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Optimization of Ilmenite Dissolution by Synergistic Effect of Oxalic Acid and Hydrochloric Acid for Preparing Synthetic Rutile

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Abstract

This study was carried out to investigate the interaction of oxalic acid with hydrochloric acid to attain the better performance for iron dissolution in comparison to absence of oxalic acid. The effects of oxalic acid on ratio of hydrochloric acid, acid concentration, ratio of liquid to solid, temperature and dissolution time are investigated for the dissolution of Fe and Ti from ilmenite to produce synthetic rutile. The DX7 software basing on an experimental design method with the central composite of response surface design is applied to specify the effects of the parameters and to optimize the leaching process. The optimum condition was determined by analysis of variance (ANOVA), indicating that the ratio of oxalic acid to hydrochloric acid for Fe dissolution and acid concentration for Ti dissolution were the most effective parameters. The results showed that the dissolution of Fe and Ti in 30% (w/w) hydrochloric acid solution was only 48.65% and 5.14%, respectively, while at the same condition and in the presence of oxalic acid with twice the ratio, these values are increased to 78.65% and 12.06%, respectively. The optimum values of parameters were as follows: oxalic acid to hydrochloric acid ratio (2:1), acid concentration (30%), ratio of liquid to solid (10), temperature (160˚C), and dissolution time (3 h). By applying the optimized parameters, Fe and Ti dissolution of 97.15% and 2.8% were predicted by the software with a desirability of 0.745. The results of leaching tests indicated that the Fe and Ti dissolution of 97.58% and 2.43%, were achieved, respectively, which are very close to the predicted value.

Keywords

Ilmenite, Oxalic Acid, Hydrochloric Acid, Synthetic Rutile, Leaching

1. Introduction

Ilmenite ($FeTiO_3$) is one of the titanium mineral resources ranking second after rutile (TiO_2) in titanium industries [1] [2] [3]. Today, the high-grade sources of titanium minerals such as rutile are diminishing; hence, for the low-grade ores like ilmenite an attempt is made to convert ilmenite into synthetic rutile [4]. Ilmenite can be upgraded to synthetic rutile using different methods of pyrometallurgy [4] [5] [6] [7], hydrometallurgy [8] [9] [10] [11], and electrometallurgy [12]. Despite some problems, utilizing the hydrothermal processes for ilmenite ore is more preferable. This is due to low energy consumption and the production of high quality TiO_2 products [12]. Many researches have reported the application of the hydrothermal process for ilmenite. Direct leaching of ilmenite can be performed using inorganic acids or organic ones. Different scholars investigated the leaching of ilmenite by sulfuric and hydrochloric acids at different conditions of acid dosages, temperatures, acid to ore ratios, particle size, and etc. [13] [14] [15] [16] [17].

Iron is the most important impurity through the production of synthetic rutile. The removal of iron content by inorganic acids requires a high temperature and high concentration of acid. Therefore, the organic acids can be used as the iron removing agents. On the other hand, most of these studies were concerned with the extraction of titania from ilmenite by H_2SO_4 and HCl [10] [11] [14] [16] [17], whereas few of the mare directed towards extracting titania by interaction with organic acid reagents. Martínez-Luévanos *et al.* stated that oxalic acid can be selected as the leaching agent when in comparison to other organic acids such as citric, malonic and acetic acids. This was due to the special properties of oxalic acid, including higher acidity, complexion power, and the reduction ability [18]. Also, oxalic acid has been used as the iron removing agent from silica in the presence of sulfuric acid. The results showed that the iron extraction was about 35% to 45% in the presence of 3 kg/ton of oxalic acid and 2 kg/ton of sulfuric acid, whereas in the same condition and only in presence of sulfuric acid, it was about 3% to 9% [19]. The dissolution of ilmenite by oxalic acid has been reported by Woranart *et al.* The results showed that 86.4% of titanium is leached by 4 mol/L of oxalic acid, 1:20 solid/liquid ratio, and 90˚C temperature, while in the same condition and 4 mol/L of sulfuric acid, the dissolution of titanium was 16.1% [20]. Some scholars reported that the capacity of oxalic acid in Fe dissolution is more than that of sulfuric acid, chloric acid, nitric acid and other organic acids [21] [22] [23].

A few decades ago, testing, interpretation, and presentation of laboratory results were boring, expensive, time consuming, and also demanding; while sample collection and preparation were overwhelming. To end that, experimental design methodology was introduced. The statistical design is an effective tool in the classification, optimization and modeling of a process [24] [25] [26].

The aim of this study was to investigate the effect of chloric acid in the presence and absence of oxalic acid through ilmenite leaching. The study outlines the optimization of parameters affecting the process and evaluation of the product. In order to understand and optimize the leaching process, the DX7 software was applied basing on statistical methods of experiments via central composite design at two levels of parameters [27].

