70.764
20	20	12	2	70	66.442
21	25	11	3	80	80.634
22	25	11	3	60	49.528
23	25	11	1	60	50.854
24	25	11	5	60	79.487
25	25	13	3	60	69.52
26	25	9	3	60	50.845
27	25	11	3	40	53.372
28	35	11	3	60	59.612
29	25	11	3	60	49.502
30	15	11	3	60	43.479

1 gr of colemanite powder was used in the experiments. The pH of prepared solution was determined with a pH meter. For extraction, an ultrasonic bath (Bandelin sonorex) with thermostatic control at 50 kHz was used. In the ultrasonic extraction procedure, the experimental conditions specified in the experimental design were used (Table 2). The content of boric acid in each filtrate was then determined by the conductometric method [18]. Boric acid yield (%) was calculated according to equation 1:

$$Boric\ acid\ yield\ (\%) = \left(\frac{C}{C_O}\right) X\ 100 \qquad (1)$$

where C is the amount of extracted boric acid (specified in Table 2) passed, and C_0 is the amount of boric acid in the colemanite ore. In the present work, Central Composite Design (CCD) was also used for the statistical analysis.

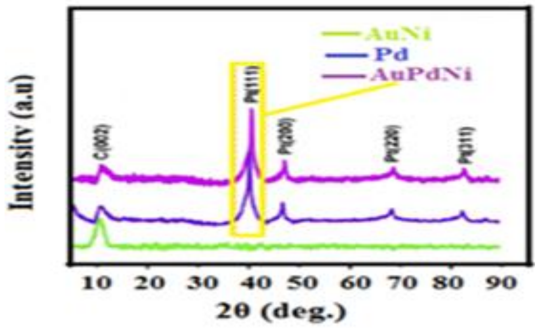
III. RESULTS AND DISCUSSION

A. CHARACTERIZATION OF AuPdNi CATALYST

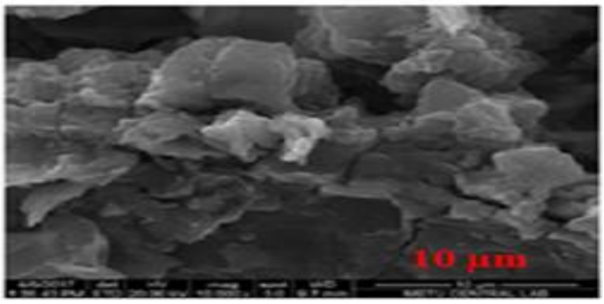
The microstructures of the synthesized AuPdNi nanocatalyst was characterized using X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM). To investigate the crystalline structure, the catalysts were identified by XRD as show Figure 1a.X-ray diffraction (XRD) analysis was implemented using a Cu Kα radiation (1.54 Å) at 40 keV and 30 mA. The diffraction peaks at 2θ = 40.22, 46.74, 68.37 and 82.21 corresponds to (111), (200), (220) and (311) diffraction planes of cubic crystallattice at around AuPdNi. The cyrstallitesizes of the AuPdNi were calculated by Debye-Scherrer'sequation [19];

$$D = \frac{0.9\lambda}{\beta Cos\theta} \qquad (2)$$

where D is the crystallite size, β is thewideness at half most in radians of the diffraction peaks, θ is the Bragg's diffraction angle, and λ is the X-ray wavelength (1.54056 °A). Besides, the peak at around 12.3° is attributed to the AuNi catalyst. The peak of the diffraction of the prepared catalyst was calculated and the lattice constant was found to be 3.887 Å, which is in good agreement with 3.890 Å for pure Pd [20]. Peak peaks on the XRD graph show that the nanoparticles of the AuPdNi catalyst are very well crystallized (Fig. 1a).



(a)



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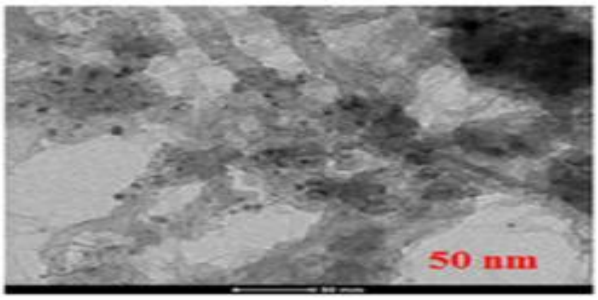

(c)

***Figure 1. (a)** XRD, **(b)** SEM and **(c)** TEM image of AuPdNi*

To better analyze the morphology, scanning electron microscopy (SEM) specimens and transmission electron microscopy (TEM) were readied by the ethanol-nanoparticle mixture drilling method and then micro propelled into a carbon-coated copper grid. The surface morphology of the prepared AuPdNi catalyst is observed by SEM analysis. As shown in Figure 1b, the sheet-like structure in the SEM image clearly shows the AuPdNi catalyst [21]. The TEM chart of the AuPdNi catalyst is shown in Figure 1c. Corner wrinkles and edges in the layers formed in the AuPdNi catalyst are visible at various locations in Figure 1c.

