REMOVAL OF METALLIC IMPURITIES FROM QUARTZ SAND USING OXALIC ACID

PENGHILANGAN LOGAM PENGOTOR DARI PASIR KUARSA MENGGUNAKAN ASAM OKSALAT

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ABSTRACT

Quartz sand of Mojosari deposit from Rembang, Central Java has been beneficiated using oxalic acid to enhance its purity, especially that is associated with the removal of iron oxide impurities. The removal of metallic impurities has been studied under experimental conditions to optimize the process parameters such as oxalate concentration (0.1-0.5M), leaching temperature (25-50°C) and pH of solution (1-5). The optimum leaching process removed iron from originally 1.44% to reach a level of 0.243% (82% removal of iron) with the SiO_2 content increases from 95.50 up to 97.77%. The obtained beneficiated quartz sand matches the required Fe level for glass insulating fibers industry, which is less than 0.3%. The best result was yielded under experimental condition using oxalic acid at concentration of 0.3M, pH 1, temperature of 40°C for 4 hours of leaching process. The experimental results of this study have opened up a practically significant and technically viable approach for the production of quartz sand suitable for glass insulating fiber industry.

Keywords : beneficiation, quartz, leaching, oxalic acid

ABSTRAK

Deposit pasir kuarsa dari Mojosari, Rembang, Jawa Tengah, dicoba diolah dengan cara pelindian menggunakan asam oksalat untuk meningkatkan kemurniannya, terutama yang berkaitan dengan upaya penghilangan besi oksida sebagai pengotor. Variabel percobaan telah diuji untuk mendapatkan parameter proses pelindian yang optimal, yaitu konsentrasi asam oksalat (0,1-0,5M), temperatur pelindian (25-50°C), dan pH larutan (1-5). Proses pelindian dapat meningkatkan kadar pasir kuarsa dengan menghilangkan besi oksida dari 1,44% menjadi 0,243%, serta meningkatkan kadar SiO_2 *dari 95,5% menjadi 97,77%. Hasil proses tersebut bisa digunakan sebagai bahan baku untuk pembuatan gelas pembungkus serat dengan persyaratan kadar besi <0,3%. Hasil terbaik ini diperoleh dalam kondisi percobaan menggunakan asam oksalat 0,3M, temperatur 40°C, pH larutan 1 dalam waktu pelindian selama 4 jam.*

Kata kunci : benefisiasi, kuarsa, pelindian, asam oksalat

INTRODUCTION

Quartz is an economically important raw material that is often used in wide variety of ceramic and glass applications, from high quality tableware and sanitary ware to glasses. There are some less common uses including glass fibre and refractory insulation bricks (Haus et al., 2012; Dal Martello et al., 2011). Quartz is a material that appears in nature combined with iron oxides, hydroxides and heavy metals. Great part of the quartz beds is contaminated by iron oxides at concentrations of 0.2-3%. The oxyhydroxides of Fe are often deposited along with the quartz, contaminating

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and making much of the quartz unusable for commercial applications due to insufficient specific properties needed. That is why the mined quartz need to be beneficiated by removal of undesirable minerals or metals before they could be considered as a suitable raw material for some of the above-mentioned purposes (Banza et al., 2006). Very low levels of iron and other impurities must be reached in the sand to permit its use for high quality crystal glass industry (<0.013% of Fe). Further target values of Fe<0.01% for optical fiber application and Fe<1 ppm for pure silicon production (99.999% SiO_2) might be significant to be considered. The British standards classified quartz sand used in terms of SiO_2 and Fe contents for glass production into 7 categories as presented in Table 1 (Mustafa et al., 2011).

