PREPARATION AND CHARACTERIZATION OF SILICA FROM THREE SELECTED CLAY MINERALS USING ULTRASONIC BATH

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Abstract

In this research work, silica particles were extracted from Montmorillonite clay minerals. The clay mineral was collected from three different sites. Elemental analysis of the clay samples were determined by EDXRF techniques. The extraction of silica from three samples was performed by using various concentration of NaOH and HCl: 2 M, 4 M, 6 M, 8 M, and 10 M. According to concentration effect the optimum concentration was 8 M for NaOH and HCl. The silica was extracted from three samples for various contact times (1-8 h). According to time effect, the optimum contact time was 4 h. To extend the effect of inorganic acid, three different inorganic acids such as 8 M HCl, 8M H_2SO_4 and 8 M HNO_3 were used. 8 M HCl was found to be the highest yield than other two acids. The silica were characterized by using EDXRF and FT IR analysis. EDXRF analysis is carried out to determine the chemical composition of prepared silica. According to FT IR spectra, prepared silica are identical to amorphous silica.

Keywords: Montmorillonite clay, FTIR spectroscopy, EDXRF, Silica

Introduction

The most common smectite is Montmorillonite, with a general chemical formula; (½Ca, Na) $(Al, Mg, Fe)_4$ $(Si, Al)_8$ O_{20} $(OH)_4$, nH_2O. Montmorillonite is the main constituent of bentonite, derived by weathering of volcanic ash. Montmorillonite can expand by several times its original volume when it comes in contact with water. This makes it useful as a drilling mud and to plug leaks in soil, rocks and dams.

Ultrasonic baths are ideal for cleaning a wide range of laboratory instruments as well as in other healthcare, medical and industrial applications. The ultrasonic activity generated in the baths allows rapid and effective clearing and processing of a wide range of instruments and components, a safer alternative to manual operations.

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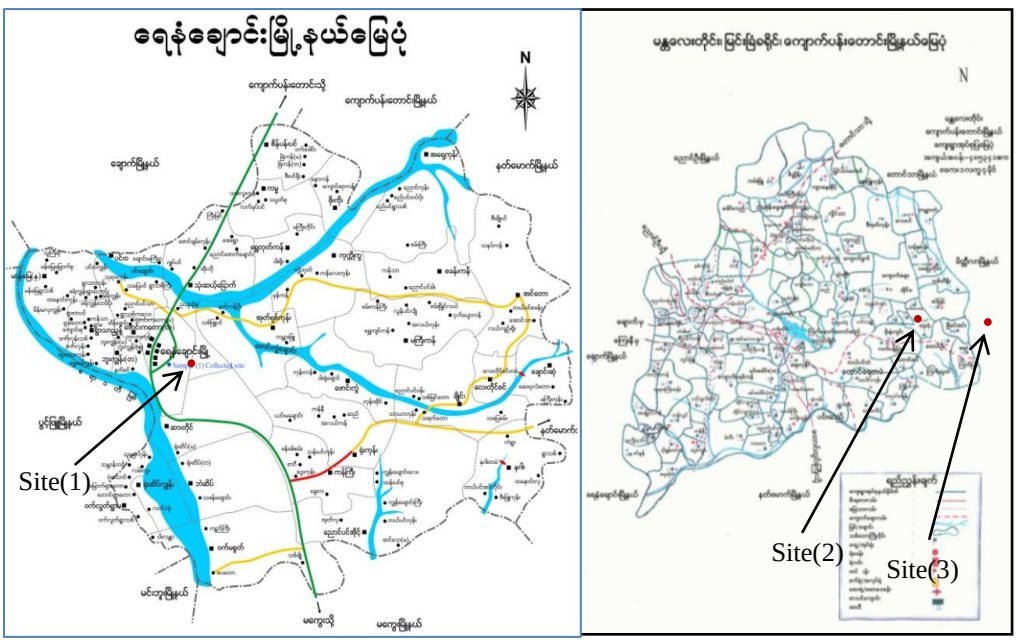
Silica is one of the most abundant oxide materials in the earth's crust. Silica occurs commonly in nature as sandstone, silica sand (or) quartzite. It can exist in an amorphous form (or) in a variety of crystalline forms. Silica is a group IV metal oxide, which was good abrasion resistance, electrical insulation and high thermal stability.

The main aim of this research is to extract silica from clay minerals by using ultrasonic bath and characterize by FT IR and EDXRF techniques.

Materials and Methods

Collection of the Samples

Three samples of clay (Montmorillonite) were collected form Ya Gyi Pyin Village, Yenanchaung Township, Magway Region, Myot Oo Pagoda, Kaukpadaung Township and Khin Phone Chone Village, Kyaukpadaung Township, Mandalay Region, during the months of October, in the year of 2016 (Figure 1 and 2).



