

EXTRACTION OF BORIC ACID FROM TINCAL MINERAL BY ETHANOL

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ABSTRACT

In this study, extraction of boric acid from tincal mineral by ethanol was investigated at supercritical and subcritical conditions. Experiments were carried out in a high pressure reactor having volume of 0.1 dm³ under the mixing rate of 800 rpm. Solid/liquid ratio was changed from 0.05 to 0.1 and different particle sizes were used. Tincal mineral decomposed at high temperature and boric acid reacted with ethanol to form triethylborate which is volatile. Characterization of the powder crystallized from ethanol phase and the powder remained in the reactor by using FTIR, XRD and TGA has revealed that boric acid was extracted from tincal and ultimately reacted with ethanol to form a triethylborate which was transported into expansion vessel. The some portion of water in tincal structure was also extracted by ethanol since there was no peak at 1650 cm⁻¹ for bending vibration of water in its IR spectrum. The amount of boric acid in the liquid ethanol phase obtained from the expansion vessel was determined by analytical titration after the addition of water to the mixture. Boric acid extraction efficiency was determined to be 32.6% in weight. at 250°C and for solid/liquid ratio of 0.05 g/cm³.

INTRODUCTION

Boron exists in the form of borate salts in nature, and the most of the boron reserves in the world are located in the western part of Turkey. Boric acid (H₃BO₃) is an important boron product which is produced from different boron minerals, such as colemanite, tincal, kernite, ulexite or brines having dissolved boron salts. Although there are more than 200 boron compounds defined in the world, only calcium borates and sodium borates are commercially important and they form the 90% of existing reserves [1]. Eti Mine Inc., the second largest producer in the world, produces boric acid from colemanite mineral. Boric acid has been widely used in the production of different boron compounds namely, zinc borate, borate esters, boron carbide, boron nitrite and etc. It is also found in a small percent in nature as the sassolite mineral. Melting point of boric acid is 170°C, however when heated slowly it is converted into metaboric acid (HBO₂) by losing water in the range of 100-130°C. Diboron trioxide (B₂O₃) is obtained as a result of heating to temperatures higher than in 160°C [2]. Although boric acid is mainly produced from colemanite mineral using sulfuric acid, there are also studies for the production of boric acid from other boron minerals, e.g., tincal and ulexite. Since tincal mineral contains soluble borax and insoluble impurities in water, it is initially separated from those impurities by dissolving it in hot water. After this separation step, it is reacted with sulfuric acid to produce boric acid and sodium sulfate as a by-product. The reaction is carried out at 90°C for ½ hour as pointed out in Equation 1, [3].



In those methods, some problems were reported regarding to environmental issues. These are an increasing amount of solid by-product with higher boron content, a discharge of large amount of water, a corrosion problem in the equipments used. In order to find solution to the above problems, using different organic and inorganic acids was investigated for the dissolution of boron minerals in literature. For instance, leaching kinetics of tincal mineral using oxalic acid [4]; dissolution kinetics of ulexite in acetic acid solution [5] were investigated. None of them replaced sulfuric acid from the use commercially since there are difficulties in the separation of by-products from mother liquor when those acids were used and most of them were not cheap enough to be used in large quantities. In industry, H_2SO_4 is the most dominantly used acid for producing boric acid from boron minerals.

In Turkey, 400,000 tons of solid waste is generated each year during the production of borax from tincal [6]. The composition of that waste was reported as 19.44% B_2O_3 ; 16.85% CaO ; 13.01% MgO ; 9.82% SiO_2 ; 10.3% Na_2O ; 1.30 Al_2O_3 ; 1.49% Fe_2O_3 and the rest was ignition loss by weight. Since the boron level in both water and solid is critically important for plants and other living species, boron content of side streams from production facility must be monitored and controlled. While European Union has decided the maximum boron level as 1 mg/dm^3 ; World Health Organization determined the level of boron in drinking water as 0.5 mg/dm^3 [7]. Instead of treating solid and liquid waste streams from production side, novel techniques must be investigated to find a solution to the problem at source.