Table 1. Bristish standards classification of sands by end-use in terms of SiO_2 and Fe contents

Grade	Type of raw material sands	SiO_2 (%)	Maximum Fe (%)
A	Optical and ophthalmic glass	99.7	0.013
B	Tableware and lead crystal glass	99.6	0.010
C	Borosilicate glass	99.6	0.010
D	Colorless container glass	98.8	0.030
E	Clear flat glass	99.0	0.100
F	Colored container glass	97.0	0.250
G	Glass for insulating fibers	94.5	0.300

Several techniques are available for upgrading quartz by partial removal of iron such as flotation, heavy-media separation or magnetic separation, but these seldom reduce the iron and other metals to an acceptable level. Other techniques available are based on the use of sulphuric acid, hydrochloric acid, hydrofluoric acid (Tuncuk and Akcil, 2014; Ledgerwood and van der Westhuyzen, 2011; Kheloufi, 2009; Banza et al., 2006). These are generally costly and have a considerable impact on the environment. In this scenario, the use of organic acids as leachant agent in the metal removal process from industrial minerals holds potential interest. The most commonly used organic acids are oxalic, citric and ascorbic acids. Organic acids dissolved the iron oxides by direct attack on H^+ ions over the mineral matrix, maintain them in solution by forming soluble complexes and chelates.

The primary advantage of using oxalic acid is in the formation during leaching of soluble complexes that are both photochemically and microbiologically degradable (Arslan and Bayat, 2009; Iveta et al., 2007; Styriakova et al., 2011). They investigated the beneficiation of quatz sand using chemical and biological leaching methods.The iron content decreased from 0.315% to 0.164% Fe_2O_3 in the bioleached quartz sand after 7 days of the process. Styriakova et al. (2012) also conducted a study on bioleaching of clay and iron oxide coating from quartz sands that performed for 63 days at 24°C. The results of bioleaching were encouraging, but it was a time consuming process. Therefore, the use of oxalic acid in chemical leaching is expected to optimize the time consuming, i.e. reducing the time of leaching to a few of hours instead of days.

The purpose of the present study is the removal of iron, aluminium and other metal impurities originated from the Mojosari quartz sand using oxalic acid leaching. An attempt was made to obtain the relatively optimum process parameters and reach a high degree of iron removal. The parameters studied were oxalate concentration, leaching temperature and pH of the solution. The whole leaching process was observed for 8 hours.

METHODOLOGY

Mineral Samples

The sample of quartz sand was taken from Mojosari, Rembang, Central Java. It was oven dried and was ground to -200 mesh particle size, then was analyzed using X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF) for characterization.

Experimental Procedures

For selective leaching studies, all experiments were conducted in a 1 L well mixed mechanically stirred glass reactor heated by a constant temperature bath (jacket water heater) having a digital controlled unit as shown in Figure 1. The experimental procedure was as follows : 400 ml of oxalic acid solution with constant total oxalate concentration (0.1-0.4M) and pre-adjusted pH value (pH 1, 2, 3, 5) was heated in the glass reactor with a pre-selected temperature (25, 30, 40, 50°C). The solution was agitated at a speed of 250 rpm. Then, a pre-weighed amount of dry quartz sand was added to the solution, creating a suspension with the appropriate pulp density (20%). The whole process was conducted within 8 hours. In the time course, sample was removed at intervals and centrifuged to remove solid suspension. Supernatans were analyzed for monitoring pH and dissolved elements. In each test, the dissolved metals concentration in solution were measured as a function of time using a varian atomic absorption spectrophotometry (AAS).

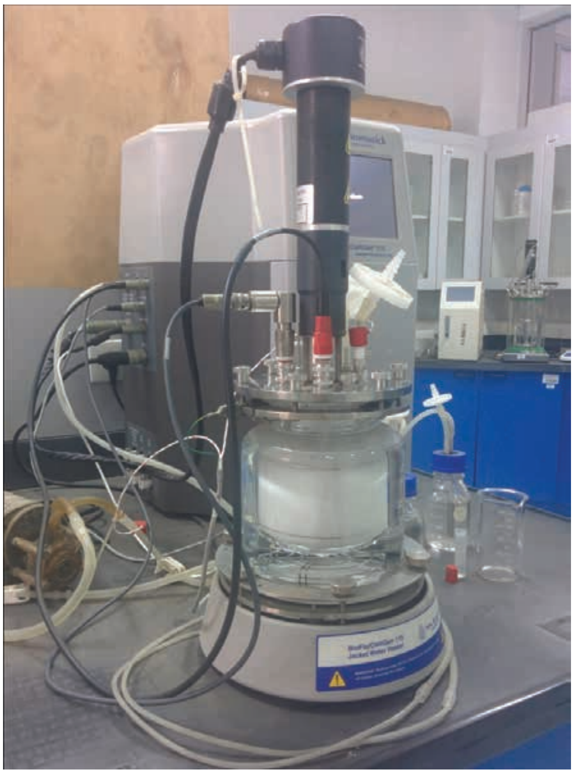

Figure 1. Leaching process in a controlled glass reactor

Analytical Measurements

For mineral characterization studies, the mineral sample was analysed using XRD and XRF instruments. The concentration of metal ions in the liquids samples taken during the leaching process was determined using an Atomic Absorption Spectrophotometer. Metrohm pH meter was used to determine the pH of leach solution.