2. Materials and Methods

2.1. Materials

The ilmenite ore samples were prepared from Qara-Aghaj deposits in northwest of Iran. After crushing and grinding the samples to 80% minus 63 microns, these samples are purified in different stages of magnetic separation and gravity separation methods. All the solid samples were characterized by powder X-ray diffraction (XRD) to check for phase purity using a Scanting diffractometer (model XDS 2000) with Cu Kα radiation (**Figure 1**). The results of chemical analysis via X-ray fluorescence (XRF) showed that the composition of the ilmenite was: Fe total 17%; TiO_2 46.2%; CaO 0.38%; MgO 2.53%; MnO 1.04%; SiO_2 0.19%; Al_2O_3 0.44%; other elements 1.34%, respectively (**Table 1**).

2.2. Methods

Acid leaching of ilmenite ore was carried out using HCl acid with a concentration of 37% (w/w) and oxalic acid with a concentration of 99% (w/w) in a 300 cm^3 three-neck glass reactor equipped with a reflux condenser and a mechanical agitator with Teflon-coated stirring rod. A stirring speed of 560 RPM was applied to keep the slurry suspended during the leaching experiment. After reaching the desired temperature, a 20 g ilmenite ore sample was added. After the

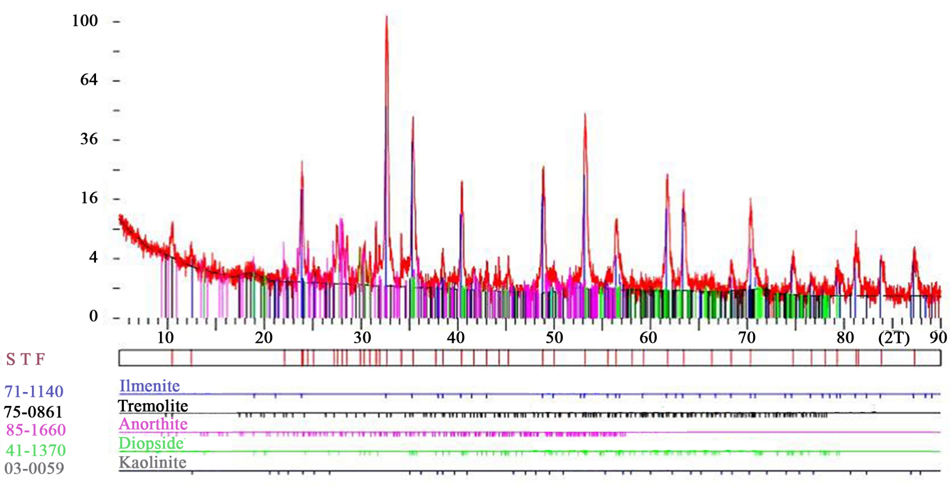


Figure 1. XRD pattern of the sample.

Table 1. Chemical composition of ilmenite concentrate (Wt %).

Composition	TiO_2	Fe_2O_3	Fe total	MnO	V_2O_5	P_2O_5	CaO	MgO	SiO_2	Al_2O_3	Co_3O_4	S	L.O.I
Purified Il	46.2	48.6	17	1.04	0.29	0.24	0.38	2.53	0.19	0.44	0.025	0.024	0.0

required reaction period, the slurry was filtered off. After washing the solid titanium with 2% HCl, the filtrated sample was dried in the air at 100˚C.

The UV-Vis spectroscopy method was used to determine the Fe content of the samples. Therefore, after diluting the sample, 0.1 ml of the sample was poured into the 10 ml flask and 0.5 ml of sulfosalicylic acid was added. After stirring the solution, 0.5 ml of ammonia was added and the absorbance was recorded at 425 nm. Total iron and ferrous iron were determined spectrophotometrically using the phenanthroline method at a wavelength 515 nm [28]. In this research, the effects of five parameters were studied in the leaching process. Thus, the leaching tests were carried out to evaluate the accuracy of the prediction in optimum conditions and validation of the process. Acid concentration (%), oxalic acid to hydrochloric acid ratio, ratio of solid to liquid (S/L) (g/L), temperature (˚C), and dissolution time (h) are used as the input parameters of the software. A software based experimental design approach (DX7) was applied at two levels of parameters to determine and model optimization through the central composite design method. The lower and upper limits of those parameters were delineated in tests and are depicted in Table 2. The designed experiments by DX7 software are shown in Table 3.

3. Results and Discussion

After entering the results of leaching tests which are obtained from the calculation conditions in the software, the optimum conditions of Fe and Ti dissolution from ilmenite were delineated. Software calculations showed the effective parameters (Table 3) and probability plot (Figure 2) with regard to responses.

From the software, the terms in the model would have a significant effect on the response if the Prob > F value is less than 0.05. There are two methods to evaluate the model accuracy: 1) residual normal plot, and 2) residual amounts vs. the predicted values.

The model can estimate the test values with appropriate precision when the obtained residuals have a normal distribution. Figure 2 shows the absolute values of residual differences between the test residuals and achieved response from the model.

