Synthesis of Zeolite A from Aluminium and Silica Powder and Applies as a Hemostatic Agent for Natural Disasters

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Abstract: ***In this paper Zeolite A was synthesized by hydrogel solution prepared from silica and aluminium precursor under hydrothermal condition at atmospheric pressure. The important parameter, the crystallization time for three experiments was chosen. Crystallization was carried out at 95±3 °C for 24 hours, 48 hours and 72 hours and which all will term as Zeolite 7 for 24 hour), Zeolite 8 for 48 hour and Zeolite 9 for 72hour). According to the SEM and XRD results, zeolite sample prepared by 48 h crystallization time (zeolite 8) had the good crystalline structure and found to be in closely agreement with reference 2θ value of Na-A. As the hemostatic agent, "Zeolite" as well as the mixture of $CaCl_2$ and Zeolite was tested successfully to stop sever bleeding. The main aim of these study is that those zeolites can be applied for using in emergency case in the fields of not only military use but also for applying as a Hemostatic Agent for Emergency Environmental Disasters.***

Keywords: Zeolite-A, Hydrogel, SEM, EDXRF, TG/DTA, ANOVA

1. Introduction

Nowadays, science and technology has been applied in many areas of our community and the wide scientific applications are also spread rapidly. Recently Zeolites become well-known in our every day and life scientific areas. Many people would like to learn more, and apply them in significant fields such as scientific research work, industries, and health related applications and soon. Zeolite occurs naturally, but it is also produced industrial purposes on a large scale. Since about December 2018, 245 special zeolite systems were identified and more than 40 naturally occurring zeolite frameworks have been observed [9].

Commercial uses and researches of zeolite materials are found widely from laboratories through industrial zones to markets in every country in the world. Zeolites are natural minerals that are minable in many parts of the world, but the most commercial zeolites are produced synthetically [1]- [6].

We also indicate less conventional characteristics of zeolites such as hospitality chemistry and advanced techniques, which are likely to lead to developments of electronics, communication, medicine and also environmental applications. In this paper, it was emphasized that a synthetic zeolite such as low silica Zeolite A can quickly be applied for hemorrhaging wounds kick to start the clotting process.

Since 2002 when the Navy and marine corps introduced fast clot and Hemcon in order to staunch battlefield injuries in which Zeolites have played an important role in first aid. [7]. Today, all US military branches carry packets of the granulated zeolite bandage to the battlefield. More sophisticated products also may be on the way of research, such as toothpaste-like clotting agents of bio-active glass with uniform pores able to deliver antibiotics or other drugs [4]- [5].

In Myanmar, the synthetic zeolites that can quickly be applied to hemorrhaging wounds in battlefields have not been used widely. Some research works dealing with zeolites are appeared in the medical laboratories by the specific technology. The experimental studies and applications become developed more and more quickly. Since zeolite hemostatic agent has been well known as Ca-A as well as Na-A zeolites including non- calcium-exchanged zeolites such as potassium zeolites, lithium zeolites, magnesium zeolites and combinations of those in the studies of zeolite application, the synthesized zeolite powders can be applied as the hemostatic agents by pouring into the wound during these experiments [8]. In this work, Zeolite A was synthesized by hydrogel process, characterized by both conventional and modern techniques, and applied as a hemostatic agent. The main aim of this study is that those zeolites can be applied for using in emergency case in the fields of not only military use but also for applying as a Hemostatic Agent for Emergency Environmental Disasters.

2. Materials

Aluminium powder, Silica powder, Sodium hydroxide (pellet) and $CaCl_2$ were purchased from ATLAS (Myanmar supply Company Ltd.). Both chemicals have been analytical and have not been washed away.

3. Experiment

A. Preparation of Zeolite A by using Hydrogel Process

Alumino silicate hydrogels having the batch molar composition of $2\ Na_2O \times 2\ SiO_2 \times Al_2O_3 \times 70\ H_2O$ were prepared by addition of sodium silicate solution into sodium aluminate solution. Sodium silicate solution was prepared by dissolution of a 6.7 g of silica (99.8 wt. %SiO_2) and 4.5 g of sodium hydroxide (98 wt. % NaOH) in deionized water. Sodium aluminate solution was prepared by dissolution of a2 g of aluminium powder and 4.5 g of sodium hydroxide in deionized water.

Then, the precipitated hydrogels were agitated for 30 min at room temperature and aged for 24 hours at 25°C. **Crystallization was carried out at 95±3 °C for 24 hours, 48 hours and 72 hours and which all will term as Zeolite 7 for 24 hour), Zeolite 8 for 48 hour and Zeolite 9 for 72 hour).** After completing crystallization, the resultant precipitate was separated from the mother liquor by filtration. The crystallization mass is then washed with deionized water until a pH range of 9-10 was reached, and dried at 97 °C for 24 hours. Synthesized Zeolite A samples (assigned as Zeolite 7, Zeolite 8 and Zeolite 9 were analyzed by SEM, XRD and EDXRF methods. Thermal analysis of synthesized zeolite sample was done by using TG/DTA method.