RESULTS AND DISCUSSION

Characterization of Mojosari's Quartz Mineral

The mineralogical analysis using XRD shows that the quartz sample used in this study consists mainly of quartz (64%) and nepheline (31%) as can be seen in Table 2. The mineralogical analysis of quartz sample reflected the presence of allophane as accessory mineral. The spectrum of mineralogical analysis is shown in Figure 2.

From the results of XRF analysis (Table 3), it can be seen that silica is the main component (95.5%) containing unwanted metals of Fe (1.44%), Al (0.773%), Ti (0.067%), Ca (0.046%), as the main

Table 2. Mineral composition of Mojosari quartz sand

Mineral	Chemical formulae	%
Quartz	SiO_2	60
High grade quartz	SiO_2	4
Nepheline	$Na_3K(Si_{0.56}Al_{0.44})_8O_{16}$	31
Allophane	$Al_2O_3.2SiO_2.3H_2O$	5

Table 3. Chemical composition of Mojosari quartz sample

Components	Chemical composition (%)
SiO_2	95,5
Fe	1.44
Al	0.773
Ca	0.046
Cu	0.026
Ti	0.067
Cr	0.022
Mn	0.009

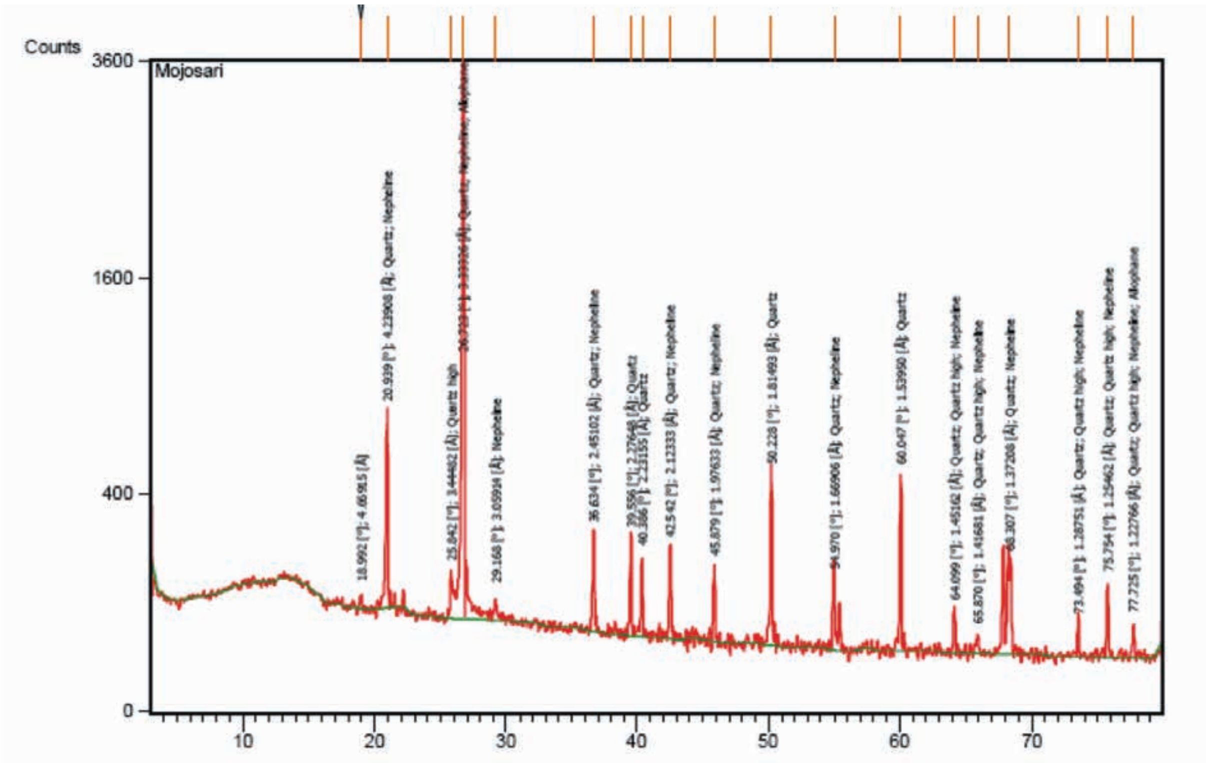

Figure 2. Characterization of Mojosari quartz sand using XRD

impurities. The chemical analysis for the raw quartz revealed that the sample is very rich in iron and aluminium, which renders this mineral sample unfit for related purposes.

Effect of Oxalate Concentration

The effect of total oxalate concentration was studied through a series of tests conducted at oxalate concentration varying between 0.1 and 0.4 M, constant pH of 1, pulp density 20% (w/v), and temperature of 40°C for 8 hours of process. In all experiments, the release of Fe, Al and other undesired metals into solution was used as indicator of metal removal and purification of quartz sand. The removal of iron as a