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Dissolution of Ulexite in Hydrochloric Acid Solutions

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Öz: Uleksit bor bileşiklerin üretiminde kullanılan önemli bor minerallerinden bir tanesidir. Bu çalışmanın amacı uleksitin kesikli reaktörde hidroklorik asit çözeltilerindeki çözünürlüğünün incelenerek borik asit üretimi için alternatif bir prosesin belirlenmesidir. Reaksiyon sıcaklığı, parçacık boyutu, katı/sıvı oranı, asit konsantrasyonu ve karıştırma hızı parametrelerinin çözünme hızı üzerine etkisi incelenmiştir. Deneme parametleri asit konsantrasyonu için 0.75*,1,1.25,1.5,2M, reaksiyon sıcaklığı için 30*,40,50,60,70°C, parçacık boyutu için -14+18*,-18+30,-30+40,-40+50,-50+60 meş, katı/sıvı oranı için 5/100,7.5/100,10/100* g/mL, karıştırma hızı için 500*,650,800 rpm olarak belirlenmiştir. Çözünme hızının reaksiyon sıcaklığı ve karıştırma hızının artmasıyla arttığı, parçaçık boyutu, asit konsantrasyonu ve katı/sıvı oranı artışıyla ise azaldığı tespit edilmiştir.

Anahtar Kelimeler — Uleksit, Hidroklorik asit, Borik asit.

Abstract: Ulexite is an important boron mineral used for the production of boron compounds. Purpose of the study has been to investigate the dissolution of ulexite in hydrochloric acid solutions in a batch reactor and to present an alternative process to produce boric acid. Reaction temperature, particle size, solid/liquid ratio, acid concentration and stirring speed have been selected as parameters on the dissolution rate of ulexite. The parameters used in experiments are; acid concentration 0.75*,1,1.25,1.5,2M, reaction temperature 30*,40,50,60,70°C, particle size -14+18*,-18+30,-30+40,-40+50,-50+60 mesh, solid/liquid ratio 5/100,7.5/100,10/100* g/mL, stirring speed 500*,650,800 rpm. It has been found that the dissolution rate has increased the reaction temperature and the stirring speed. However, increasing the particle size, acid concentration and solid/liquid ratio have decreased the rate of dissolution.

Keywords — Ulexite, Hydrochloric acid, Boric acid.

1. Introduction

Boron is an element that commonly exists in soil, rock and water on the earth. Boron exists in high concentrations in the vicinity reposing from Mediterranean and from the west regions of the USA to Kazakhstan besides, boron content of soil is generally 10-20 ppm on average. It is between the ranges of 0.5-9.6 ppm in the sea water and 0.01 - 1.5 ppm in the fresh water. Boron is seen in high concentrations and economical dimensions that mostly exist in the arid climate, volcanic regions and the regions whose hydrothermal activity is high for Turkey and the USA such as enchained compounds of boron with oxygen (Woods, 1994). Boron is a valuable element besides its industrial importance. It is found as borates (oxides) in nature. The present boron minerals are tincal ($Na_2B_4O_7.10H_2O$), colemanite ($Ca_2B_6O_{11}.5H_2O$), ulexite ($Na_2O.2CaO.5B_2O_3.16H_2O$), kernite ($Na_2B_4O_7.4H_2O$), datolite ($Ca_2B_2O_5.Si_2O_5.H_2O$), and hydroboracid ($CaMgB_6O_{11}.6H_2O$). Turkey has a significant amount of boron minerals, and besides, the world's largest boron deposits are found in the Eskişehir-Kırka region of Turkey (Durak et. al., 2014). Boron minerals and boron products have been significant substances because of being used in many fields from agriculture to energy, from defense industry to space industry. The specific boron compounds are synthesized by using the minerals that add a premium on it in terms of both economically and usage area rather than the direct consumption of boron minerals.