(a) (Site 1) (b) (Site 2 and Site 3)

Figure 1: (a) The Maps of Yenanchaung Township and (b) Kyaukpadaung Township

(a) (b) (c)

Figure 2: (a) Clay sample (1) from Yargyipyin Village, Yenanchaung Township (Site 1)
(b) Clay sample (2) from near Myot Oo Pagoda, Kaukpadaung Township (Site 2)
(c) Clay sample (3) from Khin Phone Chone Village, Kyaukpadaung Township (Site 3)

Sampling

The collected samples were dried in the shade before sieving. Afterward, pieces of microorganism matters were discarded and the clay aggregates were broken up by grinding lightly in motar and pestle. Then, it was meshed through 40 mesh size sieve and the fine powder sample was stored in plastic bag for further uses.

Determination of Mineral Contents in Three Clay Samples

The relative abundance of elements were determined in the three clay samples at the Department of Physics, University of Mandalay by EDXRF spectrometer (Perkin Elemer 700).

Preparation of Silica from Three Clay Samples for Various Reaction Times

1 g of sample was weighed accurately and placed in a test tube. Then the sample was washed with 10 mL of distilled water and filtered by filter paper. After that, the residue was used for silica extraction. 10 mL of 8 M NaOH was added to the residue in test tube. The test tube was sonicated for 1 h at 80 ºC by using ultrasonic bath (XUBA entry level). The solution was

filtered by filter paper and carbon residues were washed with 100 mL of boiling water. The filtrate and washings were allowed to cool at room temperature and were neutralized against 8 M HCl with constant stirring to pH 4. Silica gels started to precipitate when pH decreased to <10. The silica gel was washed several times with deionized water to remove sodium chloride. The extraction of silica was performed on ultrasonic bath for various times such as 1 h, 2 h, 3 h, 4 h, 5h, 6 h, 7 h and 8 h. Silica gel was aged for 18 h. And then, this gel was filtered and washed with hot water for several times at room temperature. The silica gel was heated at 250 ºC for 4 h in an oven to remove the surfactant. The dried sample was ground by using the pestle and motar to obtain silica powder.

Preparation of Silica by using Various Concentrations of NaOH and HCl

According to former procedure, silica powder was prepared by using various concentrations (2 M, 4 M, 6 M, 8 M and 10 M) of NaOH and HCl.

Preparation of Silica by using for Three Different Inorganic Acids

According to former procedure, silica powder was prepared by different inorganic acids (8 M HCl, 8 M HNO_3 and 8 M H_2SO_4).

Characterization of the prepared Silica from Clay Samples

EDXRF Analysis of prepared silica from three samples

The prepared silica powder was analyzed by EDXRF analyzer to determine the presence of elements at Monywa University.

FT IR analysis of the prepared silica from three samples

The FT IR spectra of silica were recorded by using Perkin Elmer GX System FT IR spectrophotometer at the Department of Chemistry, Monywa University.

Results and Discussion

Mineral Contents of Three Clay Samples

The relative abundance of elements containing in three types of clay sample were determined by EDXRF method. The observed spectrum indicates that 10.310 % Si, 4.210 % Fe, 3.655 % Al, 1.211 % K and 0.574 % Ca were found in clay sample 1 and 10.510 % Si, 2.702 % Al, 2.400 % Fe, 1.058 % K and 0.4778 % Ca in clay sample 2. 11.850 % Si, 5.826 % Al, 3.740 % Fe, 0.487 % K and 0.434 % Ca were found in clay sample 3 (Table 1). From these results clay sample 3 has higher abundant elemental contents than the other two clay samples. Silicon is the rich mineral in three types of clay sample. In this research work, clay sample was used as precursor in silica extraction.

Table 1: Relative Abundance of some Elements in the Clay Samples (EDXRF)

No.	Elements	Content (%)		
		Sample 1	Sample 2	Sample 3
1	Si	10.310	10.510	11.850
2	Fe	4.210	2.702	5.826
3	Al	3.655	2.400	3.740
4	K	1.211	1.058	0.487
5	Ca	0.574	0.478	0.434

Preparation of Silica from Clay Samples

Effect of Reaction Time on Silica Contents Prepared from Clay Samples

The alkaline extraction was investigated at various reaction time of 1 to 8 h. This investigation shows that the quality of silica powder increased with the increase in reaction time. Increase the reaction time, increase the percent yield of silica till (4 h). Beyond 4 h, the silica yield does not significantly change. Optimum reaction is 4 h.

The silica in the clay mineral is not dissolved in the HCl treatment. The silica particles are obtained via the following reactions:

$$NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$$

$$Na_2SiO_3 + 2HCl \rightarrow SiO_2 + 2NaCl + H_2O$$

The gel was washed several times with deionized water to remove sodium chloride resulting gel mixture was ages at room temperature. Washing with distilled water is very important for silica extraction.