As shown in Figure 2(a), Figure 2(b), the obtained results from the model have a good fit with the results of experiments. The lack of particular trends in residual values vs. the test numbers showed that there are not any systematic errors in performing the tests. Systematic errors led to an increase or decrease in the residual values.

Table 4 demonstrates the ANOVA contained responses. The ANOVA is built entirely on the premise that the factors are fixed, not random and the design is

Table 2. The lower and upper limits of five parameters.

Factor	Name	Lowe level	High level
A	[Oxalic acid:sulfuric acid]	0	2
B	Acid concentration (% w/w)	10	30
C	Ratio of liquid to solid (g/L)	5	10
D	Temperature (˚C)	70	160
E	Dissolution time (h)	2	4

Table 3. Designed experiments by DX7 software.

Run	[Oxalic: Hydrochloric] acid ratio	Acid concentration (%)	Liquid/Solid (g/L)	Temperature (˚C)	Time (h)	Fe dissolution (%)	Ti dissolution (%)
1	2	30	10	70	2	82	17
2	1	20	7.5	115	3	61	7.6
3	0	10	10	160	4	44	4.5
4	1	20	7.5	160	3	71	11.5
5	2	10	10	160	2	81	12
6	2	30	5	70	4	90	8.2
7	0	10	5	70	4	24	2.1
8	1	20	7.5	115	3	60	5.5
9	1	20	7.5	115	3	61	5.3
10	2	10	10	70	4	78	11.1
11	0	10	10	70	2	28	3
12	1	20	7.5	70	3	55	4.9
13	0	30	5	160	4	42	14.5
14	1	20	7.5	115	3	65	11.3
15	0	30	5	70	2	26	11.3
16	2	10	5	70	2	65	8.2
17	0	20	7.5	115	3	47	9.4
18	2	30	5	160	2	77	16
19	0	30	10	70	4	40	19
20	1	20	5	115	3	55	6.7
21	1	20	7.5	115	2	50	7.9
22	2	20	7.5	115	3	77	10.2
23	2	10	5	160	4	72	13.5
24	1	20	7.5	115	4	78	13.7
25	2	30	10	160	4	95	39
26	1	20	7.5	115	3	67	7.8
27	1	10	7.5	115	3	38	6.8

Continued

28	0	30	10	160	2	53	4.8
29	1	20	10	115	3	73	15
30	1	20	7.5	115	3	62	7.5
31	1	30	7.5	115	3	65	11.1
32	0	10	5	160	2	34	4.3

Table 4. ANOVA results of the equation for the responses by DX7.

Model	S.D.	C.V%	R squared	Adeq precision	F value	P value (Prob > F)
Fe dissolution	3.34	5.53	0.9856	27.298	49.27	<0.0001
Ti dissolution	2.27	22	0.9301	25.019	21.08	<0.0001

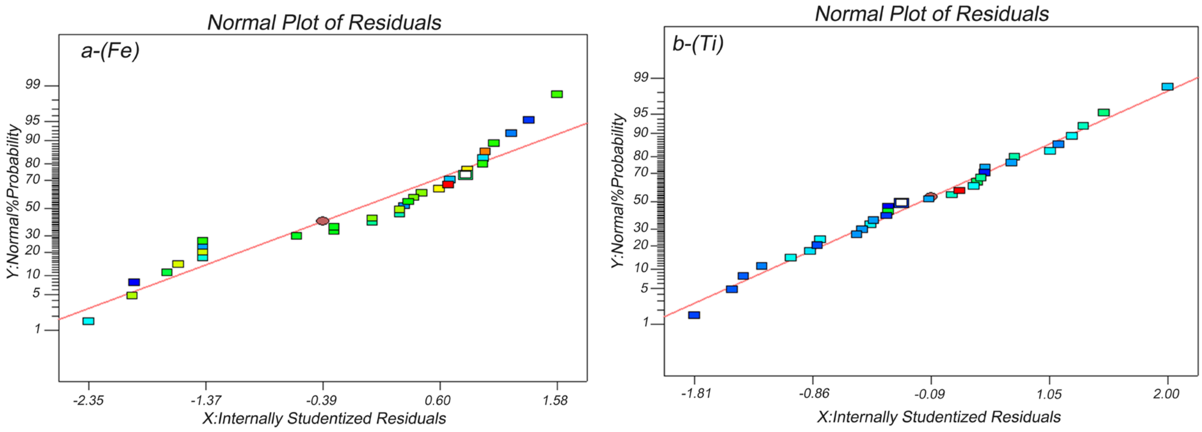
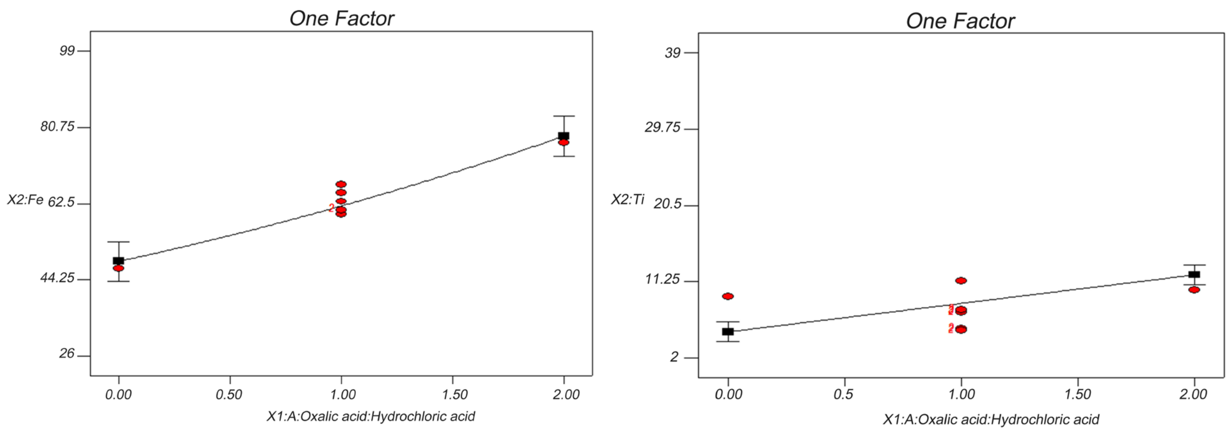


