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Full Length Research Paper

Dissolution kinetics and mechanism of pandermite in acetic acid solutions

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In this study, the dissolution kinetics and mechanism of pandermite mineral was investigated using a batch reactor employing the parameters of particle size, acid concentration, solid/liquid ratio, stirring speed and reaction temperature. From experimental data, it was determined that the conversion rate of pandermite to boric acid was increased with decreasing particle size, solid/ liquid ratio and increasing reaction temperature. Conversion rate increased up to 3 M, acid concentration then decreased with increasing acid concentration.It was observed that there was no important effect of stirring speed on the dissolution rate. Furthermore, it was observed that the dissolution mechanism was dependent on acid concentration due to restriction of dissolution in acetic acid solutions. The dissolution rate of pandermite mineral in acetic acid solution was examined according to homogeneous and heterogeneous chemical reaction model. It was determined from graphical and statistical methods that the reaction kinetics fitted to model in the form of first order pseudo homogeneous model [- ln (1 - X)] = kt and activation energy for the dissolution process was found to be 28.496 kj/mol. A mathematical model, which indicated the dissolution process was established.

Key words: Boric acid, dissolution, kinetics, mechanism, pandermite.

INTRODUCTION

Many investigations, most of which have been patented, have been conducted to produce various boron compounds from boron minerals (Wiseman, 1950; Meixner, 1955). The most common boron compounds commercially used are boric acid, anhydrous borax, borax hydrates and sodium perborates, which are generally obtained from colemanite, ulexite and tincal. Boric acid and boron salts have extensive industrial uses in the manufacture of glass and porcelain, in wire drawing, the production of leather, carpets, cosmetics and photographic chemicals, for fireproofing fabrics and weatherproofing wood. Boron compounds are used in certain fertilizers for the treatment of boron deficient soils. Boric acid, which has mild bactericidal and fungicidal properties, is used as a disinfectant and as a food preservative. Borax is widely used in welding and brazing of metals and more recently, boron compounds have found applications for hand cleansing, high-energy fuels, cutting fluids and catalysts (Sahin, 2002). Boric acid is commercially produced in Turkey by the heterogeneous solid-liquid reaction of sulfuric acid and colemanite. In this process, colemanite ore is reacted with sulfuric acid at 95°C. Gypsum forms as a by-product and precipitates in the reactor while boric acid remains in the liquid phase through the reaction. After gypsum is removed by filtration, boric acid is crystallized by cooling the solution. Filtration of gypsum has an important role in boric acid production because it affects the efficiency, purity and crystallization of boric acid.

This present process has some disadvantages, such as sulfate contamination in the final product and environmental pollution (Temur et al., 2000; Gür, 2007; Gür and Alkan, 2008). Kucuk et al. (2002) studied the dissolution kinetics of Kestelek's colemanite containing clay in water saturated with SO_2 and found that the dissolution rate was controlled by chemical reaction and the activation energy for the process was 39.53kJ.mol^{-1}. Because of these disadvantages, various studies have been performed by many investigators on the kinetics and mechanism of dissolution of boron minerals in aqueous solutions. The dissolution of colemanite was examined in

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different solutions (Kocakerim and Alkan, 1988; Kurtbas et al., 2006; Gur, 2008). In the hydrometallurgical processes, inorga-nic acids are generally used as the leaching agents. However, the acid methods are uneconomical because basic ores consume excessive acid during the leaching. Furthermore, some undesired impurities can pass into the leaching media when inorganic acids are used. Therefore, more basic lixiviants than inorganic acids (or weakly acidic reagents) may be more favorable in the leaching processes, allowing impurities in the solution to be separated more effectively. Some ammonium salts have been employed by researchers as the lixiviant. The dissolution kinetics of magnesite (Ranjitham and Khangaonkar, 1990; Raschman, 2000), colemanite (Gur, 2008), malachite (Ekmekyapar et al., 2003) and tincal (Gur, 2009) were investigated in ammonium chloride solutions. Ozmetin et al. (1996) investigating dissolution of colemanite in acetic acid solutions, determined that the dissolution rate of colemanite fitted the first-order pseudo-homogeneous reaction model in the form of $-\ln(1 - X) = kt$.

There is no study on the use of acetic acid as the leaching reactant for pandermite in the literature. Therefore, in this study, the dissolution kinetics of pandermite in aqueous acetic acid solutions was investigated. The aims of this present work were to investigate the dissolution of pandermite using acetic acid solution and to determine the effects of the experimental parameters, including solution concentration, solid-to-liquid ratio, particle size, stirring speed and temperature.

EXPERIMENTAL

The pandermite samples used in this study were provided in the region of Sultancayiri-Balikesir, Turkey. After cleaning the mineral manually from visible impurities, it was ground and sieved by ASTM Standard sieves to obtain the nominal particle size fractions of - 1.400 + 1000, - 1000 + 600, - 600 + 400, - 400 + 250 and -250 + 180 µm in diameter. The original ore sample was analyzed and the mineral content was determined to be 47.72% B_2O_3, 31.54% CaO, 17.74% H_2O and 3% insoluble matter. Particle size, solution concentration, solid-to-liquid ratio, reaction temperature and stirring speed were chosen as parameters in the leaching studies. The dissolution data obtained was plotted as a function of reacted fraction and the kinetic analysis was performed. The analysis of the dissolved mineral in the solution was performed volumetrically.