Table 2: Yield (%) of Silica from Three Types of Clay Samples at Different Reaction Time

No.	Reaction Time (h)	Sample 1		Sample 2		Sample 3	
		Wt. (g)	%	Wt. (g)	%	Wt. (g)	%
1	1	0.54	54	0.47	47	0.37	37
2	2	0.57	57	0.50	50	0.42	42
3	3	0.74	74	0.57	57	0.65	65
4	4	0.83	83	0.77	77	0.70	70
5	5	0.80	80	0.73	73	0.69	69
6	6	0.81	81	0.75	75	0.70	70
7	7	0.83	83	0.74	74	0.70	70
8	8	0.82	82	0.75	75	0.69	69

Concentration of NaOH = 8 M
Concentration of HCl = 8 M, Sample = 1 g

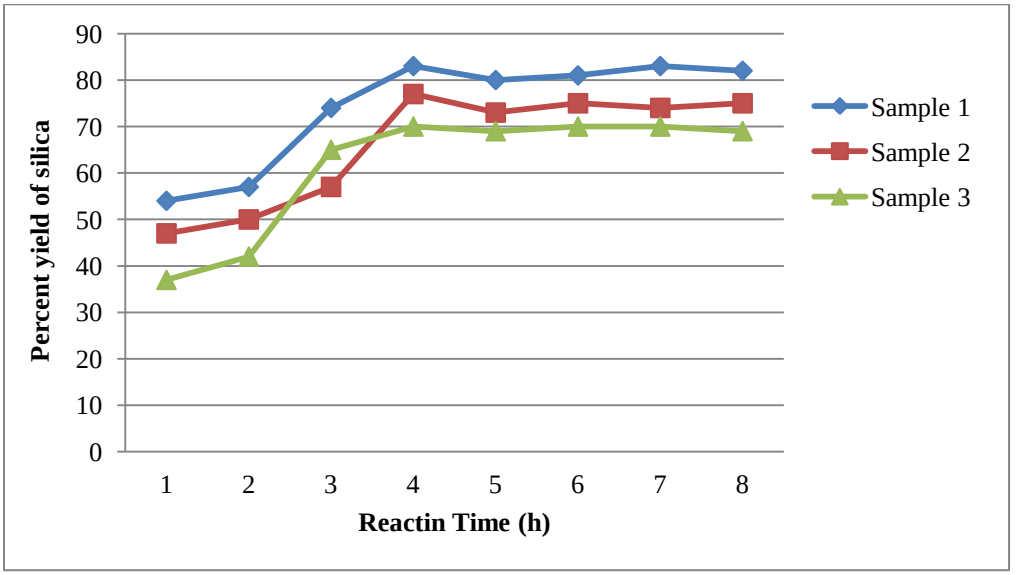


Figure 3: Reaction time *Vs* percent yield of Silica

Effect of Concentration of NaOH and HCl on Silica Contents Prepared from Clay Samples

In silica extraction, the optimum condition such as NaOH concentration in the range of 2 M to 10 M was determined. The sodium silicate was separted and then precipaitated by adding 2 M, 4 M, 6 M, 8 M and 10 M HCl. The concentration of NaOH and HCl (8 M) was found to be highest yield, 54.00 % for sample 1, 50.00 % for sample 2 and 58.00 % for sample 3. Increasing the concentration of NaOH and HCl, increase the % yield of silica till 8 M, beyond this concentration silica contents does not significantly change. Optimum concentrations of NaOH and HCl are 8 M.

Table 3: Yield (%) of Silica with Various Concentration of NaOH and HCl for Sample 1, Sample 2 and Sample 3

No.	Concentration (M)		Sample 1		Sample 2		Sample 3	
	NaOH	HCl	Wt. (g)	%	Wt. (g)	%	Wt. (g)	%
1	2	2	0.15	15	0.13	13	0.16	16
2	4	4	0.16	16	0.15	15	0.18	18
3	6	6	0.25	25	0.22	22	0.26	26
4	8	8	0.54	54	0.50	50	0.58	58
5	10	10	0.54	54	0.50	50	0.58	58