Supercritical fluids (SCF) started to being used for producing novel materials or to provide an alternative instead of conventional techniques. The use of SCF processes has been increasing as the environmental and food regulations become more and more important for the human beings and the world. The most important feature of supercritical fluid is that its property can be adjusted from gas to liquid with small pressure and temperature variations [8, 9]. Design of inorganic materials using supercritical fluid methods is accomplished through two distinctive processes. In the first one, the driving force for particle formation is a physical transformation of matter by a rapid depressurization and/or antisolvent effect. The detailed information about these processes can be found in literature [10, 11]. In the second group of process, supercritical fluids are used as a reaction media to synthesize a number of different materials, such as oxide, metals, semiconductors, and etc.[9].

Supercritical ethanol was used for drying of borate salts to obtain nano sized products [12]. It was reported that zinc borate with particle size of 20-50 nm particle size was obtained by supercritical ethanol drying and that product decreased the friction coefficient of base oil. $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and $\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ were dried by supercritical ethanol drying process in order to investigate the effects of conditions on zinc borate types [13]. Zinc borate having the oxide formula of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ partially decomposed and lost its water in the SCE drying. Zinc borate of $\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ has decomposed completely into ZnO and boric acid in SCE drying. It was anticipated that critical temperature and pressure of ethanol played a crucial role in decomposition of the zinc borates. Two major decomposition products have emerged in the SCE drying. These are the powder product, consisting of mostly ZnO , remained in the reactor and the product rich in boric acid dissolved in the ethanol. As supercritical ethanol extracted boric acid from zinc borates, the idea of extraction of boric acid from natural boron minerals, such as borax and ulexite has come in mind.

The aim of this study is to use ethanol for extracting boric acid from tincal mineral at supercritical and subcritical conditions and to investigate the interactions between boric acid and ethanol during the extraction process. For this purpose tincal obtained from Eti Mine

Works Inc. was used in extraction; the powder remained in the extractor and material dissolved in ethanol phase were characterized by advanced analytical techniques.

MATERIALS AND METHODS

Materials

Tincal mineral used in this study was supplied from Kirka Plant of ETİ MINE Works in Turkey. Ethanol (C_2H_5OH) with purity of 99.8 (v/v) (SIGMA ALDRICH) was used in the extraction experiments. Sodium hydroxide, NaOH, (%99.0, w/w MERCK), glycerol (99.5%, v/v DALAN Chemical Industrial) and phenolphthalein ($C_{20}H_{14}O_4$, MERCK) as indicator were used in the volumetric determination of boric acid. Potassium bromide, KBr, (99.99%, w/w Merck) was used to prepare pellets in IR analysis. Calibration of 0.5 M NaOH solution was done by using potassium hydrogen phthalate, $C_8H_4KO_4$.

Methods

Tincal mineral was milled and sieved by using sieves with 20, 40, 63, 106 μm sieve size. The extraction system consists of a high temperature and pressure reactor (PARR 5513), an expansion vessel, a temperature controller (PARR 4848), nitrogen cylinder, and a circulating cooling bath (Polyscience 9606). The experimental setup is shown in Figure 1.