The aqueous solution of boric acid, has a weakly acidic character; it cannot be analyzed directly by titration with a basic solution. Therefore, the addition of mannitol into the solution gives a character of mild acid to boric acid by a basic solution, such as potassium hydroxide, as follows:

$$2CH_2OH\ (CHOH)_4CH_2OH + H_3BO_3 \rightarrow (CH_2OH(CHOH)_4CH_2)_2\ BO_3H + 2H_2O \quad (1)$$

$$(CH_2OH\ (CHOH)_4CH_2)_2\ BO_3H + KOH \rightarrow (CH_2OH(CHOH)_4CH_2)_2\ BO_3K + H_2O \quad (2)$$

RESULTS AND DISCUSSION

Firstly, the effect of stirring speed was investigated on dissolution rate. The experiments were performed at stirring speeds of 300, 400, 500 and 500 rpm to determine the stirring speed effect on the dissolution rate. In these experiments, solution concentration, particle size, solid-to-liquid ratio and reaction temperature were kept at 2 M,-1000+600 mm, 0.50/50g/ml and 303 K, respectively. It was found that after a 15 min leaching time, 50.87% of XB_2O_3 at 300 rpm, 51.17% of XB_2O_3 at 400 rpm, 52.01% of XB_2O_3 at 500 rpm and 52.09% of XB_2O_3 at 600 rpm were obtained from the experimental results. From this result, it could be implied that the reagent amount of particles were fully suspended in the solution. Thus, it could be inferred that the effect of stirring speed had no important effect on the dissolution rate and stirring speed was discarded from the analysis (Ozmetin et al., 1996; Gur, 2008).

In the experimental section, the dissolution rate of pandermite was determined as a function of time by changing the solution concentration, particle size, solid-liquid ratio and reaction temperature. The dissolution experiments were carried out in a 250 ml glass reactor at atmospheric pressure. A mechanic stirrer was used and a thermostat employed to keep reaction medium at constant reaction temperature. Then 50 ml of acetic acid solution was put into the reactor. After the desire reaction temperature was reached, a given amount of pandermite was added to the solution medium and stirring was started at constant stirring speed. As soon as reaction time was finished at a certain time period, the solution was filtered. The amount of B_2O_3 in filtrate was determined by volumetric method. The data obtained were plotted as a function of conversion, described as: X = amount of dissolved B_2O_3 in the solution/ amount of B_2O_3 in the original sample, versus time. Experimental parameters and their values in dissolution process are given Table 1. The values showed with asterisks was used, when the effect of other parameters were studied.

Dissolution reactions

The dissolution process of pandermite in acetic acid solution occurred according to the following reactions;

$$CH_3COOH + H_2O \Leftrightarrow H_3O^+ + CH_3COO^- \quad (3)$$

$$4CaO.5B_2O_3.7H_2O + 8\,H_3O^+ \rightarrow 4Ca^{+2} + 10\,H_3BO_3 + 4H_2O \quad (4)$$

When pandermite was added into acetic acid solution, the overall reaction occurring in the reaction medium can be written as

$$4CaO.5B_2O_3.7H_2O + 2\ CH_3COOH + 6H_3O^+ \rightarrow 4Ca^{+2} + 10\,H_3BO_3 + 2\,CH_3COO^- + 2H_2O \quad (5)$$

Effects of parameters

Dissolution process was studied for each parameter

Table 1. Parameters and their values used in experiments.

Parameters	Values			
Particle size (µm)	- 1400 + 1000, - 1000 + 600*, - 600 + 400, - 400 + 250, - 250 + 180			
Solution concentration (mol/l)	0.5	1	2*	3
Solid-to-liquid ratio (g/ml)	0.01*	0.02	0.04	0.06
Reaction temperature (K)	293	303*	313	323
Stirring speed (rpm)	300	400*	500	600

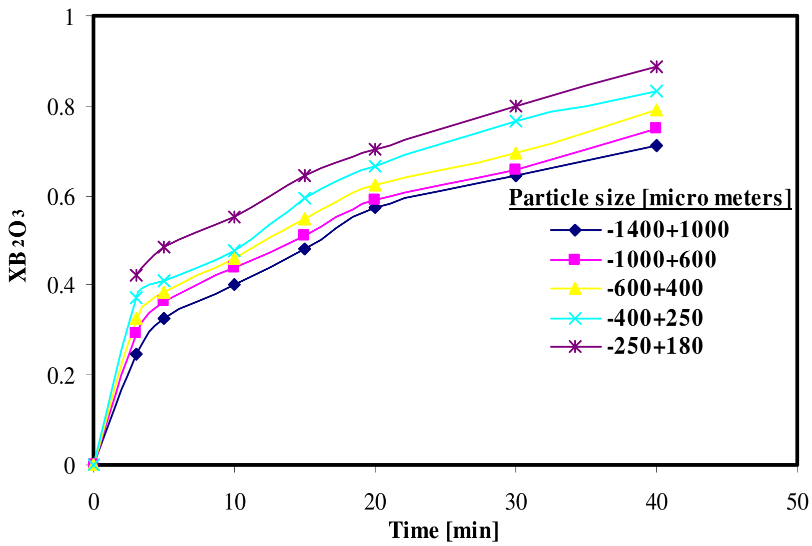

Figure 1. Effect of the particle size on dissolution rate (temperature: 303 K; acid concentration: 2 M; solid/liquid ratio: 0.5/50 g/ml; stirring speed: 400 rpm).

using the values given in Table 1. In the experiments, while the effect of one parameter was investigated, the values of the other parameters shown with asterisks in Table 1 were kept constant.

