Antibacterial Characteristic of Impregnated-Activated-Zeolite/Alumina/Glass-Ionomer-Cement Composites

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Abstract. In this present paper, we introduce the beneficial use of Indonesian activated natural zeolite, precisely from Malang area, for a potential restorative material after combined with alumina and glass ionomer cement. The activated zeolite was previously impregnated by copper (II) chloride prior to prepare the composites of impregnated-activated-zeolite/alumina/glass-ionomer-cement composites. The X-ray fluorescence (XRF) test results support the X-ray diffraction (XRD) data in revealing the crystalline phase contents. The composites comprise of mordenite, sanidine, quartz, orthoferrosilite, and tolbachite. Scanning electron microscopy (SEM) photographs dictate the uniform CuCl₂ impregnation to the activated zeolite. The CuCl₂ impregnation, moreover the addition of alumina crystalline powder and GIC polymer, increase the density of activated zeolite. Finally, the impregnated-activated-zeolite/alumina/glass-ionomer-cement composites exhibit acceptable mechanical and antibacterial characteristics for dental restorative implants.

Keywords: Antibacterial, mechanical strength, phase compositions, restorative material.

1. Introduction

Bacterial activities in the mouth may lead to broken teeth issues [1], which is mostly driven by unwanted microorganisms [2]. The painful effect of those bacterial activities is permanently-damaged areas in teeth that may develop into holes, known as dental caries. It is one of the most common and injuring oral health disease. The best way to cure the disease is to use a restorative treatment [3]. A restorative treatment for dental caries is meant for removing insensitive and demineralized outer carious dentin; glass ionomer cement (GIC) is a harmless dental restorative material as filling and luting cement even for orthodontic attachment.

Though GIC is harmless, its crushing strength, compared to other restorative materials, is relatively a low crushing strength and is easy to dissolve in mouth liquids [4-5]. Additionally, GIC is often eroded by saliva giving accumulation of secondary caries [6]. Therefore, it is important to introduce another antibacterial material that is safe for a dentistry application. Nature provides such material in the form of calcium aluminum silicate hydrate, which can be obtained from the natural zeolite. It has good structure and porous stability for ion changes. On top of that, it shows a higher mechanical strength compared to GIC [7].

Prior to practical use, the natural zeolite needs to be activated by means of physical and chemical processes to eliminate impurities and enlarge its surface area [8]. To enhance the antibacterial properties
of activated zeolite, CuCl₂ impregnation is required to control the microorganism growth. Another study reported that CuCl₂-impregnated zeolite has an excellent resistant to streptococcus mutans bacteria [9].

The desired applicable GIC-based restorative material can be obtained by not only introducing CuCl₂-impregnated activated zeolite but also adding extra metal oxides to enhance both mechanical strength and toughness. For this purpose, alumina meets all the requirements [8]. Therefore, impregnated-activated-zeolite/alumina/glass-ionomer-cement composites may contribute as secure dental restorative materials.

2. Materials and Methods
The natural zeolite sample was taken from Malang, Indonesia. The activation of the zeolite was done by washing zeolite powder and stirring for 4 h at 600 rpm in an ambient condition followed by heating at 120 °C for four h and immersing in 1% HF solution for 30 minutes and another heating at the same temperature and duration. Further treatment through 6 M HCl immersion for 30 minutes was completed, again, stirring at 600 rpm for four h. The residual powder after the second washing was immersed in 1 M NH₄Cl solution at a temperature of 90 °C for 3 h and finally sieved and heated at 120 °C for four h to obtain activated zeolite. The activated zeolite was impregnated by copper (II) ions via 0.3 M CuCl₂ solution at 600 rpm and 100 °C for one hour. The CuCl₂-impregnated activated zeolite was accomplished after washing and heating the powder at 100 °C for 24 h. Furthermore, GIC powder, impregnated activated zeolite, and alumina were mixed at various compositions by the following labelling convention: the weight fractions (%) of impregnated-activated-zeolite/alumina/GIC in sample A = 0/0/100, sample B = 50/0/50, sample C = 40/10/50, sample D = 30/20/50, sample E = 25/25/50, sample F = 20/30/50, sample G = 10/40/50, and sample H = 0/50/50. Finally, important characterizations by means of XRF, XRD, SEM, Vickers hardness, and antibacterial test.