function of time for the above experiments is depicted in Figure 3. It can be seen that the highest Fe removal rate was observed with 0.3 M oxalic acid. This leaching process removed iron from 1.44% to reach a level of 0.243% (82% removal of iron) for around 4 hours. This result was different with that found by Handayani (2004) who revealed that 0.2 M oxalic acid strength was sufficient for optimal leaching of quartz sand. The different results were attributed to the differences in mineral characteristic, metal impurities and their concentrations. Accordingly, based on the result of the current experiments, this oxalic acid concentration of 0.3M was then used subsequently in this work.

During leaching studies, some other metal ions (Al, Ca, Cu) were also dissolved from the mineral sample. Table 4 shows the removal of metallic contaminants as a function of the oxalic acid concentration. Apparently, it was observed that Fe, Al, Ca and Cu reduced progressively at all tested oxalic acid concentration, while Cr and Mn remained unchanged. Simultaneously, SiO_2 content increased with increasing time, associated with removal of Fe, Al and other metallic ions, which conforms to works of previous studies (Arslan and Bayat, 2009 ; Styriakova et al., 2012).

The chemical reaction of oxalic acid with the oxides of iron, aluminium and calcium can be drawn as follows (Hernandez et al., 2013; Salmimies et.al., 2011; Lee et al., 2007) :

In solution, oxalic acid ($H_2C_2O_4$) dissociates releasing bi-oxalate ion ($HC_2O_4^-$):

$$H_2C_2O_4 \rightarrow H^+ + HC_2O_4^-$$

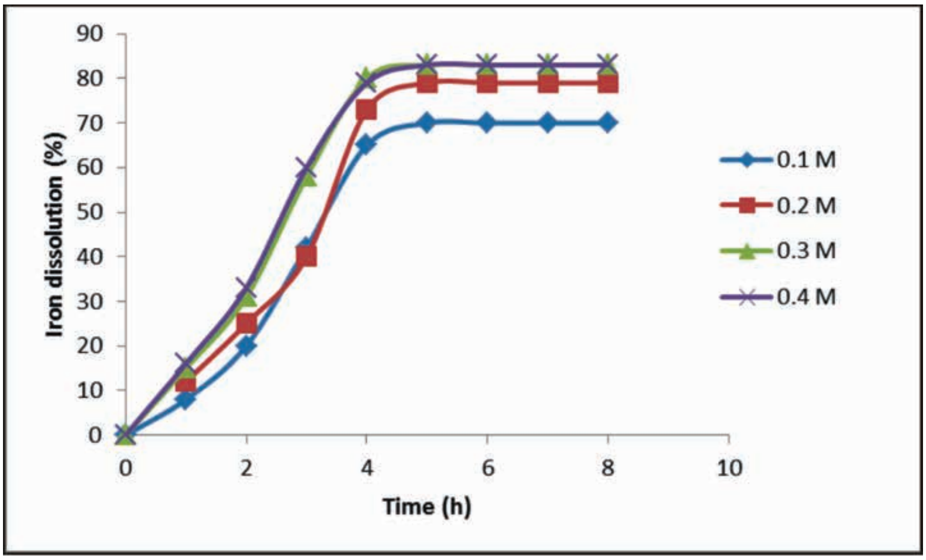

Figure 3. Iron removal during leaching with oxalic acid at different concentration.