B. RESULTS FOR EXPERIMENTAL WITHOUT AuPdNi NANOCATALYST

In our study, we used CCD to investigate the effects of independent variables (solvent/solid ratio (mL/g), pH, time (hour) and temperature (°C) on boric acid extraction (Table 1). 30 different experiments were performed for different values of these parameters. The regression analysis of experiments are submited in Table 2. Accordingly, Design Expert software is aiming for second-order polynomial equations with an R^2 value of 0.9767. For an important model it is stated that R^2 should be at least 0.80 [22,23]. These high R^2 values indicate the importance of this study.

ANOVA analysis showed that F-value (41.84) and p-value (<0.0001) were very suitable for the applied model. If the p values in the model are less than 0.05, the model is very suitable for the experiment. Each of the four experimental parameters was determined separately for the yield. Their p values are very low (Table 3). Among the coefficients, X_2X_3, X_2X_4, X_3X_4 and X_{12} (p> 0.05) did not show any significant effect on the response.

Table 2. *The regression analysis of experimental*

Source	Std. dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	8.55	0.6879	0.6359	0.5381	2597.96	
2FI	8.48	0.7698	0.6419	0.5066	2775.27	
Quadratic	3.06	0.9767	0.9533	0.8454	869.80	Suggested
Cubic	1.66	0.9971	0.9863	0.1455	6442.43	

Table 3. *Second order regression equation coefficients*

Variable	Sum of Square	df	Mean Square	F Value	P-value	
Model	5493.06	14	392.36	41.84	< 0.0001	*Highly significant*
X_1	243.33	1	243.33	25.95	0.0002	
X_2	305.24	1	305.24	32.55	< 0.0001	
X_3	1694.58	1	1694.58	180.70	< 0.0001	
X_4	1625.69	1	1625.69	173.35	< 0.0001	
X_1X_2	134.77	1	134.77	14.37	0.0020	
X_1X_3	274.48	1	274.48	29.27	< 0.0001	
X_1X_4	49.65	1	49.65	5.29	0.0373	
X_2X_3	0.80	1	0.80	0.085	0.7749	
X_2X_4	0.60	1	0.60	0.064	0.8041	
X_3X_4	0.57	1	0.57	0.061	0.8087	
X_1^2	28.57	1	28.57	3.05	0.1028	
X_2^2	277.34	1	277.34	29.57	< 0.0001	
X_3^2	537.51	1	537.51	57.32	< 0.0001	
X_4^2	654.52	1	654.52	69.79	< 0.0001	
Residual	131.29	14	9.38			
Lack of Fit	131.29	10	13.13	6538.13	< 0.0001	*significant*
Pure error	8.032×10^{-3}	4	2.008×10^{-3}			
Cor. Total	5665.30	29				

The second order polynomial model used to express the boric acid yield as a function of independent variables is shown (4) below:

$$Y = 22.95209 - 12.38836X_1 - 81.39258X_2 - 35.27854X_3 - 6.07583X_4 + 0.58045X_1X_2 + 0.82838X_1X_3 + 0.035232X_1X_4 - 0.22325X_2X_3 + 0.019350X_2X_4 - 0.018887X_3X_4 + 0.040823X_1^2 + 3.17983X_2^2 + 4.42683X_3^2 + 0.048850X_4^2 \quad (3)$$