Figure 2. Normal plot of residual for (a) Fe dissolution (b) Ti dissolution.

crossed, not nested. ANOVA makes it possible to check that the assumed model fits well with the experimental points. The small probability of p-values (0.05 or less) calls for rejection of the null hypothesis. The Fe and Ti model f-values of 49.27 and 21.08, implied by the model, respectively were significant. There is only a 0.01% chance that the "model f-values" of these large values could occur due to the noise. As to the p-values, it is noteworthy that the probability of errors in the preferred model for the leaching of ilmenite was less than 0.01%. The model adeq precision is based on the signal to noise ratio, according to which a ratio greater than 4 is desirable, and the ratio of 27.298 and 25.019 indicated the adequate signals. Therefore, these models can be used to navigate the design space.

3.1. Synergistic Effect of Oxalic Acid and Hydrochloric Acid

Figure 3 shows the effect of varying ratios of oxalic acid to hydrochloric acid at different levels of 0, 1 and 2. The experimental data indicated that the dissolution of iron is strictly increased by increasing the oxalic acid to hydrochloric acid ratio (**Figure 3(a)**). Also, the percentage of iron dissolution was higher than that of



(a) (b)

Figure 3. Effect of Oxalic acid:Hydrochloric acid ratios as a significant parameter on (a) Fe dissolution (b) Ti dissolution.

titanium dissolution, which is in good agreement with the findings of Lasheen [29].

The results showed that by increasing the ratio between the oxalic and hydrochloric acids from 0 to 2 at moderate levels of other factors (acid concentration: 20%, L/S ratio: 7.5, temperature: 115˚C, time: 3 h), one can increase the dissolution of Fe and Ti from 48.65% and 5.14% to 78.65% and 12.06%, respectively (**Figure 3(a)**, **Figure 3(b)**). It is noteworthy that this factor was involved in an interaction with the acid concentration factor.

The mechanisms of ilmenite reactions with hydrochloric acid areas reactions 1 to 3 and Oxalic acid dissociates according to the reactions 4 and 5.

$$\mathrm{FeTiO_3 + 4HCl \rightarrow TiOCl_2 + FeCl_2 + 2H_2O} \tag{1}$$

$$\mathrm{Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O} \tag{2}$$

$$\mathrm{TiOCl_2 + H_2O \rightarrow TiO_2 + 2HCl} \tag{3}$$

$$\mathrm{H_2C_2O_4 \longleftrightarrow H^+ + HC_2O_4^-},\ K_{a_1} = 5.378*10^{-2} \tag{4}$$

$$\mathrm{HC_2O_4^- \longleftrightarrow H^+ + C_2O_4^{2-}},\ K_{a_2} = 5.42*10^{-5} \tag{5}$$

According to reaction (4), $H_2C_2O_4$ is a good chelating agent and has a strong acidic effect. The protons producing according to the reactions (4 and 5) attacks to Fe^{3+} and Fe^{2+} ions particles and formed the water-soluble compounds (reactions 8 and 9) [21].

$$\mathrm{Fe_2O_3 + 6H^+ \longleftrightarrow 2Fe^{3+} + 3H_2O} \tag{6}$$

$$\mathrm{Fe^{3+} + C_2O_4^{2-} \longleftrightarrow Fe(C_2O_4)^+} \quad K = 5.89*10^8 \tag{7}$$

$$\mathrm{Fe(C_2O_4)^+ + C_2O_4^{2-} \longleftrightarrow Fe(C_2O_4)_2^-} \quad K = 3.31*10^6 \tag{8}$$

$$\mathrm{Fe(C_2O_4)_2^- + C_2O_4^{2-} \longleftrightarrow Fe(C_2O_4)_3^{3-}} \quad K = 2.75*10^4 \tag{9}$$

The reason for improving the Fe dissolution in the presence of oxalate ions can be due to the high capacity of oxalic acid in Fe mobilization [23]. Oxalate ions can form a strong bidentate ligand with Lewis acid Fe centers and labilize the Fe-O bond, whereas hydrochloric acid form weak complexes with Fe in the aqueous phase [23]. Fe(III) oxalate complex can improve the dissolution of iron ions via facilitating the electron transfer between dissolved Fe(II) and surface Fe(III) [30]. Therefore, presence of oxalic acid can improve the dissolution of iron.