Boric acid is most commonly used as a primary material in the preparation of many boron chemicals such as synthetic organic borate salts, borate esters, boron carbide, fluoroborates, and boron tri-halides. The preferred commercial method of preparing boric acid is by way of digestion of alkali and alkaline earth metal borates with concentrated mineral acids followed by crystallization of boric acid (Shiloff, 1968; Taylan et al., 2007). In Turkey, boric acid is obtained from the reaction of colemanite and sulfuric acid in accordance with heterogeneous solid–liquid reaction (Mergen et al., 2003). In this process, gypsum forms as a by-product and precipitates in the reactor while boric acid remains in the liquid phase throughout the reaction.

This process has some disadvantages such as sulphate contamination in final product, and environmental pollution. Therefore, the alternative processes have been suggested by many researchers.

Those having commercial value within 230 types of natural boron minerals in the nature are especially tincal, kernite, colemanite, inyoite, pandermite, ulexite and probertite (Kirk Othmer, 1992). Ulexite, which is a sodium–calcium borate with a chemical formula of $Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O$, is a structurally complex mineral. Many investigations have been performed related to the leaching of ulexite mineral in different solution. The solution kinetic of boron minerals in many solvents has been analyzed by using different parameters. Some of the studies that have been conducted about the dissolution kinetic of boron minerals are showed in Table 1.

Table 1. *Summary of dissolution kinetics and activation energy of boron minerals acid or gaseous solutions*

Boron minerals	Solutions	References
Ulexite	Borax pentahydrate solutions saturated with CO_2	(Kuşlu et al., 2010)
Ulexite	Ammonium carbonate	(Demirkıran and Künkül,2007)
Ulexite	Percloric acid	(Demirkıran and Künkül, 2007)
Ulexite	Phosphoric acid	(Doğan and Yartaşı, 2009)
Ulexite	Acetic acid	(Ekmekyapar et al., 2008)
Ulexite	CO_2 satured water	(Kocakerim et al., 1993)
Colemanite	Ammonium sulphate	(Tunç et al., 2006)
Colemanite	Potassium hydrogen sulphate solutions	(Guliyev et al., 2012)
Tincal	Phosphoric acid	(Durak and Genel, 2012)
Tincal	Oxalic acid	(Abali et al., 2006)

The process of boric acid generation, notably tincal (borax) and colemanite, some boron minerals are used like kernite, ulexite, probertite, hydroboracite, inderite, datolite and asharite. Two main raw materials are used in the process of boric acid generation in all over the world. In Europe and Turkey, colemanite is used for boric acid generation while tincal is used in the USA. Purpose of the study is to propose an alternative process to boric acid generation by analyzing the dissolution kinetic of ulexite in hydrochloric acid solutions.

2. Methods and Materials

Dissolution experiments have been conducted under atmospheric pressure conditions. All reagents used in the experiments have been prepared from the analytical grade chemicals (Merck) and distilled water. Ulexite ore which has been used in the study has been provided from Bigadiç, Balıkesir region of Turkey. The ore has been washed with water and dried several times after being cleaned from apparent impurities. After the process, the ore has been broken with crackers in the laboratory media then it has been separated into -14+18*,-18+30,-30+40,-40+50 and -50+60 of mesh of sieve fractions by the sieves in standards of ASTM. The result of the chemical analysis of ulexite mineral that are used in the studies is showed in Table 2. Besides XRD graphic and SEM picture of ulexite sample used in the study have also been showed in the Figure 1 and 2.