B. Preparation of the Zeolite A Based Hemostatic Agent and Application

In our experiment, 24 mice samples were collected from Biotechnology department, MIT (Medical Institute of Technology), Mandalay. And then, these mice samples were divided randomly into 8 groups of 3 animals. Following giving anesthesia, animal's tails were cut off at thickness of 2 mm by using a pair of surgical scissors. Before treatment six zeolite samples were prepared. The first three samples (Zeolite 8 at 100 °C, Zeolite 8 at 200 °C and Zeolite 8 at 400°C) were prepared by using only zeolite powder drying at respective temperatures. According to some research works [9], sometimes the use of Na-A zeolite alone leads to the anticoagulant effect because it can be removed the Ca^{2+} ion to stop the progression of the clotting pathway. So, to prevent that effect, the other three samples (Zeolite 8+$CaCI_2$ at 100°C, Zeolite8+$CaCI_2$ at 200° Zeolite 8+$CaCI_2$ at 400°C) were prepared by using the mixture of 0.5 g Zeolite powder and 1.7 ml of 0.2 M $CaCI_2$ drying at 100 °C, 200 °C and 400 °C. For the purpose of application, 30 mg of zeolite sample was simply poured into the wound. After treatment with above mentioned agents, the clotting time was measured using a scaled test-tube and chronometer. In this paper, what is referred to as clotting time is the time required from the instant that the blood taken into a blood collecting tube is started on its coagulation process to the time when the blood no longer flows when the tube is placed in an inverted position. Analysis of variance (ANOVA) was used for comparing the means of each parameter in the 8groups.

4. Results and Discussion

A. Characterization of Synthesized Zeolite A by SEM

The SEM results as shown in Figure 1, Figure 2 and Figure 3 indicated the different forms of surface conformations. The SEM photograph indicates the more or less crystalline character. Among the results from the SEM microphotograph, the prepared **Zeolite 8**and **zeolite 9** (crystallization time at 48 h and 72h) were clearly observed that they have more crystalline character than the zeolite 7 (crystallization time at 24h). In the different surface conformations of SEM photographs as shown in Figures (1, 2 and 3), it was found that the surfaces of all samples were composed of cluster of SiO_2 and numerous voids and pores. In this work, the sample Zeolite 8 was chosen for further research works. Because of the shorter crystallization time, if compared with Zeolite 9, which has excellent crystal structure as Zeolite8.