Reaction time - 1 h, Sample - 1 g

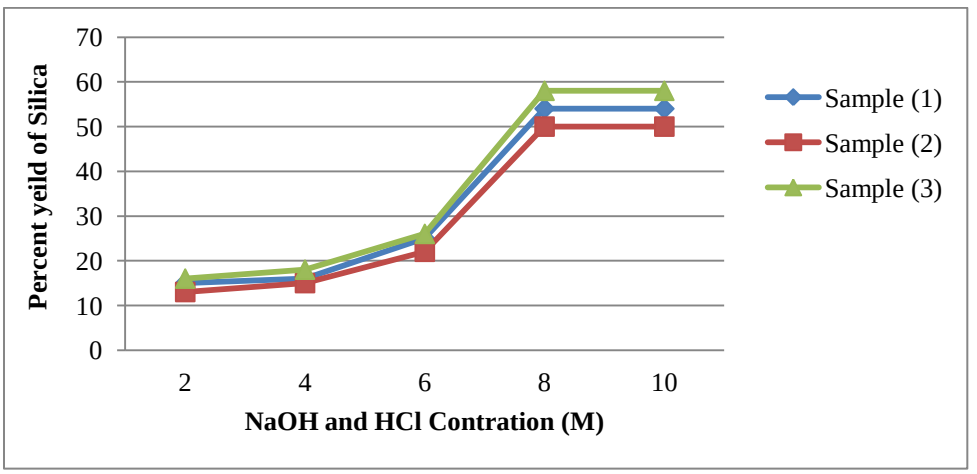


Figure 4: NaOH and HCl concentration *Vs* percent yield of silica

Effect of Various Acids on Silica Contents Prepared from Clay Samples

In Silica extraction, various inorganic acid; 8 M H_2SO_4. 8 M HCl and 8 M HNO_3 were used. High yield of silica 54 % for sample 1, 47 % for sample 2 and 37 % for sample 3 were obtained using 8 M HCl. The optimum inorganic acid is 8 M HCl.

Table 4: Yield (%) of Silica from Various Acids for Sample 1, Sample 2 and Sample 3

Type of Acid	Concentration (M)		Sample 1		Sample 2		Sample 3	
	Base	acid	Wt.(g)	%	Wt.(g)	%	Wt.(g)	%
H_2SO_4	8	8	0.13	13	0.11	11	0.12	12
HCl	8	8	0.54	54	0.47	47	0.37	37
HNO_3	8	8	0.47	47	0.40	40	0.32	32

Reaction time = 1 h, Weigh of sample = 1 g

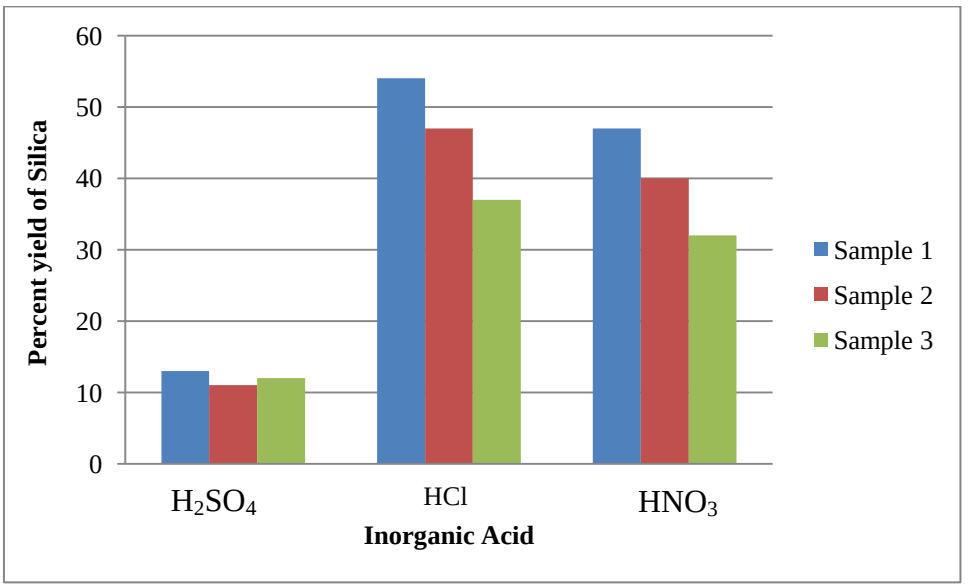


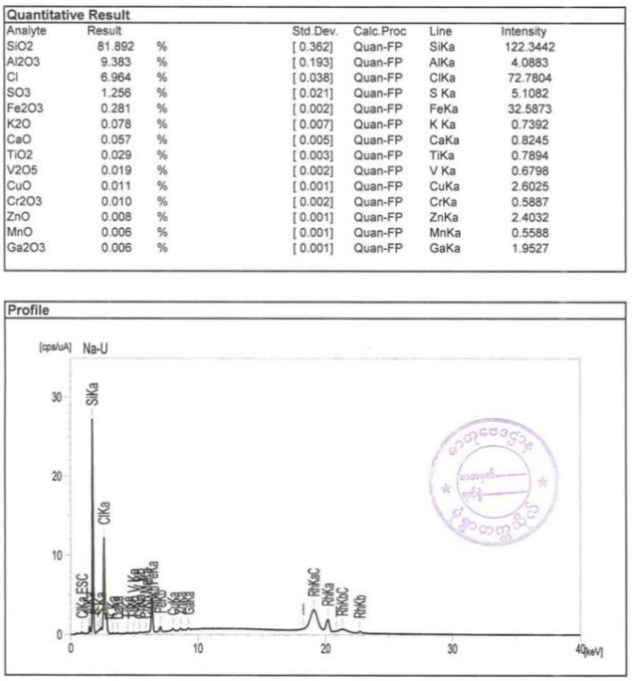
Figure 5: Inorganic acid Vs percent yield of silica

Characterization of the Prepared Silica (8 M NaOH and 8 M HCl)

EDXRF Spectral Results of Prepared Silica (8 M NaOH and 8 M HCl) from Three Samples

For qualitative determination of elemental oxide in prepared silica, EDXRF technique was used. EDXRF spectra of the prepared silica are shown in Figure 6, 7 and 8. The relative abundance of metal oxide in these samples are presented in Table 5.