Table 2. *Chemical analysis of tincal ore used in this study*

Component	**% Composition**
B_2O_3	42.83
Na_2O	6.38
CaO	14.22
MgO	4.58
H_2O	29.67
Other	2.32

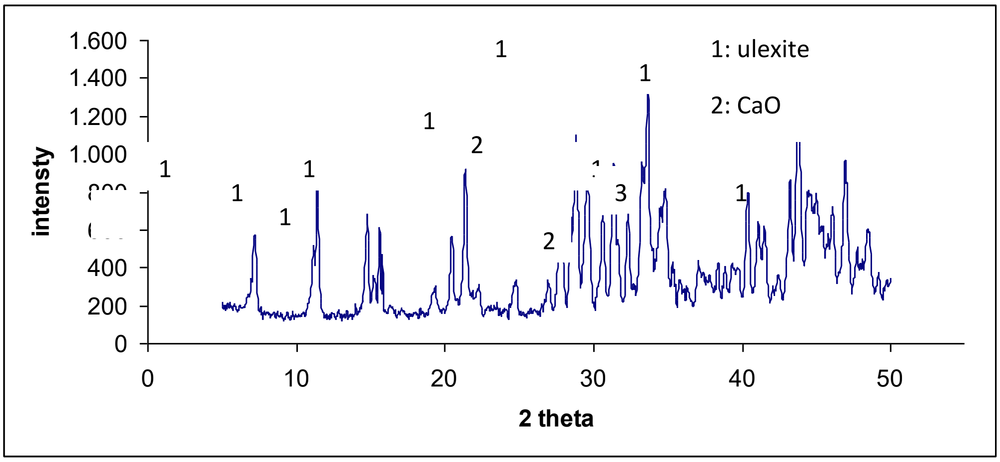

Fig. 1. *XRD diffractogram of ulexite minerals used in this study.*

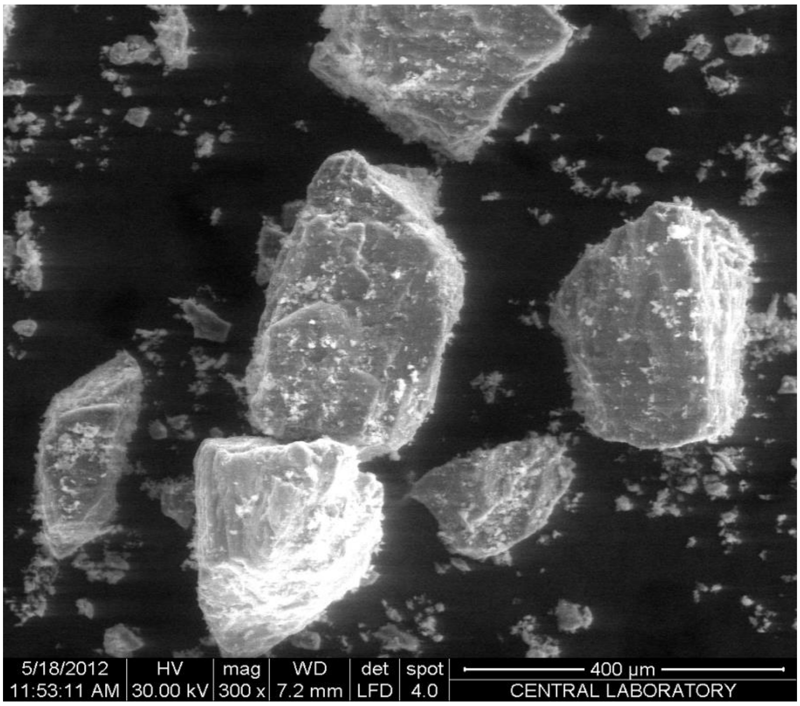

Fig. 2*. SEM photograph of ulexite minerals used in this study*

2.1. Experimental procedure

The solution treatments have been carried out in a 250mL-spherical glass reactor within atmospheric pressure. For mixing process, mechanics mixer and in order to keep temperature constant a constant heat water circulator has been used.

The parameters that have been used in solution process have been displayed in Table 3. Each experiment has been repeated twice, and the arithmetic averages of the results of the two experiments have been used in the kinetic analysis.