3.2. Effect of Acid Concentration

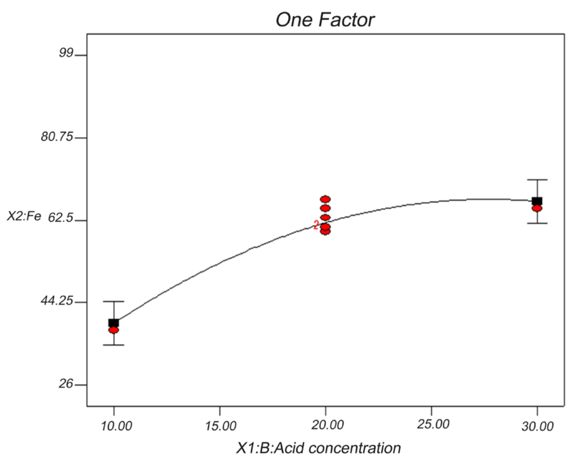
Acid concentration is an important parameter, controlling the rate of leaching process. The leaching tests were carried out at different concentration of acids varying from 10 to 30% (w/w). The results showed that the dissolution of Fe and Ti from ore are increased by increasing the acid concentration from 10% to 30% (**Figure 4(a)**, **Figure 4(b)**). It was due to increasing the number of oxalate and chloride ions interacting with a surface of the dissolving solid with increasing the acid concentration. As shown in **Figure 4**, the dissolution of Fe and Ti goes up from 39.65% and 4.41% to 66.65% and 12.79% at the aforementioned condition, respectively. It shows that the oxalic acid is a good iron dissolution agent along with the hydrochloric acid.

3.3. Effect of Liquid to Solid Ratio (L/S)

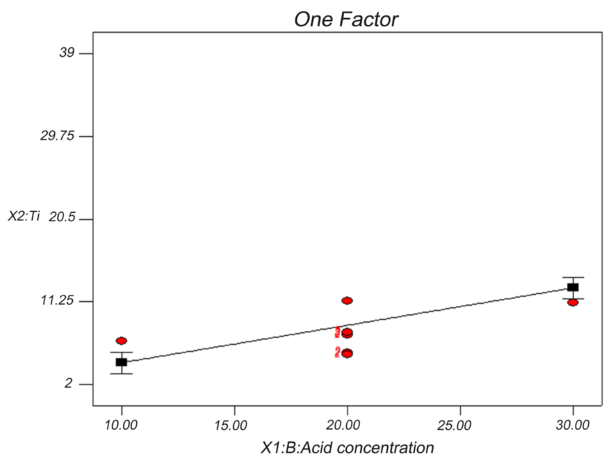
The liquid to solid ratio is the other factor affecting the leaching process. Leaching tests were performed at different L/S ratios (ranging from 5, 7.5 and 10). The results showed that the dissolution of Ti and Fe from ilmenite are increased by increasing the L/S ratio (**Figure 5**). It was due to low hydrolyzing the titanium dioxide [31] [32] [33] [34]. The low levels of L/S ratio result in precipitating the titanium in the pores and preventing the formation of $TiOCl_2$ species as a dissolved ones [33].

3.4. Effect of Temperature

The experiments were carried out at different temperatures varying from 70˚C



(a)



(b)

Figure 4. Effect of acid concentration on (a) Fe dissolution (b) Ti dissolution.