To observe the effect of particle size on dissolution rate, the experiments were carried out using the following size fractions: - 1400 + 1000, - 1000 + 600, - 600 + 400, - 400 + 250 and - 250 + 180 µm. The results shown in Figure 1 indicated that the particle size had a significant effect on the dissolution of ulexite. As seen in Figures 1 and 2, when the particle size decreased, the conversion factor of pandermite to boric acid increased, which can be attributed to the increase of the contact surface, on which the main dissolution reaction occurs, with the decrease of the particle size per amount of the solid.

To study the effect of the acetic acid concentration on dissolution rate, the experiments were carried out in concentrations of 0.5, 1.0, 2.0 and 3 M. The experiment was carried out to see the effect of acetic acid concentration on dissolution rate with increasing acid concentration up to 2 M. The result showed that the dissolution rate decreased with increasing acid concentration (Figures 3 and 4). In the investigation of dissolution mechanism of pandermite mineral in acetic acid solutions, it was observed that the dissolution rate was restricted by increasing acid concentration. When the acid concentration increased, a certain value of boric acid reached a saturation value near the solid particle. It then formed a difficult-soluble solid film layer around the particle, causing the system to have diffusional character which resulted in the slowing down of the dissolution process (Ozmetin et al., 1996).

To investigate the effect of solid-to-liquid ratio on the conversion fraction of pandermite to boric acid, the solid-to-liquid ratio was studied in the range of 0.5/50 - 3/50 g/ml. These figures indicated that the dissolution rate of pandermite decreased with an increase in solid-to-liquid ratio, which could be explained by the decrease of solid amount per amount of the reagent in the suspension (Figures 5 and 6 shows the effect of this parameter).

The effect of the reaction temperature on the dissolution rate under certain reaction conditions was investigated in the range of 293-323 K, where the results are presented in Figures 7 and 8. According to the results given in Figures 7 and 8, increasing reaction temperature has an increasing effect on the dissolution of pandermite, as expected because of the exponential dependence of the rate constant in the Arrhenius equation.

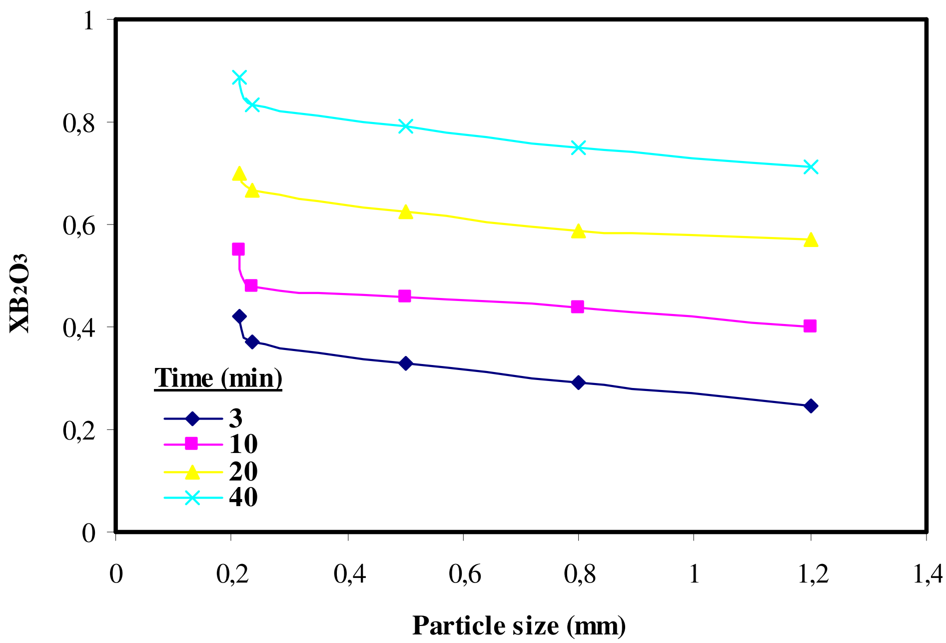

Figure 2. Effect of the average particle size on dissolution rate at certain times (temperature: 303 K; acid concentration: 2 M; solid/liquid ratio: 0.5/50 g/ml; stirring speed: 400 rpm).