In solution processes, 0.1 L hydrochloric acid solution has been put in reactor for each experiment and then the mixing process has been started by closing the reactor cap. After the temperature of solution in reactor has reached to the desired value, reaction has been launched by putting a certain amount of ore.

At the end of the determined duration, mixing process has been finished and then some substances have been filtered in G-4 glass crucible by means of squinch in a short time by receiving the substance that is enough for analyzing from reactor. The B_2O_3 in the solution has been analyzed according to volumetric method with mannitol (Scott, 1963).

Table 3. *Parameters and their ranges used on the experiments*

Parameter	**Value**
Particle size (mesh)	-14+18*,-18+30,-30+40,-40+50,-50+60
Concentration of hydrochloric acid (M)	0.75*,1,1.25,1.5,2M
Solid/liquid ratio (g/mL)	5/100,7.5/100,10/100*
Stirring speed (rpm)	500*,650,800
Reaction temperature (^{o}C)	30*,40,50,60,70^{o}C

* The constant values used when the effect of other parameters was investigated

The conversion quantity has been found by transferring the dissolving H_3BO_3 quantity at the end of the reaction into B_2O_3 quantity.

The conversion fraction of the ore in terms of B_2O_3;

$$X_{B_2O_3} = \frac{\text{Amount of dissolved } B_2O_3 \text{ in the solution}}{\text{Amount of } B_2O_3 \text{ in the original sample}}$$

3. Result and analysis

3.1. Dissolution reactions

Hydrochloric acids resolve their ions in one phase. When hydrochloric acid dissolves in water, principally, it sends its 1 proton to medium.

$$HCI + H_2O \rightleftharpoons H_3O^{+} + CI^{-} \qquad Ka= 10^{7}$$

It is regarded as that the dissolvability of ulexite in hydrochloric acid solutions and it originates according to the following equations.

$$Na_2O.2CaO.5B_2O_3.16H_2O + 6\,HCI_{(aq)} \rightarrow 2Na^{+}_{(aq)} + 2Ca^{+2}_{(aq)} + 10\,H_3BO_{3(aq)} + 6CI^{-}_{(aq)} + 4H_2O$$

The leach solution obtained from the dissolution of ulexite includes sodium, calcium, chlorine ions, and dissolved boric acid. Boric acid can be crystallized from the leach solution. Furthermore, NaCl and $CaCl_2$ may be obtained as by-products from the solution.

3.2. Effect of the parameters

The parameters that influences dissolution ratio of ulexite in hydrochloric acid solutions such as temperature, particle size, solid/liquid ratio, acid concentration, stirring speed have been selected and the effect of these parameters on dissolution ratio has been analyzed. Before studying on the effects of other parameters that may influence the dissolution rate, firstly effect of the stirring speed has been performed. Experiments have been carried out at stirring speeds of 500, 650 and 800 rpm to observe the effect of the stirring speed on the dissolution rate. In these experiments, hydrochloric acid concentration, particle size, solid-to-liquid ratio, and reaction temperature have been fixed at 0.75 M, -14+18 mesh, 10/100 g/mL, and 30 ^{o}C, respectively. From the obtained results, it has been observed that the dissolution rate has been practically independent of the stirring speed. Therefore, all subsequent experiments have been carried out at stirring speed of 500 rpm.

3.3. Effect of the reaction temperature

The effect of temperature on dissolution ratio of ulexite has been analyzed at 30,40,50,60 and 70^{o}C. In the experiments, particle size has been kept constant as -14+18 mesh of sieve, solid/liquid ratio as 10/100 g/mL, stirring speed as 500 rpm and 0.75M HCI acid concentration. According to the obtained results, as the temperature of reaction increases, dissolution rate increases as it is seen from the Fig. 3.