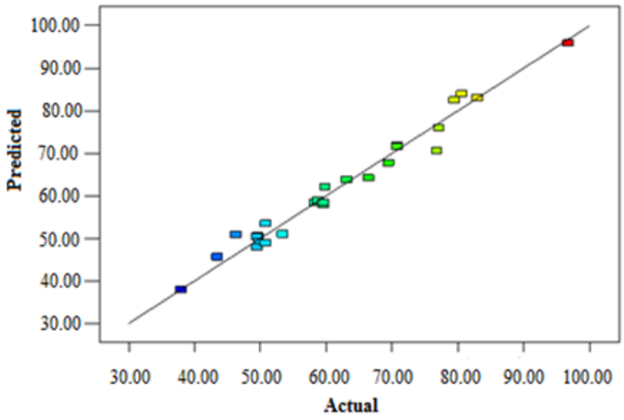

***Figure 2.** The plot of actual and predicted values for the response*

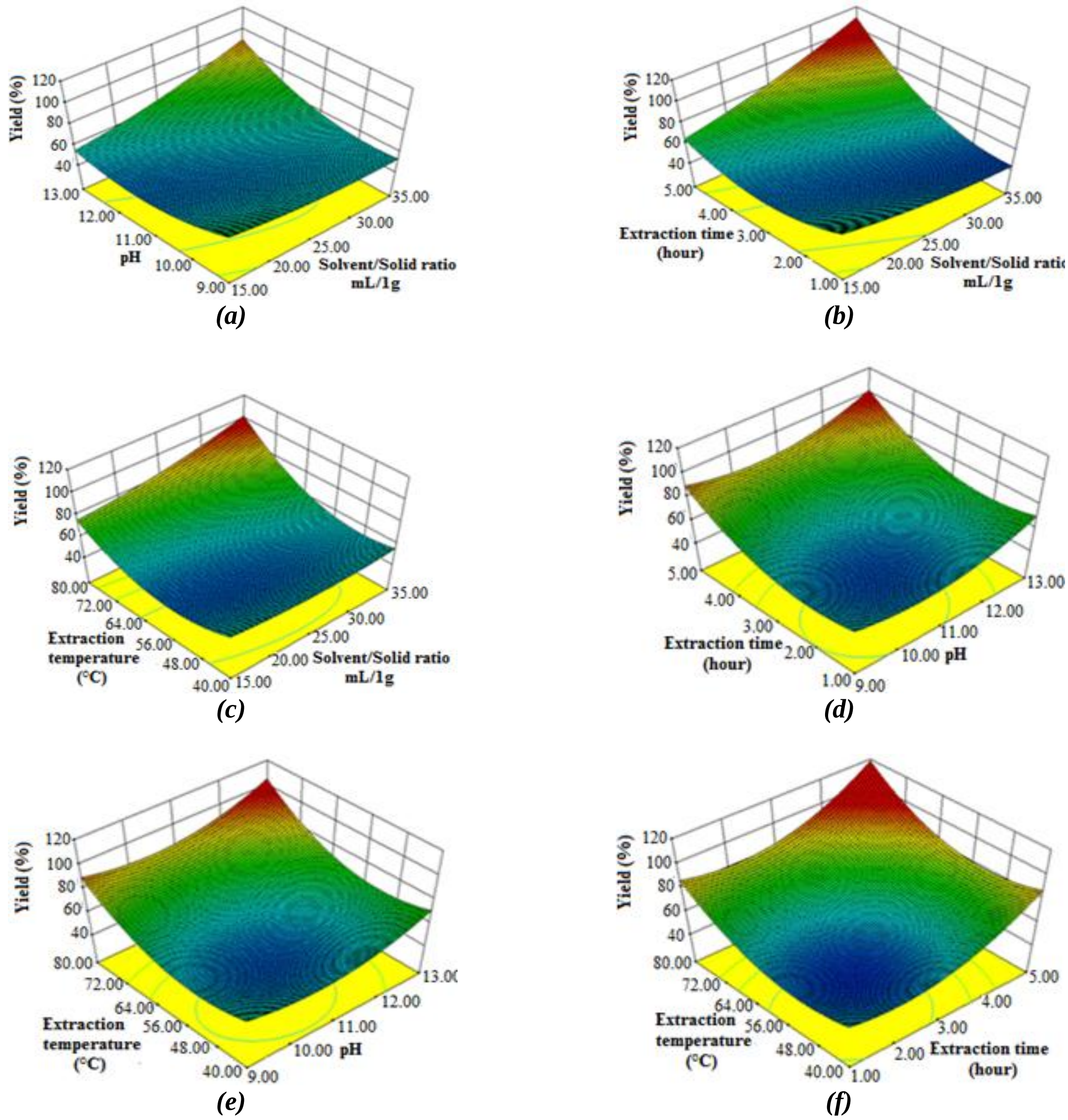

***Figure 3.** Response surface plats displayingimpacts of variables on the boric acid extraction yield (%)*

Actual and predicted values in the plot are shown in Figure 2. The observed values are very close to the predicted values. The reaction surface in Figure 3A has shown that higher alkaline pH increases the permeation with a higher solvent/solid ratio. This can be seen as a red/orange color zone in the surface plan. In Figure 3B, the boric acid extraction yields a red zone (optimum zone) when the pH of solution changes from 25 to 35 mL and the extraction period is at minimal 4 hours (Table 2). According to this extraction temperature and solvent/solid ratio (Figure3C), a comparative relationship was researched; higher temperature and higher HCl volume are required to achieve higher efficiency. In Table 4, this reciprocal relationship (X_1X_4) showed a p-value of 0.03. However, the surface plot showed that both parameters had a very significant effect on the yield separately.