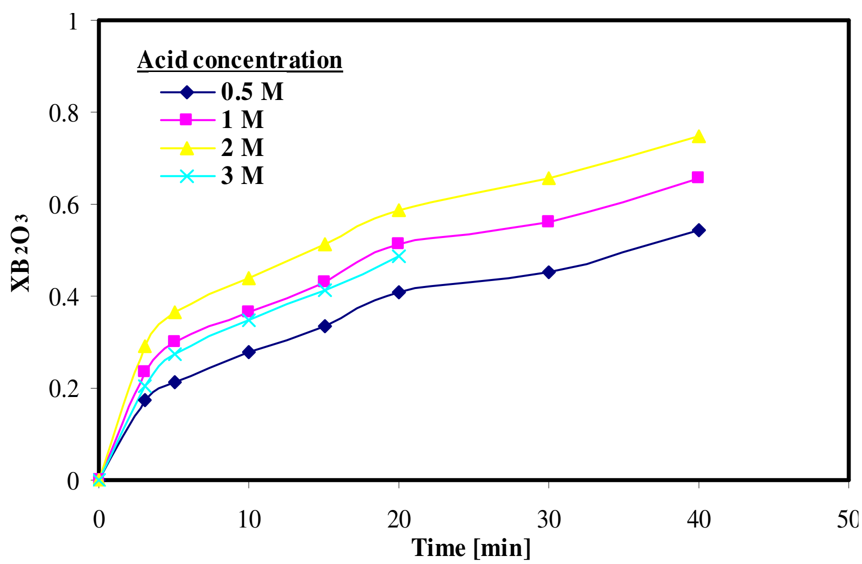

Figure 3. Effect of the acid concentration on conversion fraction (temperature: 303 K; particle size: -1000+600 µm; solid/liquid ratio: 0.5/50 g/ml; stirring speed: 400 rpm).

Kinetic analysis

In the end of the experimental results, the kinetic data of the present study were analyzed according to heterogeneous and homogeneous reaction model using graphical and statistical methods. As the experimental results were analyzed using the non-catalytic heterogeneous reaction models (According to these models, the rate of reaction between solid particle and the leaching reagent may be controlled by one of the following steps: diffusion through the fluid film, diffusion through the product layer, or the chemical reaction at the surface. The particle size can stay constant or decrease during the reaction) by graphical and statistical methods (Levenspiel, 1999; Wen, 1968), it was found that the data fit none of the heterogeneous reaction kinetic models.

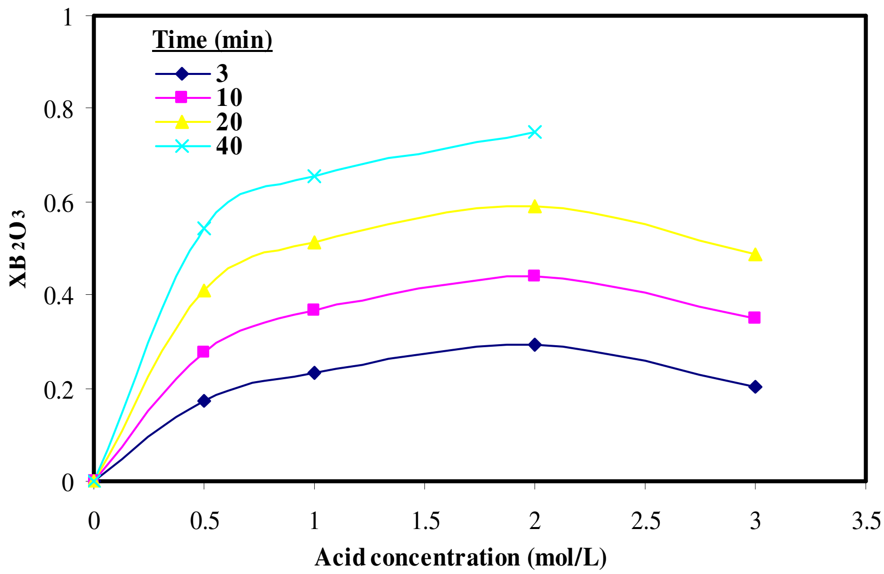

Figure 4. Effect of the acid concentration on conversion fraction at certain times (temperature: 303 K; particle size: - 1000 + 600 µm; solid/liquid ratio: 0.5/50 g/ml; stirring speed: 400 rpm).

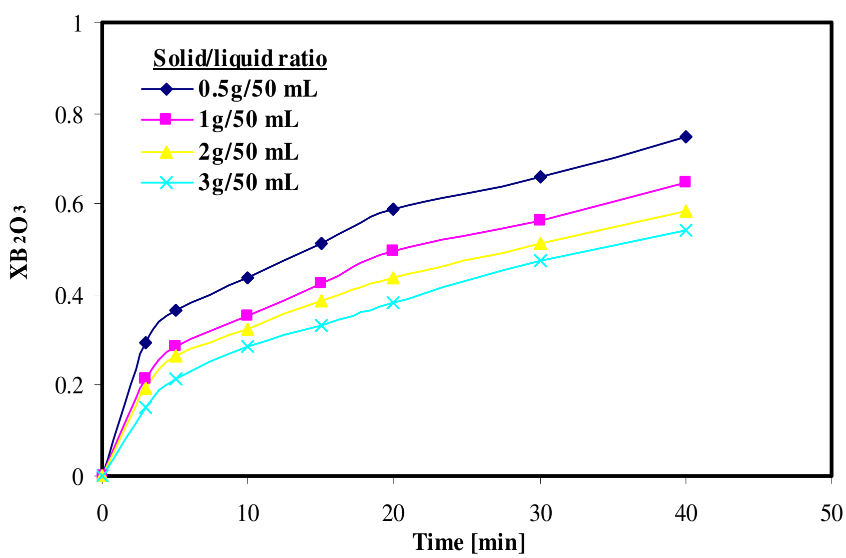

Figure 5. Effect of the solid/liquid ratio on dissolution rate (temperature: 303 K; particle size: -1000+600 µm; acid concentration 2 M; stirring speed: 400 rpm).