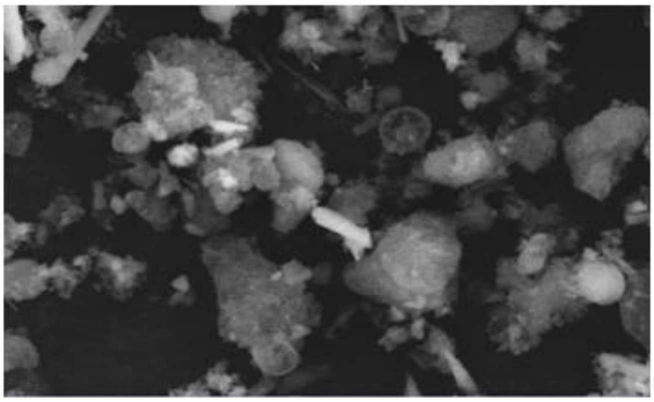

Figure 1: SEM Image of Zeolite7

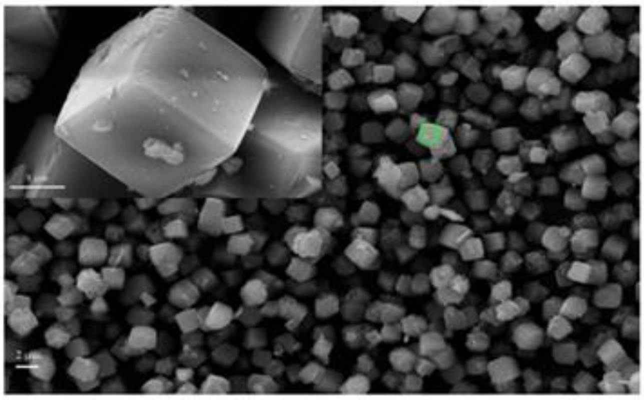

Figure 2: SEM Image of Zeolite8

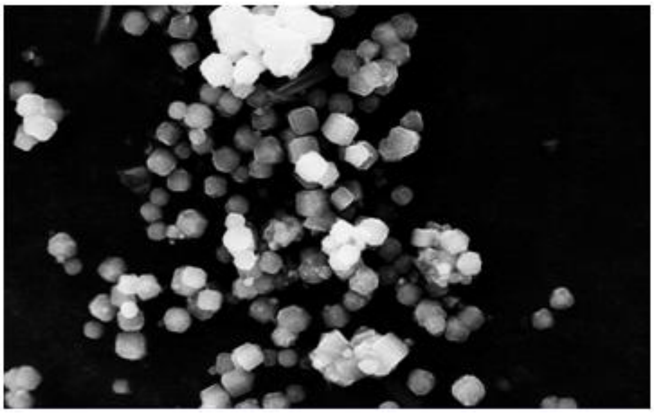

Figure 3: SEM Image of Zeolite9

B. Characterization of Synthesized Zeolite A by XRD

The reference 2θ value of Zeolite A was reported in database of International Zeolite Association (IZA). According to the XRD spectrum, the sample Zeolite 8 was found to be closely in agreement with the reference 2θ value of Na-A. From the XRD spectrum of synthesized Zeolite A, 2θ values of various samples of zeolites were approximately 30 to 40 during this work.

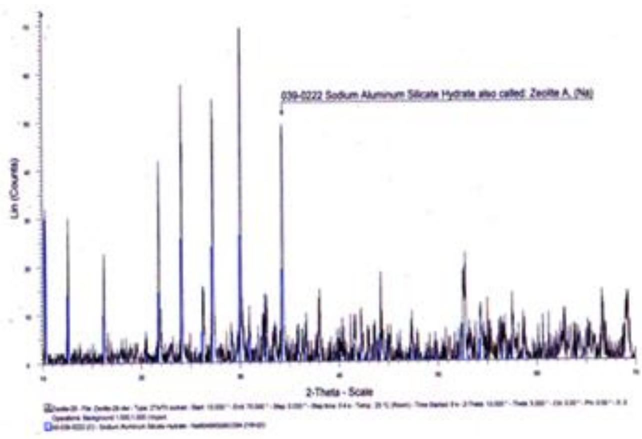

Figure 4: XRD Result of Zeolite 8

C. Determination on the Elemental Composition of Synthesized Zeolite A by EDXRF Technique

The Zeolite sample was determined by using EDXRF as shown in Table. I. The results from this figure, the concentration of element in the sample can be calculated. From the EDXRF result, thesampleZeolite8wasfoundtobeclosely agreement with the molar ratio of SiO_2 and Al_2O_3 of Zeolite A (approximately 1:1) and the hydrogel solution with a molar composition of $2Na_2O$: Al_2O_3: $2SiO_2$: $70H_2O$ and pH (13-14). The chemical composition of SiO_2, Al_2O_3, Fe_2O_3 and CaO were calculated.

Table I: EDXRF Results of Synthesized Zeolite 8 Sample

No	Formula	Z	Line 1	Net int (KCPs)	Cal Conc%	Start error
1	O	8	O KAI	1.935	9.93	0.15%
2	Na	11	Na KAI-HR-Min	4.667	15	1.09%
3	Al	13	Al KAI-HR-Min	18.39	16.4	0.95%
4	Si	14	Si KAI-HR-Min	23.1	17.2	0.84%
5	S	16	S KAI-HR-Min	0.234	0.066	9.10%
6	Ca	20	Ca KAI-HR-Min	14.22	1.71	1.07%
7	Fe	26	Fe KAI-HR-Min	5.2	0.0502	2.00%

D. Analysis of Synthesized Zeolite A by TG/DTA Techniques

During this experimental work, thermal analysis of Zeolite A such as TG/DTA techniques was carried out and discussed these results as follows. The schematic TG/DTA curve of the Zeolite 8 was presented in Figure5. The first small weight loss due to the removal of adsorbed water / alcohol below 100˚C and the second exothermic loss of 30.7% is attributable to decomposition of zeolite materials and crystallization of zeolites crystals. The theoretical weight loss (30.87%) calculated by conversion of the hydroxide precursor to Al_2O_3 is in good agreement with the measured value. The process accounts for approximately one third of the total weight loss in the whole decomposition process from 100 to 800˚C according to the TGA thermogram with the major loss occurring between 200-400 ˚C. A change in weight occurs at 200-400 ˚C, which corresponds to dehydration of the sample. This dehydration also shows up on DTA as an endothermic event.