Table 4. Chemical composition of quartz sample before and after leaching with oxalic acid at different concentration

Component	Raw Material (%)	After leaching with oxalic acid at different strength			
		0.1 M	0.2 M	0.3 M	0.4 M
SiO_2	95.5	96.90	97.28	97.77	97.80
Fe	1.44	0.435	0.299	0.243	0.239
Al	0.773	0.188	0.159	0.158	0.055
Ca	0.046	0.039	0.037	0.006	0.005
Cu	0.026	0.008	0.005	0.001	0.001
Ti	0.067	0.067	0.063	0.053	0.050
Cr	0.022	0.022	0.022	0.022	0.022
Mn	0.009	0.009	0.009	0.009	0.009

The bi-oxalate ion formed dissociates releasing the oxalate ion ($C_2O_4^{2-}$):

$$HC_2O_4^- \rightarrow H^+ + C_2O_4^{2-}$$

Of these species, it is considered that the bi-oxalate is responsible for the dissolution of the iron:

$$Fe_2O_3 + H^+ + 5HC_2O_4^- \rightarrow 2Fe(C_2O_4)_2^{2-} + 3H_2O + 2CO_2$$

$$Fe_2O_3 + 6H_2C_2O_4 \rightarrow 2Fe(C_2O_4)_3^{3-} + 6H^+ + 3H_2O$$

$$2Fe(C_2O_4)_3^{3-} + 6H^+ + 4H_2O \rightarrow 2FeC_2O_4.2H_2O + 3H_2C_2O_4 + 2H_2O$$

$$Fe_2O_3 + 3H_2C_2O_4 + H_2O \rightarrow 2FeC_2O_4.2H_2O + 2CO_2$$

Reactions with aluminium oxide :

$$Al_2O_3 + 6H_2C_2O_4 \rightarrow 2Al(C_2O_4)_3^{3-} + 6H^+ + 3H_2O$$

$$2Al(C_2O_4)_3^{3-} + 6H^+ + 4H_2O \rightarrow 2AlC_2O_4.2H_2O + 3H_2C_2O_4 + 2H_2O$$

$$Al_2O_3 + 3H_2C_2O_4 + H_2O \rightarrow 2AlC_2O_4.2H_2O + 2CO_2$$

Reactions with calcium oxide :

$$Ca(OH)_2 + H_2C_2O_4 \rightarrow Ca(C_2O_4) + 2H_2O$$

Figure 4 presents representative quartz sand before and after leaching with oxalic 0.3M. The release of Fe, Al, Ca and Cu impurities from the quartz resulted in whiter colour development of

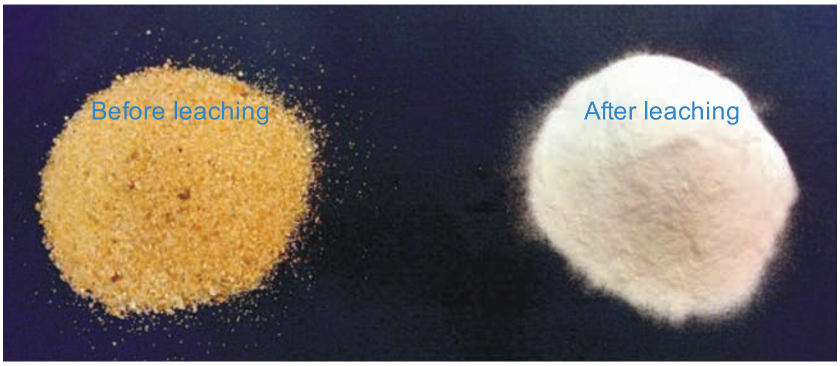

Figure 4. Representative quartz sand before and after leaching with oxalic acid 0.3M

the mineral sample. The chemical properties were also improved and could be suitable raw material for more extensive use in ceramic industry.