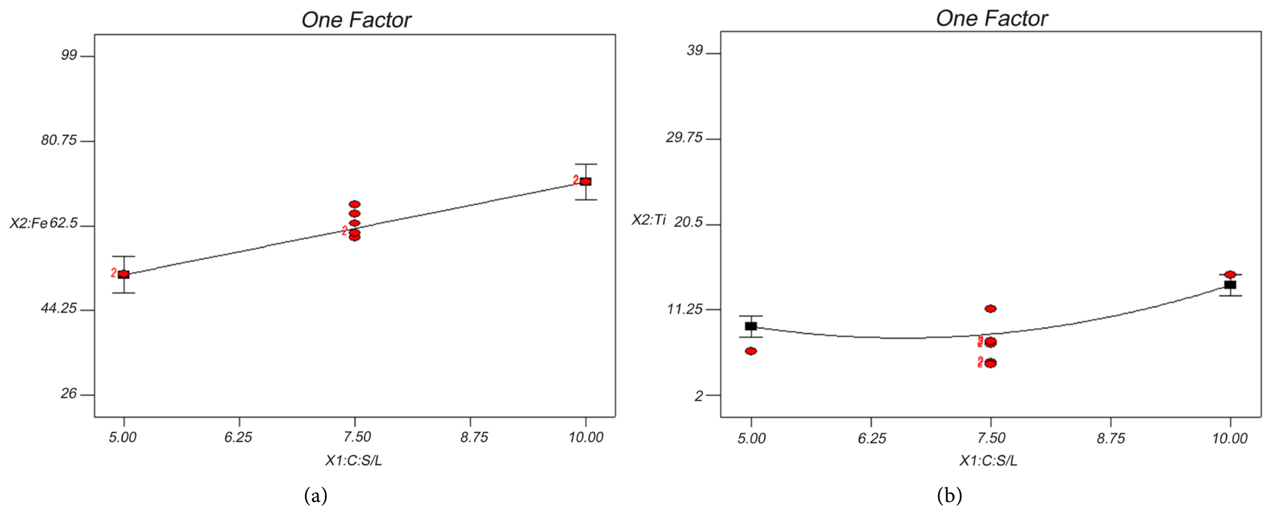


Figure 5. Effect of L/S ratio on (a) Fe dissolution (b) Ti dissolution.

to 160˚C. Inasmuch as the temperatures below the boiling point has not very effective on the Fe extraction and Ti recovery [35]. Therefore, some experiments were performed at 160˚C.

As shown from **Figure 6(a)** and **Figure 6(b)**, the dissolution of Fe and Ti at higher temperatures (up to the boiling point) are significant. These were not only due to the fast polymerization of ilmenite and hydrolysis the $TiOCl_2$ at high temperature, but also the exothermic nature of Fe dissolution from ore [31] [32] [35].

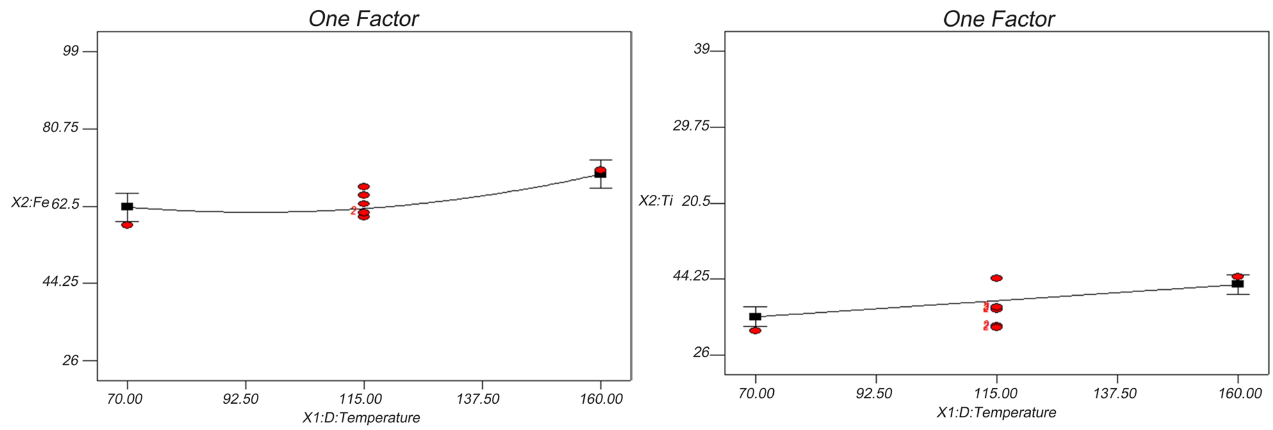
3.5. Effect of Dissolution Time

In order to investigate the effect of dissolution time on Fe and Ti dissolution, leaching tests were performed for 2, 3 and 4 h (**Figure 7(a)** and **Figure 7(b)**). It is clear from **Figure 7(a)** and **Figure 7(b)**, increasing the time result in increasing the Fe dissolution and Ti recovery [35]. It is expected that after long times there will be a little dissolution in Fe and Ti content of ore [32].