According to EDXRF analysis, it can be observed that silica contents were found to be the highest in these samples.



Quantitative Result

Analyte	Result		Std.Dev.	Calc.Proc	Line	Intensity
SiO2	81.892	%	[0.362]	Quan-FP	SiKa	122.3442
Al2O3	9.383	%	[0.193]	Quan-FP	AlKa	4.0883
Cl	6.964	%	[0.038]	Quan-FP	ClKa	72.7804
SO3	1.256	%	[0.021]	Quan-FP	S Ka	5.1082
Fe2O3	0.281	%	[0.002]	Quan-FP	FeKa	32.5873
K2O	0.078	%	[0.007]	Quan-FP	K Ka	0.7392
CaO	0.057	%	[0.005]	Quan-FP	CaKa	0.8245
TiO2	0.029	%	[0.003]	Quan-FP	TiKa	0.7894
V2O5	0.019	%	[0.002]	Quan-FP	V Ka	0.6798
CuO	0.011	%	[0.001]	Quan-FP	CuKa	2.6025
Cr2O3	0.010	%	[0.002]	Quan-FP	CrKa	0.5887
ZnO	0.008	%	[0.001]	Quan-FP	ZnKa	2.4032
MnO	0.006	%	[0.001]	Quan-FP	MnKa	0.5588
Ga2O3	0.006	%	[0.001]	Quan-FP	GaKa	1.9527

Figure 6: EDXRF spectrum of prepared silica from sample 1

Quantitative Result

Analyte	Result		Std.Dev.	Calc.Proc	Line	Intensity
SiO2	80.005	%	[0.312]	Quan-FP	SiKa	116.9246
Al2O3	10.514	%	[0.186]	Quan-FP	AlKa	4.5283
Cl	7.263	%	[0.033]	Quan-FP	ClKa	75.7571
SO3	1.212	%	[0.018]	Quan-FP	S Ka	4.9265
Fe2O3	0.832	%	[0.003]	Quan-FP	FeKa	95.5773
TiO2	0.081	%	[0.003]	Quan-FP	TiKa	2.1873
CaO	0.032	%	[0.003]	Quan-FP	CaKa	0.4588
ZnO	0.022	%	[0.001]	Quan-FP	ZnKa	6.1902
CuO	0.011	%	[0.001]	Quan-FP	CuKa	2.6225
V2O5	0.010	%	[0.002]	Quan-FP	V Ka	0.3747
Ga2O3	0.006	%	[0.000]	Quan-FP	GaKa	2.0039
Cr2O3	0.005	%	[0.001]	Quan-FP	CrKa	0.3216
MnO	0.004	%	[0.001]	Quan-FP	MnKa	0.3541
NiO	0.003	%	[0.001]	Quan-FP	NiKa	0.5188

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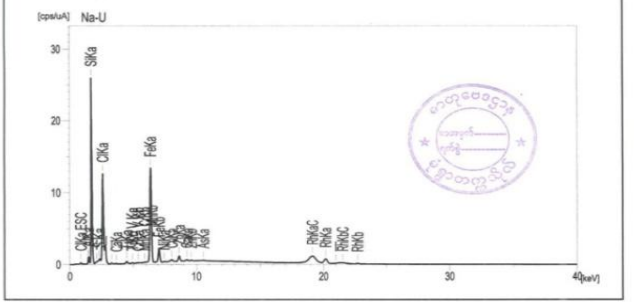

Figure 7: EDXRF spectrum of prepared silica from sample 2

Quantitative Result

Analyte	Result		Std.Dev.	Calc.Proc	Line	Intensity
SiO2	78.162	%	[0.344]	Quan-FP	SiKa	119.7223
Al2O3	11.519	%	[0.216]	Quan-FP	AlKa	5.2590
Cl	8.282	%	[0.040]	Quan-FP	ClKa	91.4621
SO3	1.124	%	[0.018]	Quan-FP	S Ka	4.8625
Fe2O3	0.635	%	[0.003]	Quan-FP	FeKa	75.8338
K2O	0.076	%	[0.006]	Quan-FP	K Ka	0.7414
V2O5	0.073	%	[0.003]	Quan-FP	V Ka	2.7257
TiO2	0.043	%	[0.003]	Quan-FP	TiKa	1.2158
ZnO	0.020	%	[0.001]	Quan-FP	ZnKa	5.9364
CaO	0.020	%	[0.004]	Quan-FP	CaKa	0.2975
Ga2O3	0.012	%	[0.001]	Quan-FP	GaKa	4.0902
CuO	0.012	%	[0.001]	Quan-FP	CuKa	3.0437
MnO	0.006	%	[0.001]	Quan-FP	MnKa	0.6218
PbO	0.006	%	[0.001]	Quan-FP	PbLb1	1.4513
Cr2O3	0.006	%	[0.001]	Quan-FP	CrKa	0.3721
Tl2O3	0.003	%	[0.001]	Quan-FP	TlLa	0.5410