Effect of Temperature

To determine the effect of temperature on the purification of quartz sand, experiments were also conducted at 25, 30, 40 and 50°C. Figure 5 and Table 5 show the effect of changing the conditioning temperature on metal removal. The degree of metal removal increases with increasing temperature until certain value. These results showed a significant reduction in Fe content from 1.44 to 0.243% with raising the temperature from 25 to 40°C. However, there was no significant change in Fe dissolution when the temperature was increased to 50°C.

It is clear that the increase in conditioning temperature is beneficial for improving the grade of quartz. It seems that increasing temperature can affect the rate of solubility of metal contaminants. The results indicate that the selective leaching process was sensitive to reaction temperature at relatively lower temperature (25 to 40°C) when the metal removal appreciably increased, but after that, the rate of increase in SiO_2 and corresponding reduction in Fe and other metal contents was almost flated.

Removal of metallic contaminants may be related to chemical bonding between metallic elements as well as reaction of metal ions and leaching solution. Therefore, low removal efficiency of Ti, Cr and Mn in oxalic acid solution is considered to be caused mostly by the bonding between metallic contaminants and mineral. Apart from

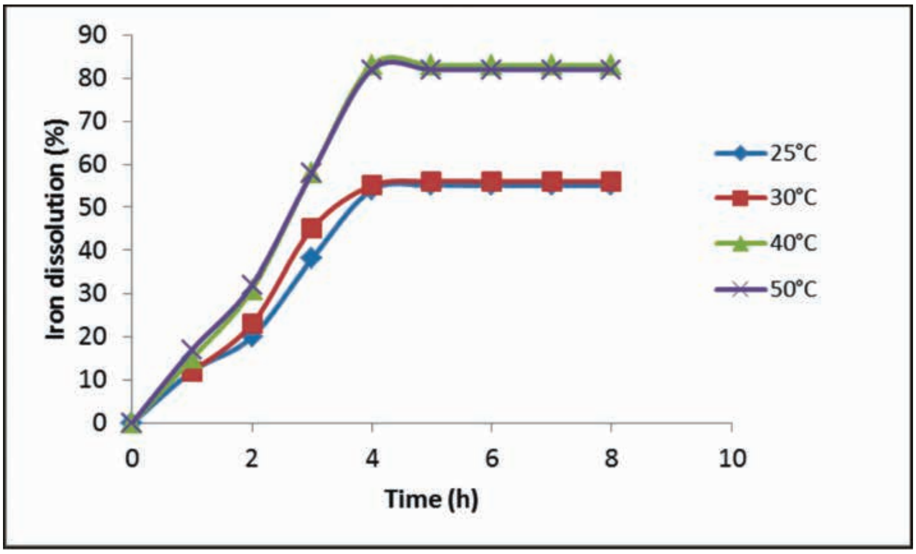

Figure 5. Iron removal during leaching with oxalic acid at different temperature

Table 5. Chemical composition of quartz sample before and after leaching with oxalic acid at different temperature

Component	Raw Material (%)	After leaching with oxalic acid at different temperature			
		25°C	30°C	40°C	50°C
SiO_2	95,5	96.78	96.96	97.77	97.79
Fe	1.44	0.655	0.641	0.243	0.253
Al	0.773	0.174	0.172	0.159	0.058
Ca	0.046	0.035	0.031	0.009	0.006
Cu	0.026	0.019	0.018	0.007	0.001
Ti	0.067	0.066	0.066	0.061	0.053
Cr	0.022	0.022	0.022	0.022	0.022
Mn	0.009	0.009	0.009	0.009	0.009

being chemical bonding, it might also be due to reaction rate of Ti, Cr and Mn is lower compared to Fe, Al, Ca, Cu againts oxalate. As a results, it was found that weak acid of oxalic acid, does not have an enough ability to remove Ti, Cr and Mn from mineral surface, but it is effective to remove Fe, Al, Ca and Cu, even at relatively low concentration and low temperature.

Effect of pH

Effects of varying pH on the purification on quartz sand were also examined. To study the effect of pH, a series of test was conducted at pH of 1, 2, 3 and 5, total oxalate concentration of 0.3 M and pulp density of 20%. In the case of Fe ion, based on Eh-pH (Pourbaix) diagram, it is impossible to truly study the dissolution above pH 5 since the iron hydroxide starts precipitating in the liquid. The Fe dissolution versus time is plotted in Figure 6. The results show that the Fe removal was highly dependent on pH of solution. A gradual decrease in Fe dissolution was observed by increasing pH. The optimum iron removal is observed at pH 1-2, while in less acid solutions, the dissolution rate decreases significantly. These results are in agreement with those from the tests carried out by Mandal and Banerjee (2004) where the dissolution increased as pH decreased, and the highest iron dissolution was noted at pH 1.25, which is higher than the pK of oxalic acid.