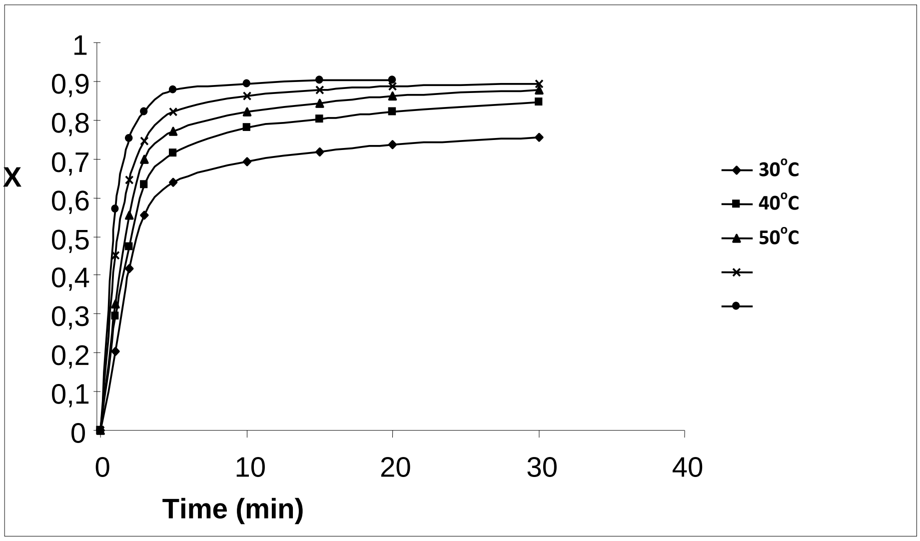

Fig. 3. *Effect of reaction temperature on dissolution rate of ulexite*

3.4. Effect of concentration of hydrochloric acid

The effect of acid concentration on dissolution rate of ulexite has been researched in the concentration of 0.75M, 1M, 1.25M, 1.5M and 2M. In the experiments, particle size has been kept constant as -14+18 mesh of sieve, temperature as 30^{o}C, solid/liquid ratio as 10/100 g/mL, stirring speed as 500 rpm.

In the experiment of acid concentration, dissolution ratio has showed decrease in inversely proportion to the increasing acid concentration. It is obviously seen in Figure 4.

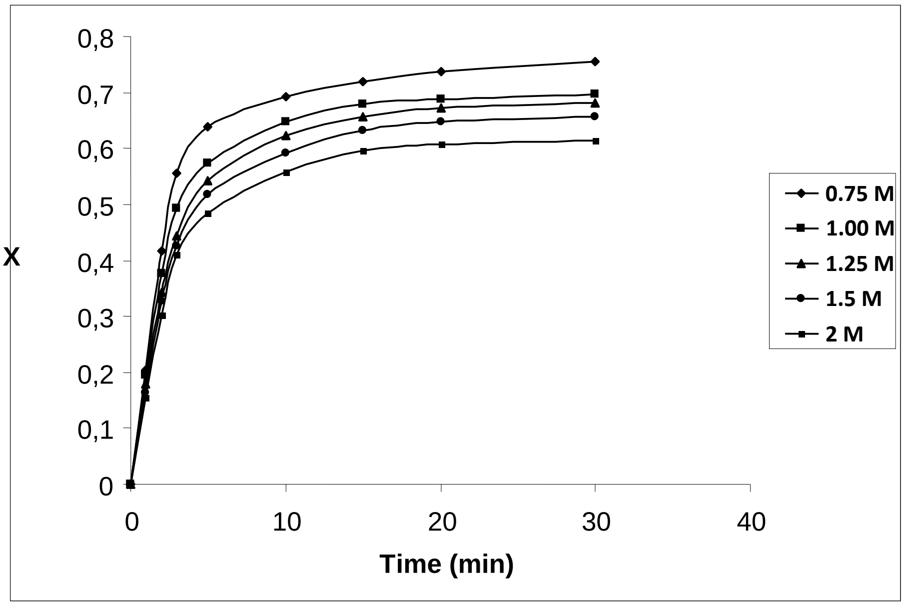

Fig. 4. Effect of concentration of hydrochloric acid on dissolution ratio of ulexite