3.6. Synergistic Effect of Factors

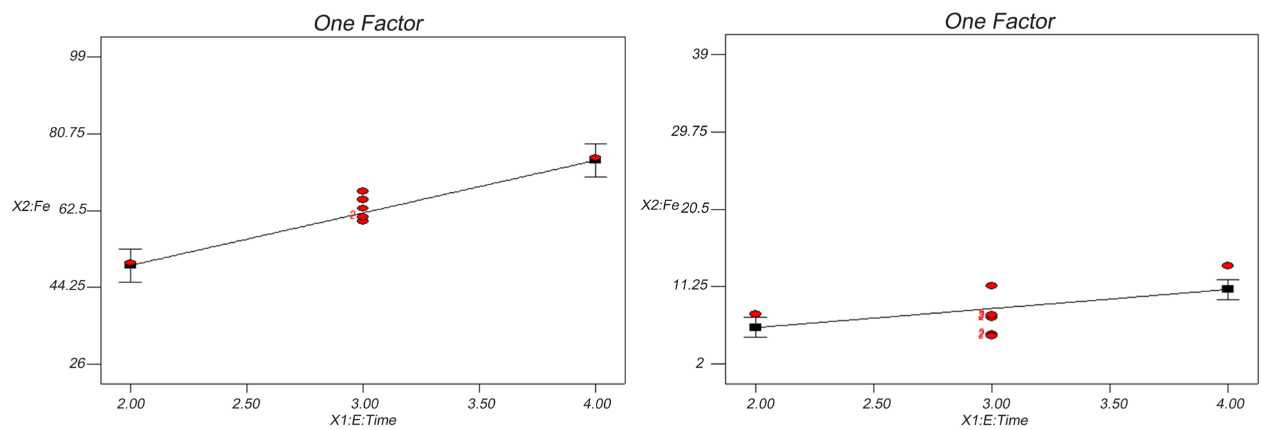
The results of models showed that the interaction of oxalic acid: hydrochloric acid ratio with acid concentration and liquid to solid ratio were the significant factors on the dissolution of Fe and Ti (**Figure 8**). It can be understood that the presence of oxalic acid as a solvent agent reinforces the dissolution of Fe. The Ti dissolution from ilmenite can be mainly attributed to hydrochloric acid because the previous works of scholars proved that the oxide of Ti was not dissolved in $H_2C_2O_4$ solution [21]. Also, it is apparent that the dissolution of iron is strongly influenced by the interaction of the parameters.

According to Equation (1) and Equation (2), it is indicated that the dependency of Fe dissolution on the presence of oxalic acid and Ti dissolution on acid concentration is more rather than that of other factors. Also, the interaction of factors is considerable.



(a) (b)

Figure 6. Effect of temperature on (a) Fe dissolution (b) Ti dissolution.



(a) (b)

Figure 7. Effect dissolution time on (a) Fe dissolution (b) Ti dissolution.

The final equations for the dissolution of Fe and Ti from ilmenite ore in terms of coded factors of the model are given by Equation (10) and Equation (11):

$$\text{Fe dissolution} = 61.94 + 15.00A + 13.50B + 10.00C + 3.89D + 12.50E + 2.19AB + 0.69AC \quad (10)$$

$$\text{Ti dissolution} = 8.61 + 3.46A + 4.19B + 2.26C + 1.96D + 2.28E - 0.19AB + 2.13AC \quad (11)$$

A comparison the phase purity of leaching residue and feed sample using a XRD pattern showed that the XRD peaks at the angle of 32 degrees, related to ilmenite, completely disappeared and turned into the synthetic rutile (**Figure 9**).

4. Conclusions

This work studied the effect of different parameters on the dissolution of iron and titanium from ilmenite in the oxalic acid and hydrochloric acid solution. The results showed that the most significant parameters in the leaching tests for iron dissolution were as follows:

Ratio of oxalic acid to sulfuric acid (2:1), Acid concentration (30% w/w), dissolution time (4 h), ratio of liquid to solid (10), and temperature (160˚C) with standardized effect values of 15, 13.5, 12.5, 10, and 3.89, respectively.