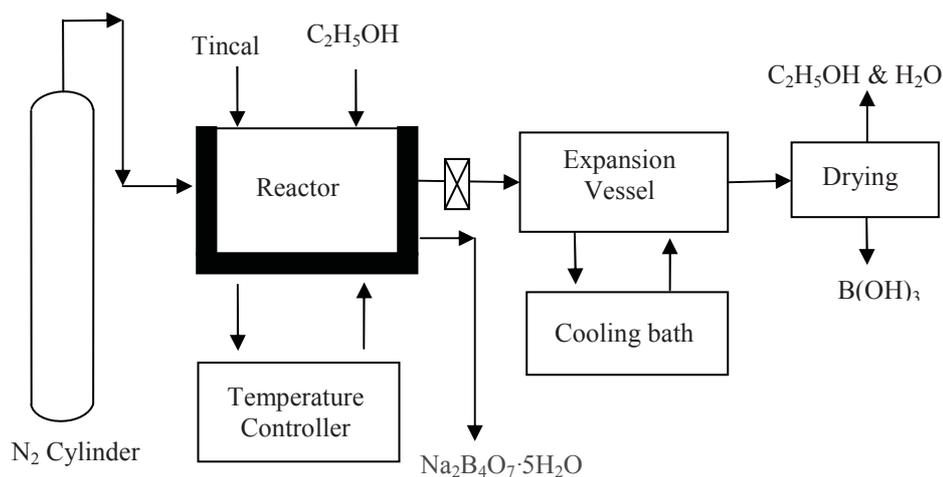


Figure 1. Experimental Setup

Experiments were carried out in the high temperature and high pressure reactor having 0.1 dm^3 volume. Different solid/liquid (S/L) ratios (0.05-0.1) were used in the experiments as shown in Table 1. Before heating the reactor, nitrogen gas was passed through the system to remove any remaining oxygen in the reactor and pipelines. In the experiments, tincal-ethanol mixture was heated to temperatures of 200°C and 250°C, and to the corresponding pressures under the mixing rate of 800 rpm for different extraction times. When the reactor reached to the desired pressure, it was kept under these conditions for a predetermined extraction time, and then mixing was stopped and the mixture was transferred into the expansion vessel at 10°C by opening the valve between them and keeping the reactor temperature constant during the transfer. When the pressure in the reactor decreased to the atmospheric pressure, the system was again purged with N_2 gas. 0.010 dm^3 of the ethanol phase in the expansion vessel was transferred to a Petri-dish and dried at room temperature in fume hood. The chemical

structure of the white powder crystallized from ethanol phase and powder remained in the reactor was examined by Infrared Spectroscopy (FTIR), X-Ray Powder Diffraction equipment (XRD) and thermal gravimetric analyzer (TG/DTA). In ethanol phase, the amount of boric acid was determined by analytical titration in the presence of H₂O.

Table 1. Experimental conditions of boric acid extraction from tincal

Exp. No	Temperature, °C	Pressure, MPa	Tincal used, g	Solid/Liquid Ratio, g/cm ³	Particle Size, μm	Extraction Time, min
Exp-1	250	7.4	2.50	0.05	+20-40	5
Exp-2	250	7.4	3.75	0.075	+20-40	10
Exp-3	250	7.2	3.75	0.075	-20	5
Exp-4	200	3.0	2.50	0.05	+40-63	5
Exp-5	200	3.0	2.50	0.05	+20-40	10
Exp-6	200	2.9	2.50	0.05	-20	5
Exp-7	200	3.0	2.50	0.05	+20-40	0

In the characterization experiments, X-Ray diffractometer (Philips Xpert-Pro) was used to analyze the crystal structures of the colemanite with CuK_α radiation at 45 kV and 40 mA. The registrations were performed in the 2θ range of 5-80°. The transmission spectra of KBr pellets prepared by mixing 4.0 mg of sample and 196 mg of KBr in an agate mortar and pressing the mixture under 8 tons were obtained using FTIR spectrophotometer (Perkin Elmer Spectrum BX). TGA were performed in Perkin Elmer-Diamond TG/DTA. Powder samples (10-15 mg) were loaded into an alumina pan and heated from 20°C to 800°C at 10°C.min⁻¹ under N₂ flow (40 ml.min⁻¹).

RESULTS

Extraction of boric acid was investigated at supercritical and subcritical conditions of ethanol in the high pressure and temperature reactor. B₂O₃ contents of ethanol phase and the solid phase remained in the reactor were determined by analytical titration. Table 2 shows the results obtained in the extraction experiments.

Table 2. Results of extraction experiment by ethanol from tincal mineral

Exp. No	Solid remained in the reactor, g	C ₂ H ₅ OH outlet, ml	Initial amount of B(OH) ₃ , g	B(OH) ₃ in ethanol, g	B(OH) ₃ in solid, g	Extracted B(OH) ₃ , %
Exp-1	1.49	48.0	1.21	0.40	0.89	32.69
Exp-2	2.36	48.5	1.82	0.52	1.40	28.68
Exp-3	2.45	47.5	1.63	0.48	1.08	29.60
Exp-4	1.59	48.0	1.29	0.30	1.04	22.98
Exp-5	1.54	48.0	1.21	0.31	0.90	25.30
Exp-6	1.61	48.5	1.09	0.27	0.75	24.75
Exp-7	1.61	48.0	1.21	0.30	0.94	22.22

The comparison of Exp.1 and Exp.5 has revealed that decreasing the temperature from 250°C to 200°C reduced the extraction efficiency by 7%, w/w at the expense of higher extraction

time. When Exp-4 was compared with Exp-6, it was seen that boric acid extraction efficiency for the particle size of (+40-63 μm) was less than the particle size of (-20 μm). Since the particle size is directly related to surface area, when particle size is decreased, surface area of that powder increases, and extraction will be higher for particles having larger surface area. On the other hand, it was found that increasing the solid/liquid ratio caused 4%, w/w decrease in extraction efficiency. The maximum boric acid extraction efficiency was determined as 32.6%, w/w at 250°C and solid/liquid ratio of 0.05.