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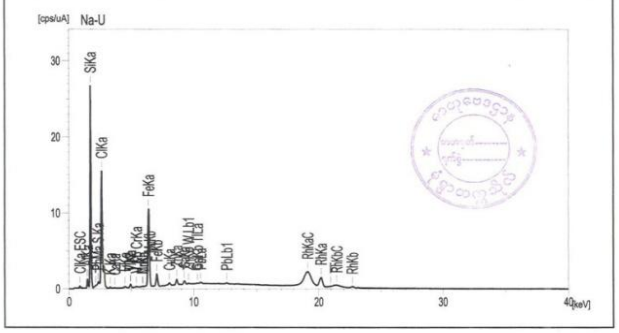


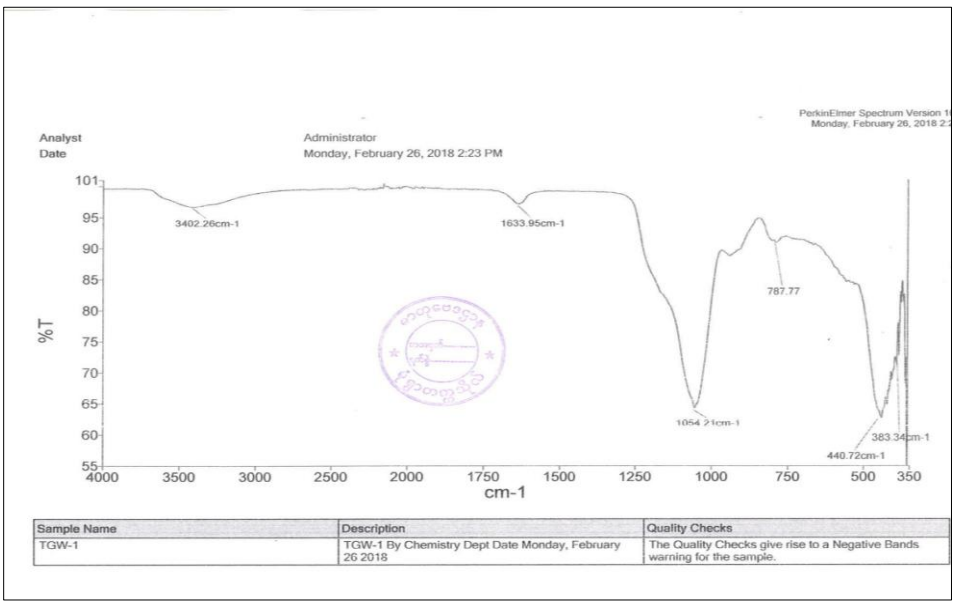
Figure 8: EDXRF spectrum of prepared silica from sample 3

Table 5: EDXRF Spectral Results of Prepared Silica from Sample 1, Sample 2 and Sample 3

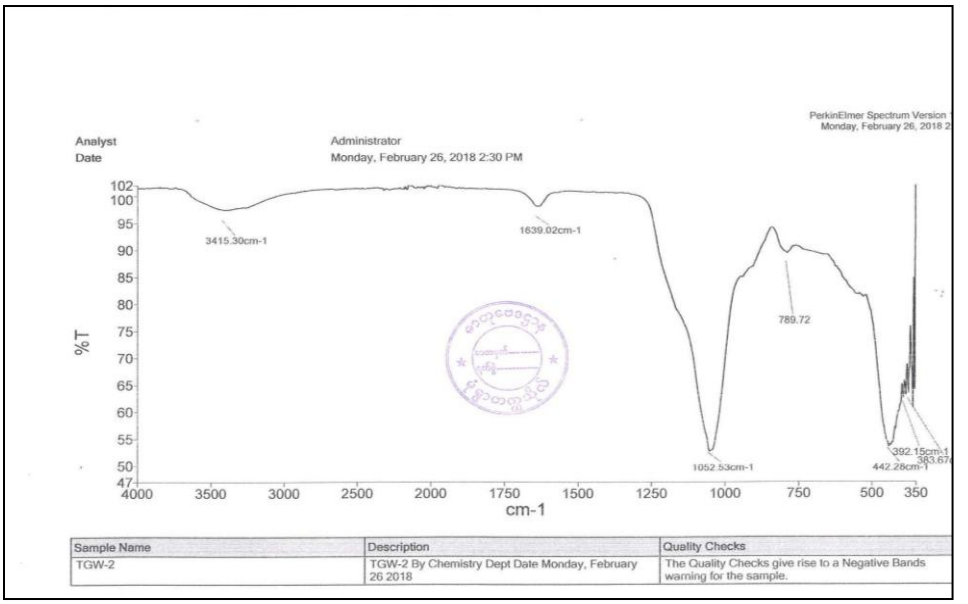
No	Analyte	Relative Abundance (%)		
		Sample 1	Sample 2	Sample 3
1	SiO_2	81.892	80.005	78.162
2	Al_2O_3	9.383	10.514	11.519
3	Cl	6.964	7.263	8.282
4	SO_3	1.256	1.212	1.124
5	Fe_2O_3	0.281	0.832	0.635