When the data were analyzed using the homogeneous models, it was found that the process could be expressed by a first-order pseudo homogeneous reaction kinetic model:

$$dX/dT = k(1 - X) \qquad (6)$$

or

$$- \ln (1 - x) = kt \qquad (7)$$

The straight lines shown in Figures 9 - 12 can adequately represent the dissolution process and confirmed the suitability of the first-order pseudo homogeneous chemical reaction controlled model. As can be seen graphically in Figures 9 -12, there are good linear agreement between formula of the first-order pseudo homogeneous reaction kinetic model and time for different particle size, acid concentration, solid/liquid ratio and reaction temperature Rate expression for this process could be written as follows:

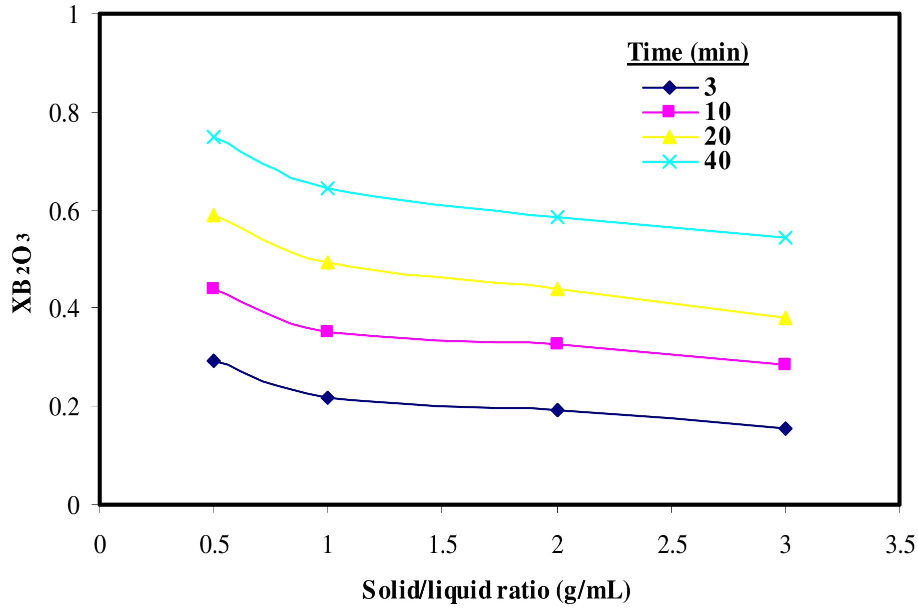

Figure 6. Effect of the solid/liquid ratio on conversion fraction at certain times (temperature: 303 K; particle size: -1000 + 600 µm; acid concentration 2 M; stirring speed: 400 rpm).

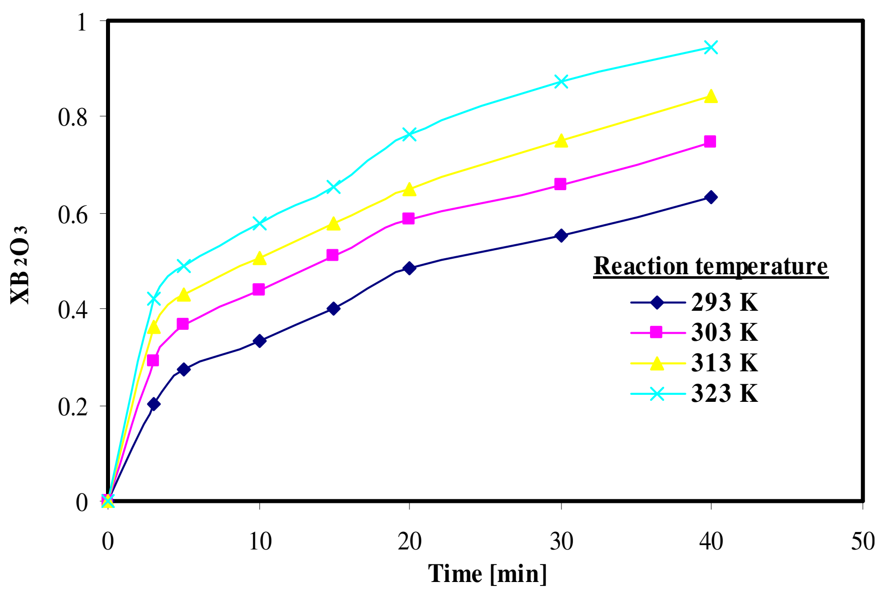

Figure 7. Effect of the reaction temperature on dissolution rate (particle size: - 100 + 600 µm; solution concentration 2 M; solid/liquid ratio 0.5 g/ml; stirring speed: 400 rpm).