XRD Analyses: Figure 2 shows the XRD patterns of tincal used in the experiments and the powder remained in the reactor at the end of extraction carried out at 250°C and 7.4 MPa. Beside borax, calcite, dolomite, sodium carbonate and quartz were in the mineral according to XRD pattern data. The peaks at 2θ values of 15.5°; 18.2°; 20.0°; 30.8°; 34.3°; 37.8°; 47.5° were assigned to borax structure based on the data of JCPDS 75–1078. However, there are some minor compounds in tincal mineral as impurity. Those major peaks were also investigated. The peak at 2θ of 30.0° belongs to calcite (JCPDS 87–1863); the peak at 2θ of 25.85° related to quartz (JCPDS 81–1665); the peak at 2θ of 30.9° represents the presence of dolomite (JCPDS 84–1208), and finally the peak at 2θ of 33.35 shows the presence of sodium carbonate (JCPDS 86–0315). XRD pattern data support the composition of tincal mineral (17.50% Na_2O ; 6.58% MgO ; 6.88% CaO ; 4.58% SiO by weight) found by XRF. In the ethanol extraction, the crystal structure of tincal has changed substantially as shown in Figure 2.b. The major peak at 2θ of 30.9° in Fig. 2 b) belongs to dolomite structure. As inferred from the comparison of Fig 2 a) and Fig 2 b), major peaks of borax vanished as water and some boric acid were extracted from its structure.

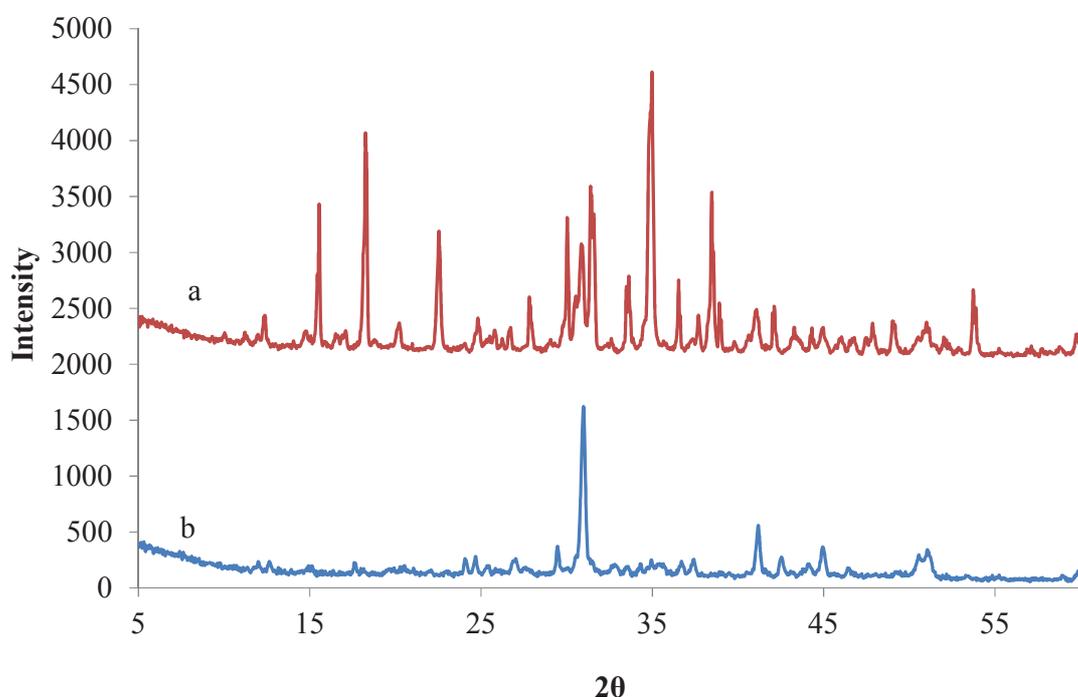


Figure 2. XRD patterns of a) tincal and b) powder remained in the reactor (E-2)