In Figure 3D, it was observed that the optimum yield zone was reached when the yield was kept for more than 4 hours at 9 to 13 pH values. However, it can be seen that higher yields can be obtained when the pH rises. This is shown as a red zone with a larger area.The interaction between the extraction temperature and the pH was found to be similar to that of Figure 3D (Figure 3E). Figure 3D and 3E show that the temperature or extraction time can be varied over a wide range of pH to obtain maximum efficiency when changed. In addition, since the p-value is > 0.7, the correlation coefficient of two variables is weak (Table 4). As can be seen in Figure 3F, higher yields are obtained when extractions are carried out at 64 °C for at least 3 hours. However, unlike Figure 3D and 3E, this effect is not apparent on the surface drawing. It is seen that the efficiency of pH is lower than that of extracting time and temperature.

It has been reported by Tekin and Okur in the literature that the reduction of the particle size is a major effect on the solubility of colemanite in producing boric acid [24]. In our study, colemanite powder with a particle size of 0.075 mm (200 mesh) was used. The yield results obtained by using such a small grain size are shown in Table 2. In this finding, ultrasound-assisted is a consequence of a positive effect on the dissolution of the colemanite mineral [25].

C. COMPARISON OF RESULTS FOR ULTRASOUND-ASSISTED EXTRACTION (UAE) WITH AuPdNi NANOCATALYST

It is seen that in almost all experiments, higher yields are obtained at different pH, time, temperature and solids/solid ratios, with the aid of AuPdNi nanocatalyst and without AuPdNi nanocatalyst (Figure 4). In each of the images in Figure 4a, 4b, 4c and 4d, when the AuPdNi nanocatalyst is used, the maximum amount of boric acid is reached.

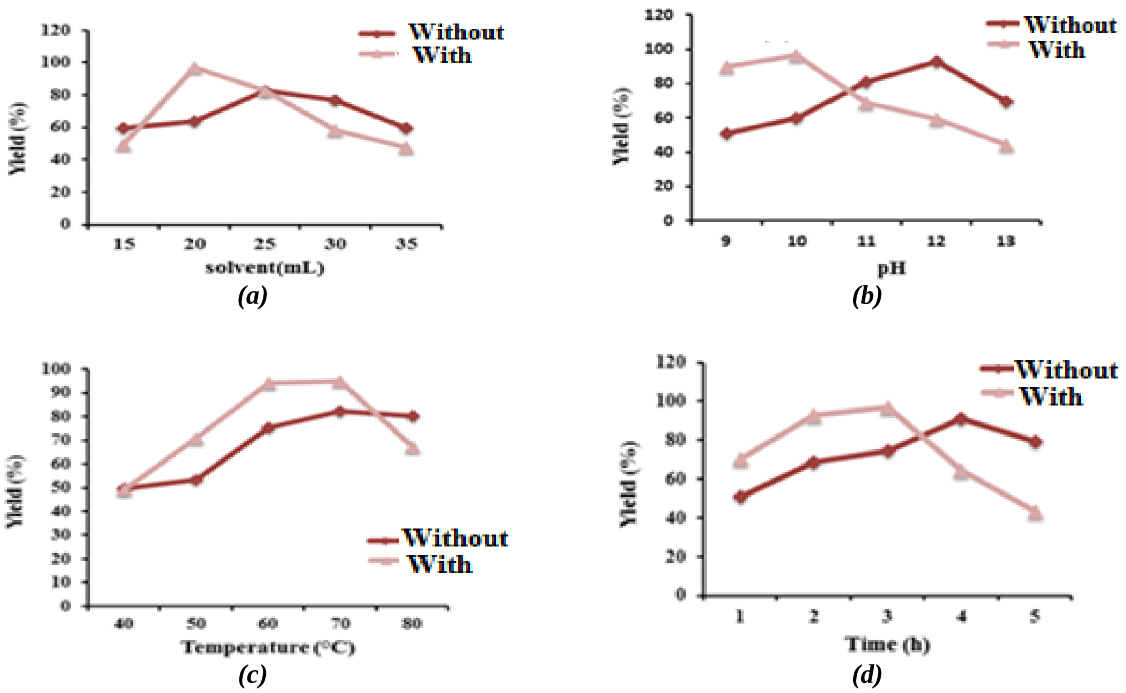

Figure 4. *Comparison of yields with and without AuPdNiof independent variables*

D. OPTIMIZATION OF THE EXTRACTION PROCESS

Optimization is one of the most commonly used methods for optimizing the multiple-response processes in science and engineering [26]. It describes the properties of the extracts obtained by the reaction variant during extraction. Some of these variables have to be maximized, others have to be minimized. The purpose of this study is to determine the best experimental conditions for extraction. Table 4 obtained the optimum conditions and yield of four independent variables.