$$- \ln (1 - X) = k. \quad (8)$$

To include the effect of the reaction parameters on the rate constant of reaction, a semi empirical model could be written as

$$k = ko\,(D)^{a}\,(C)^{b}\,(S/L)^{c} \exp (- Ea/RT) \quad (9)$$

Combining Equations (7) and (8), the following equation is obtained:

$$- \ln (1 - X) = ko\,(D)^{a}\,(C)^{b}\,(S/L)^{c} \exp (- Ea/RT)\, t \quad (10)$$

The constants a, b and c were estimated from the appa-

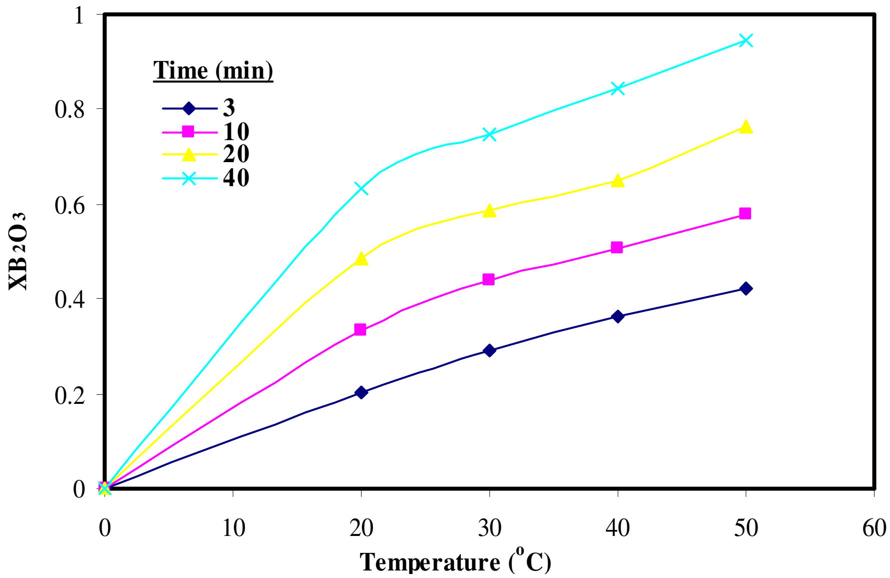

Figure 8. Effect of the solid/liquid ratio on conversion fraction at certain times (particle size: - 100 + 6 µm; solution concentration 2 M; solid/liquid ratio 0.5 g/ml; stirring speed: 400 rpm).

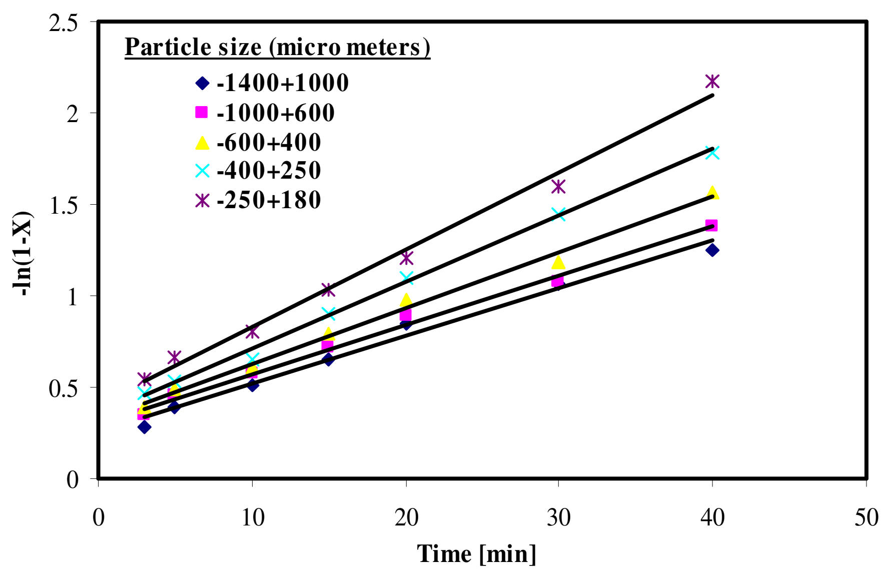

Figure 9. Agreement of experimental data with the first-order pseudo homogeneous kinetic model [- ln (1 - X)] versus time for particle size.

rent rate constants given in Table 2. The values of these constants were calculated as - 0.2933, 0.3899 and - 0.2878, respectively. The activation energy of the dissolution process was determined from the Arrhenius equation. The Arrhenius plot of the process is shown in Figure 13. From the slope of the straight line in this figure, the activation energy of the process was calculated to be 28.496kj/mol. As a result, the following kinetic expression including the parameters used in this dissolution process can be written:

$$[- \ln (1 - X)] = [6.68 \times 10^{3} (R_p)^{-0.2933} (C_A)_o^{0.3899} (K/S)^{-0.2878} e^{-3427.47/T} .t] \quad (11)$$