3.5. Effect of the ulexite particle size

The effect of particle size on the dissolution ratio of ulexite ore in hydrochloric acid solutions have been studied in the fractions of -14+18, -18+30, -30+40, -40+50, -50+60 mesh of sieve. In the experiments, heat has been kept constant as 30^{o}C, acid concentration as 0.75M, solid/liquid ratio as 10/100 g/mL, stirring speed as 500 rpm.. In Figure 5, the effect of particle size on dissolution ratio is showed. Dissolution rate increases with the decrement of particle size.

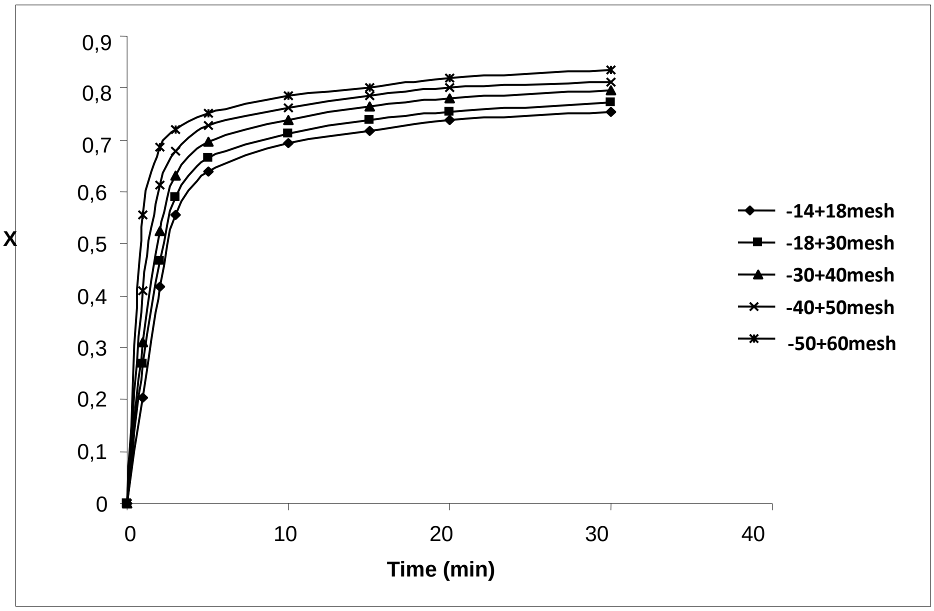

Fig. 5. *Effect of particle size on dissolution ratio of ulexite*

3.6. Effect of the solid/liquid ratio

The effect of solid/liquid ratio on the dissolution rate of ulexite ore in hydrochloric acid solutions have been studied in the values of 5/100, 7.5/100 and 10/100 g/mL. In the experiments, particle size has been kept constant as -14+18 mesh of sieve, reaction heat as 30^{o}C, acid concentration as 0.75M, stirring speed as 500 rpm. As seen in Figure 6, as solid/liquid ratio increases, dissolution rate decreases.