FT IR Spectra of Prepared Silica (8 M NaOH and 8 M HCl) from Three Samples

The FT IR spectra of prepared silica are shown in Figure 9 (a) (b) (c) and (d). The bond assignment of prepared silica is tabulated in Table 6. According to FTIR data, 1052 cm^{-1} and 1054 cm^{-1} (Si-O stretching vibration), 789 cm^{-1} and 787 cm^{-1} (Si-O-Si stretching vibration), 442 cm^{-1}, 449 cm^{-1} and 440 cm^{-1} (Si-O in-plane bending vibration) were observed in these samples. The bond around at 3437 cm^{-1} is due to -OH stretching vibration of the water molecules on the silica surface.



(a)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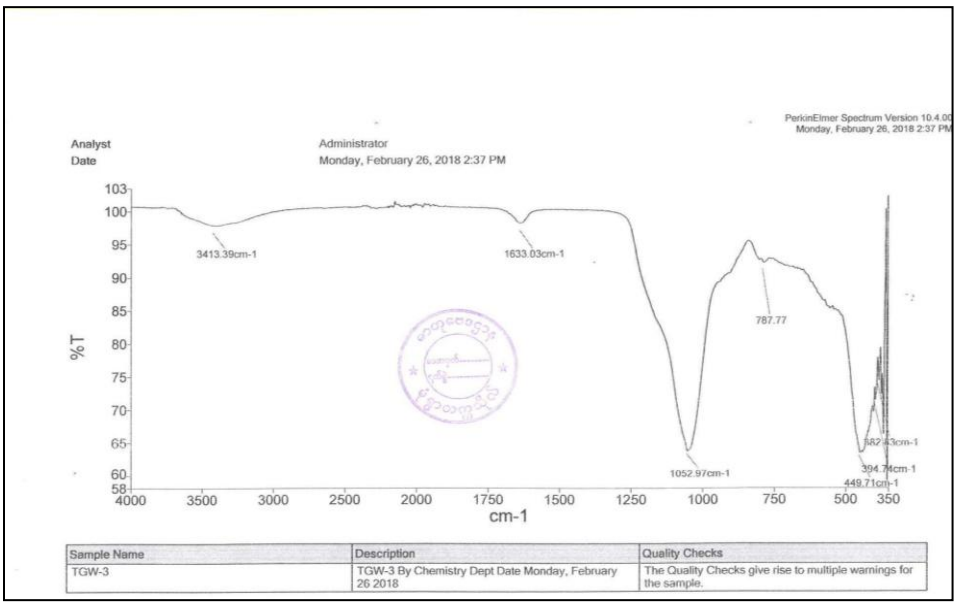
(b)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Quality Checks
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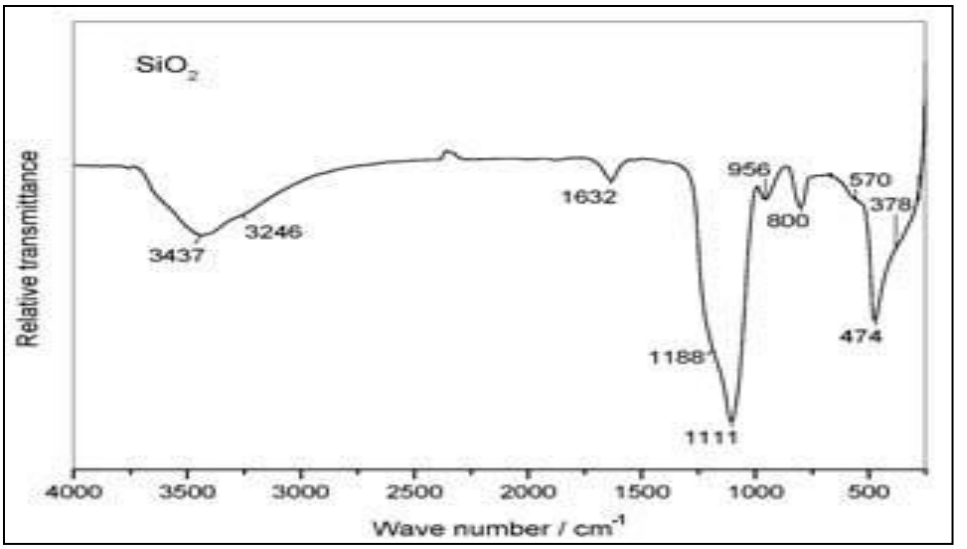
(c)