Conclusion

In this present study, the dissolution kinetics of pander-

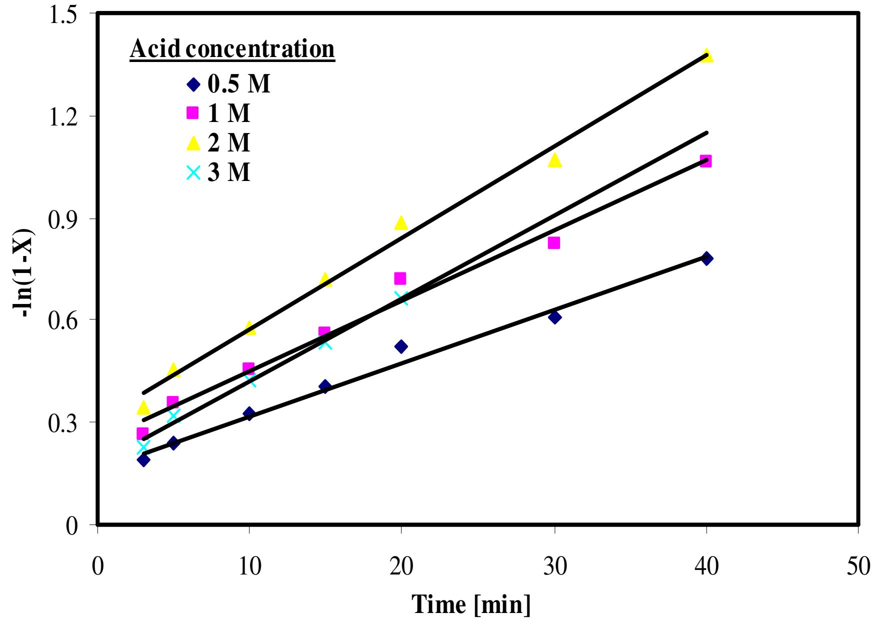

Figure 10. Agreement of experimental data with the first-order pseudo homogeneous kinetic model [- ln (1 - X)] versus time for acid concentration.

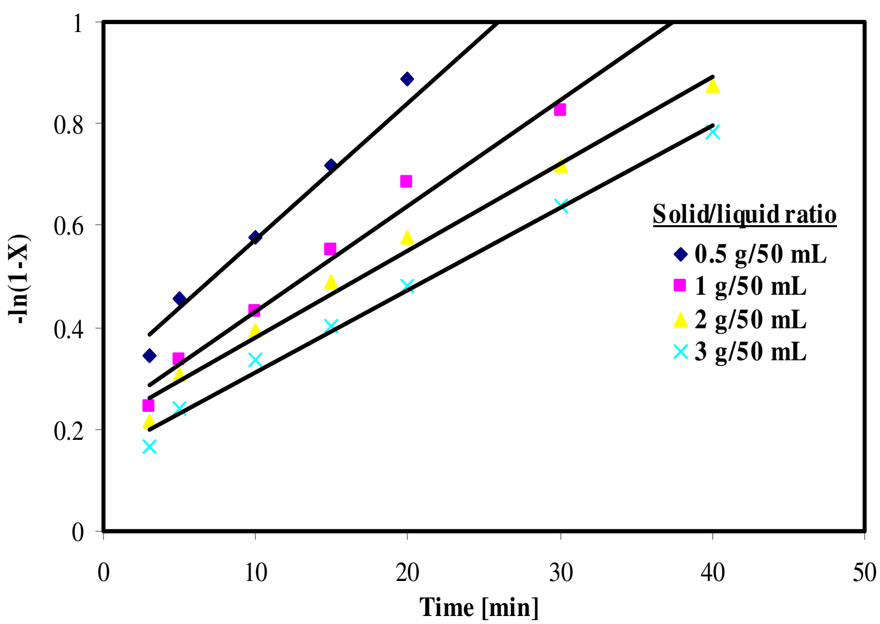

Figure 11. Agreement of experimental data with the first-order pseudo homogeneous kinetic model [-ln (1-X)] versus time for solid/liquid ratio.

mite was investigated in acetic acid solutions in a batch reactor. The dissolution rate increased with increasing acetic acid concentration, reaction temperature and with decreasing particle size and solid to liquid ratio, while there was no effect of stirring speed on the process. Employing the graphical and statistical methods to heterogeneous and homogeneous reaction kinetic model, it was obtained that dissolution kinetics of pandermite in acetic acid solutions was described by the first order pseudo homogenous reaction control model. The activation energy for dissolution process of pandermite in acetic acid solution was determined to be 28.496 kJ mol^{-1}. Consequently, it could be said that acetic acid solution is a good leachant for pandermite mentioned in text. In