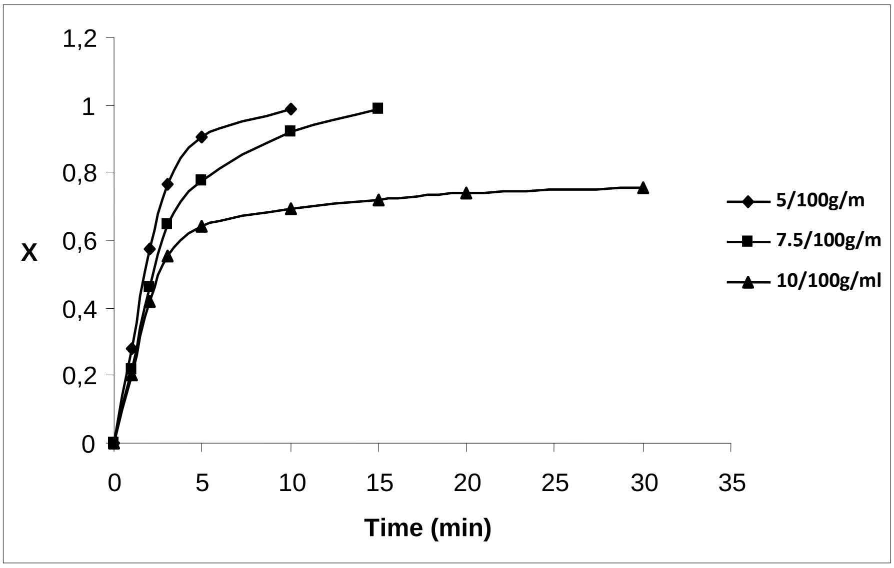

Fig. 6. *Effect of solid/liquid ratio on dissolution rate of ulexite*

3.7.Effect of the stirring speed

The effect of stirring speed on the dissolution ratio of ulexite ore in hydrochloric acid solutions have been studied at a rate of 500, 650 and 800 rpm. In the experiments, particle size has been determined as -14+18 mesh of sieve, solid/liquid ratio as 10/100 g/mL, reaction heat as 30^{o}C, acid concentration as 0.75M. According to experimental data, as seen from Figure 7, while stirring speed increases, dissolution rate increases.

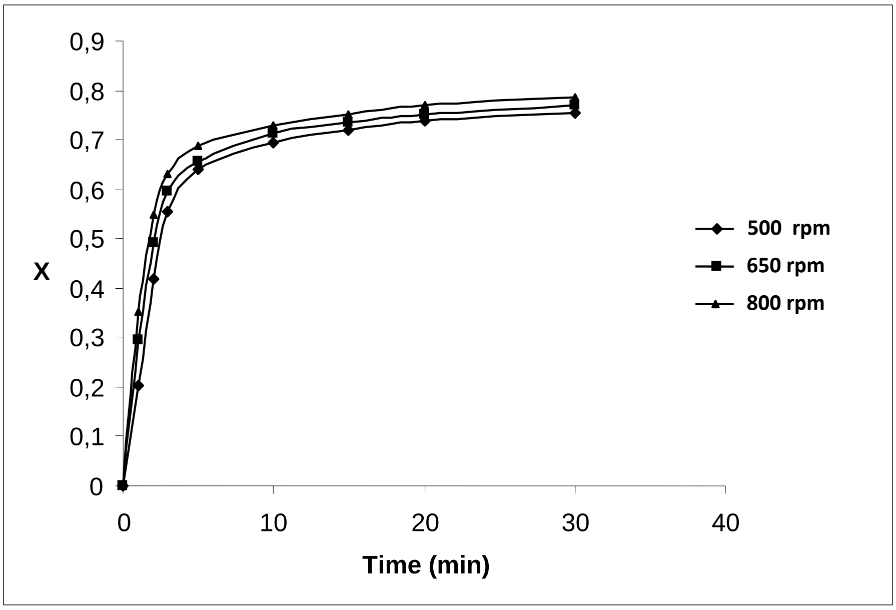

Fig. 7. *Effect of stirring speed on dissolution ratio of ulexite*

4. Discussion and conclusion

In this study, the dissolution kinetics of ulexite in hydrochloric acid solutions has been investigated in a batch reactor. Ulexite has been examined by taking into consideration to the acid concentration in hydrochloric acid solutions, stirring speed, particle size, solid/liquid rate and temperature parameters. It has been determined that the rate of solution increases by increasing temperature and stirring speed while it decreases by increasing of solid/liquid rate, acid concentration and particle size. Dissolution of ulexite in hydrochloric acid solution of different parameters has been examined in this study as a result.

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