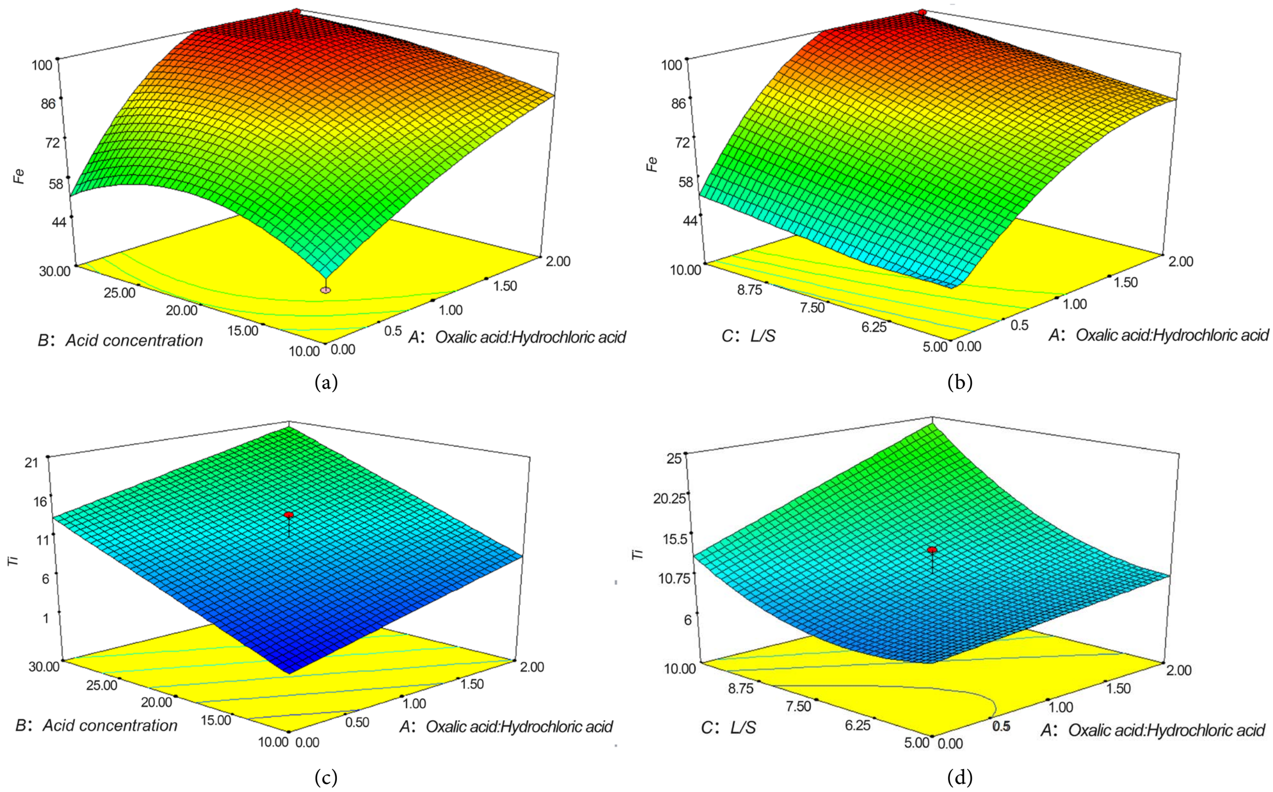


Figure 8. Interaction of factors A, B and C on ((a), (b)) Fe dissolution ((c), (d)) Ti dissolution.

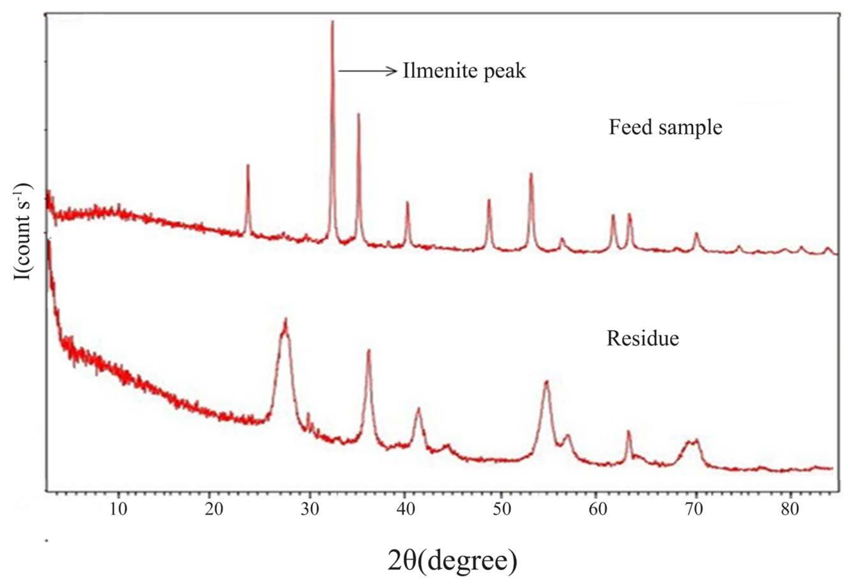


Figure 9. XRD pattern of the feed sample and leaching residue.

Also, the high concentration of oxalic acid results in the increasing the dissolution of Fe. This was due to some properties of oxalic acid in comparison to hydrochloric acid, including good chelating agent, high capacity in Fe mobilization, forming a strong bidentate ligand with Lewis acid Fe centers, labilizing the Fe-O bond, and facilitating the electron transfer between dissolved Fe(II) and surface Fe(III).

The results of analysis of variance (ANOVA) demonstrated that prediction of the model for dissolution of Fe and Ti in a mixture of oxalic acid and hydrochloric acid solution is significant. This was due to the p-value of the model that is less than 0.001. Also, the software predicted the optimum condition for maximum dissolution of Fe and minimum dissolution of Ti with desirability of 0.745. Applying these conditions resulted in a product with 97.15% Fe dissolution and 2.8% Ti dissolution.

For validating the model under optimum conditions of factors, leaching experiments were performed. Five confirmation tests were carried out under predicting optimum conditions, including oxalic acid to hydrochloric acid ratio 2, acid concentration: 30%, L/S ratio: 9, temperature: 160˚C, time: 3 h. Finally, the mean value of Fe and Ti dissolution for five tests reached 97.58% and 2.43%, respectively, which are very close to the predicted values. Therefore, the results of the model showed that the optimization of leaching conditions was successfully performed for producing the synthetic rutile. On the other hand, there is some inadequate information about the interaction and mechanism of the solvents on the dissolution of different elements from ores. On behalf of these results, this investigation can be a good project with an eye on the potential of mixed organic and inorganic acids as the solvent in the leaching process for researchers.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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