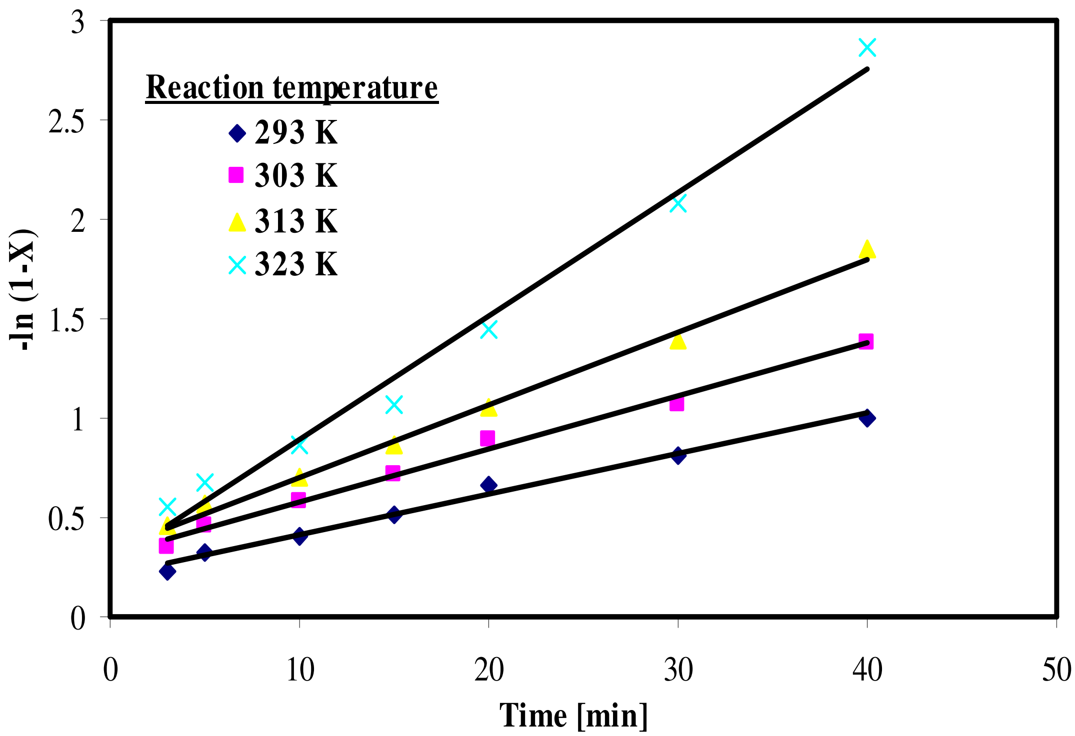

Figure 12. Agreement of experimental data with the first-order pseudo homogeneous kinetic model [- ln (1 - X)] versus time for reaction temperature.

Table 2. The apparent rate constant and correlation coefficient values.

First-order pseudo homogeneous reaction kinetic model -ln (1 - x) = kt		
Parameters	**k (min^{-1})**	**R^2**
Particle size (mm)		
- 250 + 180	0.0423	0.9961
- 400 + 250	0.0364	0.9985
- 600 + 400	0.0305	0.9971
- 1000 + 600	0.0268	0.9965
- 1400 + 1000	0.0261	0.9925
Concentration (mol/l)		
0.5	0.0156	0.9931
1.0	0.0206	0.9923
2.0	0.0268	0.9965
3.0	0.0243	0.9951
Solid-to-liquid ratio (g/ml)		
0.5/50	0.0268	0.9965
1/50	0.0207	0.9947
2/50	0.0171	0.9939
3/50	0.0161	0.9964
Temperature (K)		
293	0.0204	0.9944
303	0.0268	0.9965
313	0.0365	0.9977
323	0.0620	0.9934

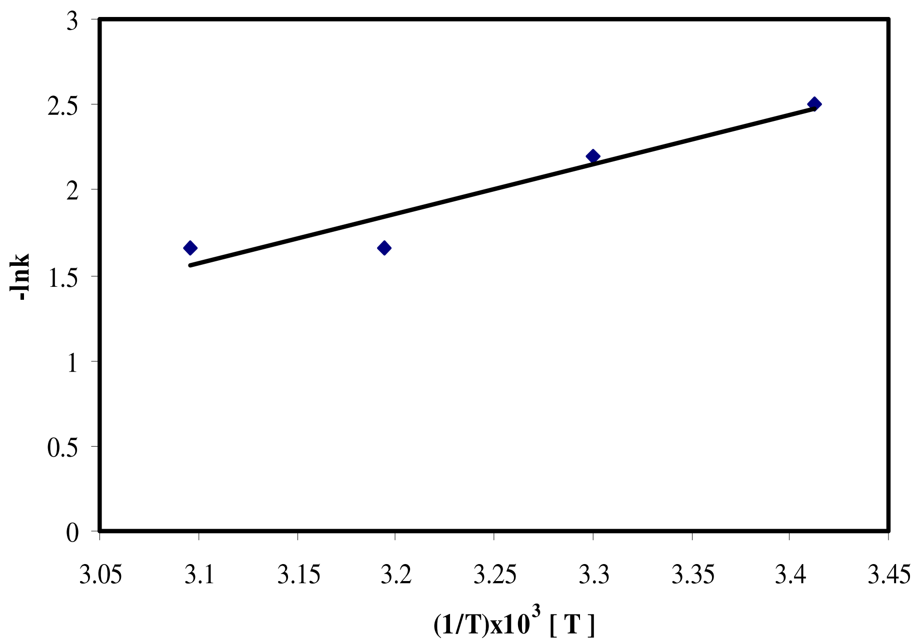

Figure 13. Arrhenius plot for the dissolution process.

addition, leaching pandermite in acetic acid is environmental friendly.

Nomenclature

a, b, c = constants in Equation. [10]
C = concentration of acetic acid [mol/cm^3]
D = particle diameter [mm]
Ea = activation energy [kJ/mol]
k = apparent rate constant for the first order pseudo homogeneous model [min^{-1}]
ko = frequency or pre-exponential factor [s^{-1}]
R = universal gas constant [J/mol K]
Ro = average radius of solid particle [cm]
S/L = solid-to-liquid ratio [g/ml]
T = temperature [K]
t = reaction time [min]
x = converted fraction of B_2O_3

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