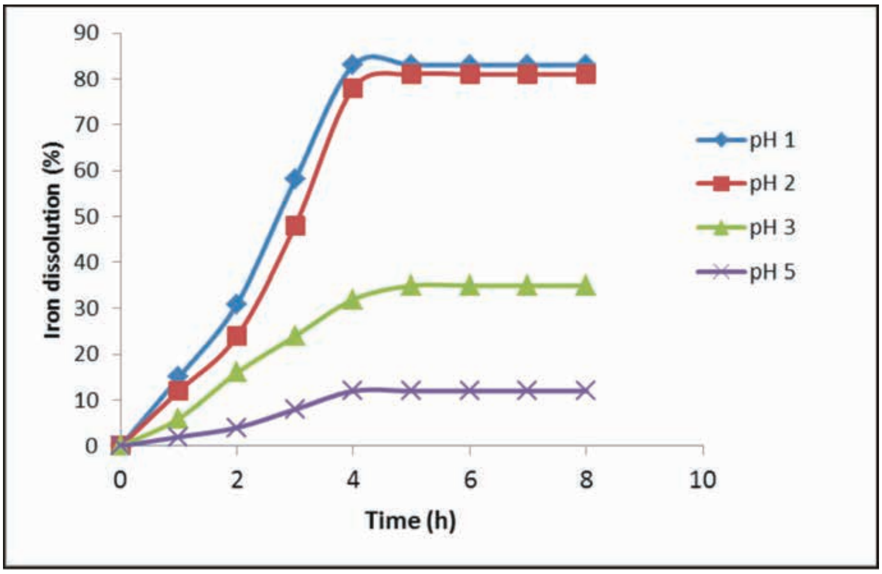

Figure 6. Iron removal during leaching with oxalic acid at different pH solution

Generally, pH is one of the most important factors in metal dissolution since it can influence the property and solution chemistry of the metal ions (Huang et al., 2006). Precipitation, hydrolysis, complexation and redox reactions are among the changes in solutions with pH. In this experiment, maximum removal of Fe and Al was recorded at pH 1-2, followed by pH 3 as can be seen in Table 6. The drop in metal loading beyond pH 2 might be explained by the reduced availability and solubility of the metal ions with the onset of precipitation of metal hydroxides. The above findings reveal that metal loading is strongly influenced by the solution's pH. An efficient removal was observed at pH 1-2 for all metal ions.

Table 6. Chemical composition of quartz sample before and after leaching with oxalic acid at different pH solution

Component	Raw Material (%)	After leaching with oxalic acid at different pH solution			
		pH 1	pH 2	pH 3	pH 5
SiO_2	95,5	97.77	97.74	96.72	95.73
Fe	1.44	0.243	0.274	0.941	1.270
Al	0.773	0.158	0.156	0.261	0.528
Ca	0.046	0.006	0.005	0.006	0.039
Cu	0.026	0.001	0.001	0.001	0.013
Ti	0.067	0.053	0.052	0.057	0.058
Cr	0.022	0.022	0.022	0.022	0.022
Mn	0.009	0.009	0.009	0.009	0.009

CONCLUSION

The effectiveness of iron and other impurities removal was significantly dependent on oxalate concentration, leaching temperature and pH of the solution. Under optimum experimental condition in this study, the iron content decreased from 1.44 to 0.243% (83% Fe removal), reaching SiO2 purity of 97.77% with oxalic acid 0.3M, pH 1 at 40°C for 4 hours. This product does not meet yet the requirement for raw material of high quality crystal glass or advance technology that is the Fe content must be <0.013%. Nevertheless, in terms of iron content, the present experimental results have shown the technical feasibility of this leaching process for making glass insulating fiber (Fe<0.3%). Through further optimization of influencing parameters such as pulp density and particle size of the mineral, possibilities of enhancing iron removal may exist to reach a higher purity of quartz sand.

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