FTIR Analyses: Infrared spectrum of tincal and the powder remained in the reactor were given in Figure 3. The characteristic peaks of borax ($\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8(\text{H}_2\text{O})$) was explained by Jun and his coworkers [14]. Since majority of tincal mineral was composed of borax, the

main peaks belonged to borax structure. The peak at 1650 cm^{-1} wavenumber shows the presence of crystal water in structure of tincal and the broad peak at $3300\text{-}3500\text{ cm}^{-1}$ were caused by vibration of hydrogen bonded O-H groups. It was determined that some water were extracted from tincal structure as there was no peak at 1650 cm^{-1} and the height of the broad peak $3200\text{-}3600\text{ cm}^{-1}$ was decreased. Since bound hydroxyl groups are reacted to form water at high temperature, some part of extracted water comes from this reaction.

The liquid ethanol phase obtained at the end extraction was examined by FTIR-ATR. The presence of a weak peak at 1490 cm^{-1} in the spectrum showed that there is triethyl borate in the mixture. It was concluded boric acid extracted from tincal structure reacted with ethanol at extraction conditions. It was considered that transportation of boric acid by ethanol to the expansion vessel was induced by ester formation. However, not only boric acid but also some water was extracted from tincal structure. Recovery of boric acid from nuclear wastes performed by using the same methodology as reported in a previous investigation [15]. In that technique, boric acid first reacted with alcohol in excess amount and then evaporated from solid phase. Finally it was mixed with water to separate alcohol and boric acid. The presence of water in ethanol-boric acid mixture caused ester hydrolysis. As the esterification reaction is an equilibrium reaction, formation of ester is limited by the presence of water in the mixture. Thus, the transported triethyl borate was converted into boric acid and ethanol in the expansion vessel. 0.010 dm^3 of the ethanol-boric acid mixture in the expansion vessel was dried naturally in petri-dish at room temperature. Triethyl borate was converted into boric acid and ethanol in the presence of water.

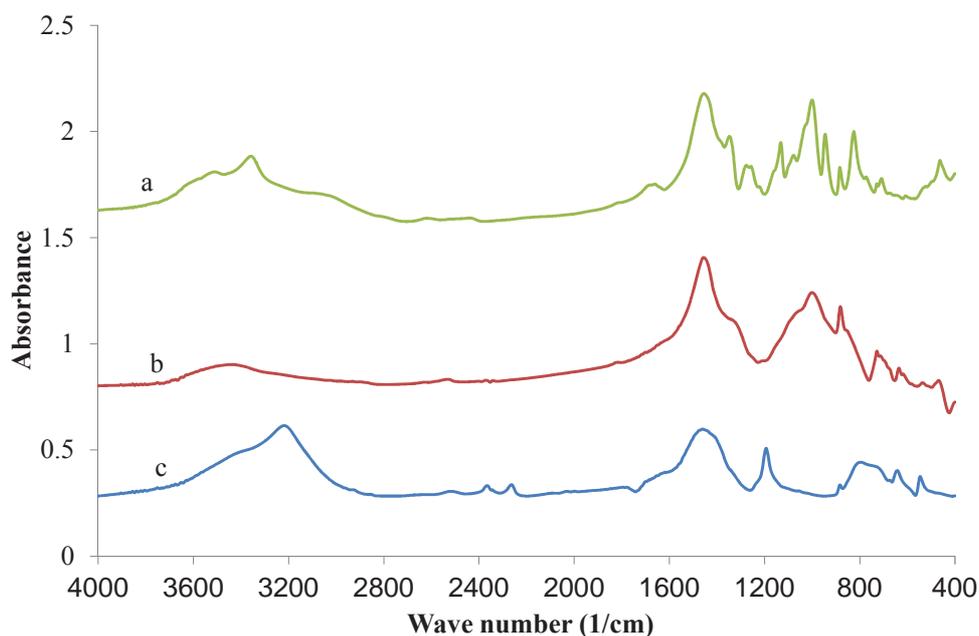


Figure 3. FTIR spectra of a) tincal b) the powder remained in the reactor, and c) the powder crystallized from ethanol phase (E-2)

Ethanol was evaporated from the liquid phase transported into the expansion vessel so that any dissolved compound could be crystallized. The white powder obtained at the end of drying was analyzed by FTIR spectroscopy and its spectrum is given in Figure 3 c. It was determined that crystallized powder product had the characteristic peaks of boric acid at $1454, 1192, 880, 790, 640$ and 546 cm^{-1} wavenumber [14].