Table 4. *The conditionsoptimum of yield boric acid*

Solvent/solid ratio *(mL (1 g colemanite)$^{-1}$)*	**pH**	**Extraction time** *(h)*	**Extraction temperature** *(°C)*	**Yield (Boric acid)** *(%)*
X_1	X_2	X_3	X_4	Y
25.90	10.76	4.60	75.65	87.13

Table 5. *Comparisons with conditions that yield boric acid from colemanite with and without AuPdNi*

Solvent/solid ratio *(mL/1g)*	**pH**	**Time** *(h)*	**Temperature** *(°C)*	**Yield** *(%)*	**PdAuNi Catalyst**
26	11	5	80	87.19	-
26	11	5	80	87.01	-
26	11	5	80	87.17	-
26	11	5	80	95.03	+
26	11	5	80	95.37	+
26	11	5	80	95.18	+

According to the results, we can see that in case of AuPdNinanocatalyst there is a significant increase in productivity. The AuPdNinanocatalyst increased the yield of boric acid (Table 5). In our work, the use of RSM is used for optimization without AuPtNi catalyst. Optimum conditions were determined as25.90 mL / g, 10.76, 4.60 hours and 75.65 ° C thanks to the Central Composite Design (CCD) (Table 4). Six separate experiments were performed under the conditions indicated in Table 4. The yield values obtained were averaged. It is estimated that the yield of boric acid is about 87.10% under the optimizedconditions (without AuPtNi). The experiment was repeated using the AuPtNi catalyst as described in Table 5. The boric acid yield was compared to the yield values obtained without catalyst and with catalyst.

Researchers have shown that higher temperatures result in higher yields [25,27]. In this study, the low extraction temperature was found at 75.65 °C [28,29].

E. REUSABILITY OF AuPdNi NANPARTICLES (NPs) AS CATALYST

The reusability of the AuPdNi nanocatalyst was investigated using the model reaction under optimized reaction conditions (Figure 5). First, the catalyst was washed three times with ethanol and washed with distilled water and then vacuum dried. In Figure 5, it is observed that there is no significant reduction in the catalytic function of the AuPdNi catalyst. For this reason, availability has increased six fold. It seems to be a very stable and reusable catalyst. During the reaction, only some agglomeration (increase in particle size) was observed after aggregation in catalyst 6. The decrease in percent conversion after a catalyst has been used can be explained by increasing the particle size of the AuPdNi Ns.

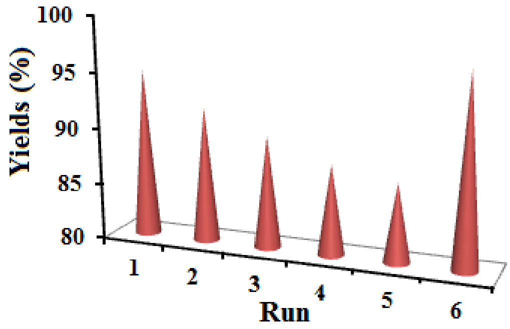

Figure 5. *Reusability of AuPdNi nanoparticles as catalyst*

IV. CONCLUSIONS

This study showed that CCD is a powerful method for the production of boric acid by the UAE method. The highly efficient AuPdNi nanocatalyst has been successfully synthesized. An effective and practical synthetic method was developed. The highest yield value was obtained at the lowest extraction time.Moreover, the efficient operation of the catalyst, simple or insensitive to ambient air or humidity, provides a great advantage in terms of high efficiency.

Compared to prior works, this work contains pure and economical boric acid production. Solvent/solids ratio (1 g colemanite)$^{-1}$, pH, extraction time (h) and extraction temperature (°C) were evaluated using the response surface design. Extraction yield was investigated the determined parameter values. Results showed that parameters used in the experiment were quitesignificant for production yield. Optimum conditions were 25.90 mL (1g colemanite)$^{-1}$ for solvent/solids ratio, 10.76 for pH, 4.6 hours for extraction time and 75.65 °C for extraction temperature. In summary, boric acid extraction yield was reached with the aim of about 95.37% with the help of AuPdNi catalyst.

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