(d)

Figure 9: FT IR spectra of prepared silica from (a) sample 1 (b) sample 2 (c) sample 3 and (d) reference silica

Table 6: Vibrational Mode for SiO_2 Groups per Unit Cell (Sample 1, 2 and 3)

Assignment	Spectral region assigned for polymorphs of SiO_2(cm^{-1})			
	Sample 1	**Sample 2**	**Sample 3**	**Literature value***
Si-O stretching vibration (motion primarily associated with the oxygen atom)	1052	1052	1054	1200 – 1000
Si-O stretching vibration (motion primarily associated with the silicon atom)	789	787	787	825 – 600
Si-O bending vibration	442 392	449 394	440	600 – 390
Distortion modes	383	382	383	380 – 100

* Ellis, 1958

Conclusion

In this research work, silica was extracted from montmorillonite, clay mineral. The clay mineral was collected from three different sites. The silicon contents found in clay minerals were determined by EDXRF technique. The observed spectra indicated that the amount of silicon was the highest, 10.310 % in sample 1, 10.510 % in sample 2 and 11.850 % in sample 3.

Silica was extracted from clay mineral by using base digestion method. The extraction of silica from three clay samples were performed by chaining the contact times (1 h - 8 h). From the observed data, the optimum contact time was found to be 4 h for all samples. The extraction of silica were performed by using various concentration of NaOH and HCl: 2 M, 4 M, 6 M, 8 M, 10 M. According to concentration effect, the optimum concentration for silica extraction was 8 M for NaOH and HCl. Then, silica was prepared from the samples using different inorganic acids; 8 M HCl, 8 M H_2SO_4 and 8 M HNO_3. From the observed data, the optimum inorganic acid was found to be 8 M HCl.

Each extracted silica was characterized by using FT IR and EDXRF analysis. From EDXRF data, the amounts of silica were found to be 81.892 % for sample 1, 80.005 % for sample 2 and 78.162 % for sample 3.

From FT IR spectra, the peaks at 1052 cm^{-1} for sample 1, 1052 cm^{-1} for sample 2, 1054 cm^{-1} for sample 3 indicated the presence of Si-O stretching modes involving motion primarily associated with the oxygen atom.

In this research work one of the abundant clay minerals, montmorillonite can be converted into silica, valuable product used for several applications in industry. In addition, the silica was used in treatment of toxic metal contaminant waste water. Silica can reduce pollutant level of waste water. The silica obtained is very amorphous. The prepared silica is much valuable product.

Acknowledgements

I am extremely grateful to Dr Khin Maung Oo, Rector, Dr Thidar Aung, Professor and Head, Department of Chemistry, Magway University, for their permitting, understanding, kind helps and good guidance on my study.

References

Amonette, J.E., Zelazny, L. W., Eds. (1994). *Quantitative Methods in Soil Mineralogy;* Soil Science Society of America Miscellaneous Publication: Madison, WI.

Barnhisel, R., Bertsch, P. (1989). Chlorites and Hydroxy-Inter-layered Vermiculite and Smectite. In *Minerals in Soil Environments;* Dixon, J., Weed, S., Eds.; Soil science Society of America: Madison, WI, 729-788.

Brindley, G.W. (1955). "Clays and clay Technology". California Division of Mines, Sanfrancisco. Bulletin 169, P.33.

Ghosh, R., Bhattacherjee, S. (2013). "A Review Study on Precipitated Silica and Activated Carbon from Rice Husk", *Chemical Engineering & Process Technology*, Department of Chemical Engineering, Calcutta Institute of Technology, India, **4** (4) 1-7.

Madrid, R., *et. al.* (2009). "Production and Characterization of Amorphous Silica from Rice Husk Waste", *4th International Conference on Engineering for Waste and Biomass*, Technical University of Lisbon, Portugal, 10-13.

Mehta, A., Ugwekar, R. P. (2015). "Extraction of Silica and other related products from Rice Husk", *Abhishek Mehta Int. Journal of Engineering Research and Applications*, Laxminarayan Institute of Technology, India, **5** (8) 43-48.

Pandey, J. K., Ahn, S. H., Lee, C. S., Mohanty, A.K. and Misra, M. (2010). "Recent Advances in the Application of Natural Fiber based Composites". Macromol. Mater. Eng, Vol. 295 (11), P.975.

Schultz, D. (1989). An Introduction to Soil Mineralogy. In *Minerals in Soil Environments;* Diox. J., Weed, S., Eds.; Soil Science Society of Merica: Madison, WI, 635-676.

Sone, H., Fugetsu, B., Tanaka, S. (2009). "Selective elimination of Lead (II) Irons by alginate/polyurethane composite foams," Journal of Hazardous Materials, Vol. 162, pp.423-428.