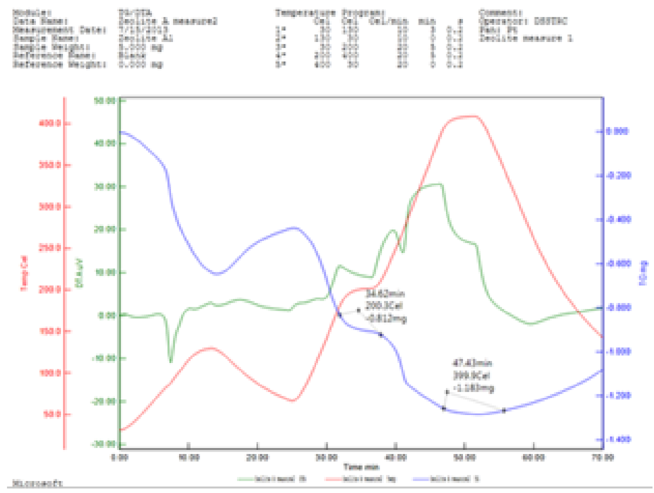

Figure 5: TG/TDA Thermogram of Zeolite

E. Test of Synthesized Zeolite A as Hemostatic agent

The average values of the clotting time in control animals (1st and 2nd group) were 2.26 min and 2.4 min respectively (Table. II). In the 3rd group, in which the animals were treated with zeolite 8 at 100°C, the average value of the clotting time was 0.21 min. In the 4th group, in which the animals were treated with Zeolite 8 at 200°C, the average value of clotting time was 4.5min. In the 5th group, in which the animals were treated with Zeolite 8 at 400°C, the average value of clotting time was 7 min. In the 6th group, in which the animals were treated with Zeolite 8+ $CaCl_2$ at 100 °C. The average value of the clotting time was 1.58 min. In the 7th group, in which the animals were treated with Zeolite 8+ $CaCl_2$ at 200 °C, the average value of the clotting time was 1.43 min. In the 8th group, in which the animals were treated with Zeolite 8+ $CaCl_2$ at 400°C, the average value of the clotting time was 1.44 min.

From the results, the shortest clotting time 0.21 min was obtained when the Zeolite 8 at 100 °C was applied. But, the other two samples (at 200 °C and 400 °C) were found to be increased in the clotting process. Assumed that, drying zeolite samples at higher temperatures, 200 °C and 400 °C for this case, leads to the anticoagulant effect because it can be removed the Ca^{2+}ion from blood to stop the progression of the clotting pathway. To verify this, $CaCl_2$ was mixed with the zeolite samples at 100 °C, 200 °C and 400 °C. As shown in Table. I, the clotting time becomes shorter for the two samples, 1.43min for Zeolite

8+ $CaCl_2$ at 200 °C and 1.44 min for Zeolite 8+ $CaCl_2$ at 400 °C. For the sample Zeolite 8+ $CaCl_2$ at 100 °C the clotting time becomes longer, but still shorter, if compare with the control samples. Assume that, the large amount of water residue from zeolite+$CaCl_2$ mixture can decrease the dehydration level of sample and slow the clotting time. [10]–[11]. Therefore, the optimum drying temperature for the preparation of zeolite+ $CaCl_2$ mixtures must be higher than 100°C.

Table II: Comparison of Clotting Time between Control Mice's Blood and the other Tested Samples with Treatment of Different Materials

Sr No	Name of Sample	Amount of sample mg	Clotting Time (min)
1	Control I	No Treatment	2.26
2	Control II	No Treatment	2.4
3	Zeolite 8 at 100°C	30	0.21
4	Zeolite 8 at 200°C	30	4.5
5	Zeolite 8 at400°C	30	7
6	Zeolite 8 + $CaCl_2$ at 100°C	30	1.58
7	Zeolite 8 + $CaCl_2$ at 200°C	30	1.43
8	Zeolite 8 + $CaCl_2$ at 400°C	30	1.44

5. Conclusion

In this paper, it has been informed the chemical structures of zeolites including characterization by SEM, XRD and EDXRF techniques. This paper emphasizes for the synthesis of Zeolite A and its application as hemostatic agent. In the present work, Zeolite A was prepared via hydrogel method from silica and aluminium under hydrothermal condition at atmospheric pressure. Characterization of the prepared Zeolite A was carried out using SEM, XRD and TGA thermos gram. The results revealed that zeolite sample prepared by 48 h crystallization time had the good crystalline structure.

The ANOVA method was used to determine the significant properties of Zeolite A that has the availability of clotting function in the blood. As the hemostatic agent, "Zeolite" as well as the mixture of $CaCl_2$ and Zeolite was tested successfully to stop, sever bleeding. According to the tests, zeolite sample drying at 100 ˚C and the zeolite mixture (containing zeolite + $CaCl_2$) drying at 200 ˚C have the shorter clotting times 0.21 min and 1.43 min, respectively, if compared with other samples. Shorter clotting times 0.21min and 1.43 min respectively when compared with the other samples.

According to the tests, the volume of blood lost and the bleeding time of the tested mice group, which are treated with these two zeolite samples also reduce about half time, when compared with the control groups.

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