TGA Analyses: Thermal behaviors of the solid product remained in the reactor and the powder crystallized from ethanol phase were investigated to support the data found in the XRD and FTIR. The powder remained in the reactor has decomposed in two steps analyses as shown in Figure 4. The first step began about 200°C and ended at about 500°C. A mass loss of 9% occurred up to 500°C which is caused by the release of 2 moles of water from the structure. A mass loss of 11% was calculated in the second step of dehydration, which is due to the elimination of water formed by reaction of hydroxyl groups in the tincal structure. Total mass loss occurred as 20% which is approximately half of the water content of initial tincal mineral (43.2%).

The crystallized powder from the ethanol phase has decomposed in one step as seen in Fig. 4-b. The mass loss of 44.0% at 300°C occurred in the decomposition of powder is comparable with the theoretical water content of boric acid (43.75%, wt). Thus, a white powder that was separated from ethanol phase was boric acid as supported by TGA.

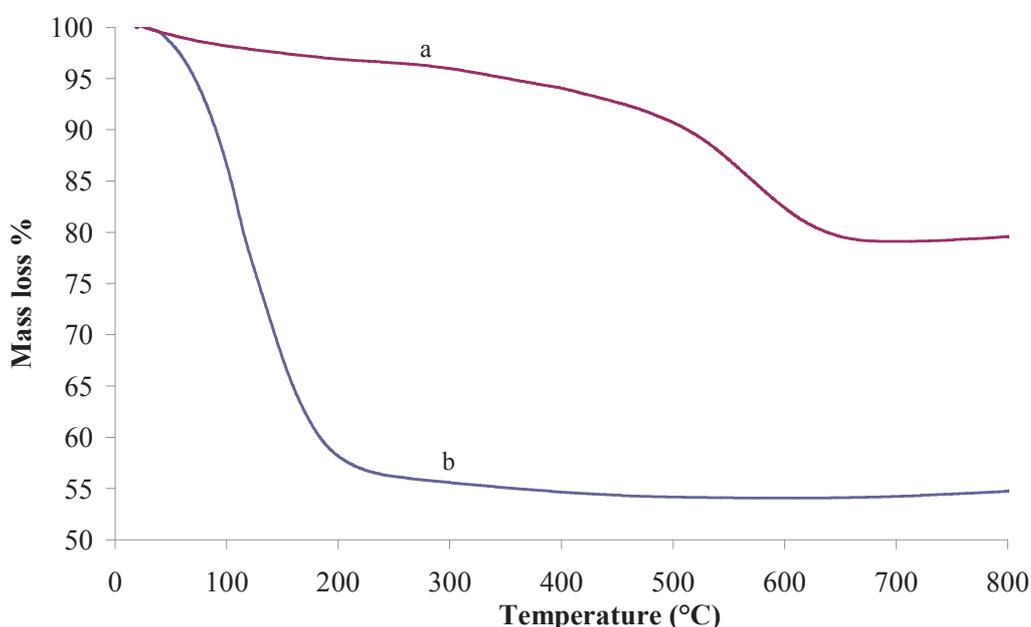


Figure 4. TGA graphs of a) powder remained in the reactor and b) powder crystallized from ethanol phase (E-2)

Thus, the following overall reaction (Eqn 2) occurred during supercritical ethanol extraction of tincal mineral.



Impurities remain unchanged or reacted with NaOH formed from borax in the reactor.

CONCLUSION

The effects of temperature, solid/liquid ratio, particle size and extraction time were investigated in the extraction of boric acid from tincal at supercritical and subcritical ethanol conditions. The interaction between boric acid and ethanol at supercritical and subcritical conditions was determined. Approximately half of the water content of tincal was removed in ethanol extraction. Characterization of the ethanol phase by FTIR-ATR has shown that boric acid extracted from tincal structure gave an esterification reaction with ethanol. The formed triethyl borate can be hydrolysed at the end by the addition of water to the mixture. It was

determined that the maximum boric acid extraction efficiency was about 32.6%, w/w in the conditions of at 250°C, S/L ratio of 0.05 g/ cm³, particle size of 20 µm and extraction time of 5 minutes. If the extraction efficiency is increased by the addition of a catalytic material to the mixture, this technique can be used to extract boric acid by esterification and recover it by hydrolysis.

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