3. Results and Discussion

Previous to XRD test, an elemental tracking of the zeolites, which can be seen in Table 1, was conducted by means of XRF. Table 1 shows elements (above 1%) within the prepared sample. Si is the most predominant atom, followed by Ca and Fe. As it is expected, Cu appears only after CuCl₂ impregnation. The atomic fractions for the constituents, except Al, tend to decrease because of the impregnation. Oxide compounds, detected by XRD, are based on these atoms.

| Sample                        | Atomic fraction (%) |
|-------------------------------|---------------------|
|                               | Si      | Fe      | Ca      | Al      | K      | Cu     |
| Activated zeolite             | 54.3    | 17.4    | 13.7    | 7.9     | 5.4    | -      |
| CuCl₂-impregnated activated   | 49.3    | 10.2    | 4.8     | 8.3     | 4.4    | 9.6    |
| zeolite                       |         |         |         |         |        |        |

The XRD patterns of purified activated zeolite before and after CuCl₂ impregnation are shown in Figure 1. Changes in XRD patterns are detected in terms of diffractions peaks and intensities. Further analysis using RIR method was conducted and the results are represented in Figure 2. The crystalline constituents in the activated zeolite, in line with the XRF results, are 45% mordenite (Ca₃Al₂Si₄O₁₄(H₂O)₃), 23% quartz (SiO₂), 21% sanidine (K(AlSi₃)O₈), and 11% orthoferrosilite (FeSiO₃). Meanwhile, CuCl₂-impregnated activated zeolite contains 37% mordenite (Ca₃Al₂Si₄O₁₄(H₂O)₃), 32% sanidine (K(AlSi₃)O₈), 14% quartz (SiO₂), 13% orthoferrosilite (FeSiO₃), and 4% tolbachite (CuCl₂). Physically, CuCl₂ impregnation changed the color of the activated zeolite from yellowish-white to grey-white.
Figure 1. XRD patterns of activated zeolite and CuCl$_2$-impregnated activated zeolite.

(a)

(b)

Figure 2. Phase identifications using RIR approach of (a) activated zeolite and (b) CuCl$_2$-impregnated activated zeolite.
Figure 3. Microstructure pictures of activated zeolite before (left) and after (right) CuCl$_2$ impregnation. The scale-bar represents 2 µm in length.

Figure 3 shows the SEM images of the zeolites. Both unimpregnated and impregnated zeolites perform similar particulates distribution, surface shape, and roughness. It is driven by the uniform CuCl$_2$ impregnation. Si/Al ratio, from SEM-EDX data, for activated zeolite and CuCl$_2$-impregnated activated zeolite, are respectively 4.63 and 5.31. Si/Al ratio for zeolite indicates the adsorption and ion transfer abilities. The larger Si/Al ratio of the impregnated sample provides better characteristics of zeolite. The particles of the impregnated activated zeolite are slightly denser than that of the pre-impregnated sample. It is due to impurities dissolution after acid pretreatment and CuCl$_2$ impregnation.

The composite of 25%-impregnated-activated-zeolite/25%-alumina/25%-GIC (sample E) and pure GIC polymer XRD profiles are given in Figure 4. Besides mordenite, sanidine, quartz, orthoferrosilite, and tolbachite, corundum-Al$_2$O$_3$ XRD peaks are found in the Bragg angles of 25.6°, 35.1°, 37.8°, 43.5°, 52.6°, 61.3°, 68.4°, and 77.6°. Broad XRD profiles of GIC represents that amorphous phase of the GIC polymer.

Figure 4. XRD patterns of GIC and 25%-impregnated-activated-zeolite/25%-alumina/25%-GIC.
Figure 5. SEM image of 25%-impregnated-activated-zeolite/25%-alumina/25%-GIC.

The corresponding SEM image of sample E is shown in Figure 5. Unlike the microstructures of impregnated activated zeolite, the composite of sample H shows even denser aggregates due to the presence of GIC polymer and alumina. This is the desired microstructural properties of the dental restorative material to fill the holes in human teeth.

Figure 6(a) represents the mechanical strength regarding Vicker’s hardness number (VHN) and Figure 6(b) shows the antibacterial characteristic regarding the inhibition zone diameter. Note: the inhabitant of the composites was tested to *Streptococcus mutans* bacteria. To test the antibacterial performance, the composites were dissolved in water and incubated overnight. The incubation will provide an inhibition zone with which its diameter can easily be measured. A slow release agent mechanism due to copper (II) ions diffusion to the cell membrane of *Streptococcus mutans* bacteria. The oligodynamic properties of copper (II) ions within the composites reduce the growth of the microorganism.

Figure 6. (a) Mechanical strength and (b) antibacterial characteristic of impregnated-activated-zeolite/alumina/GIC composites.
Other reports showed that the concentration of silver nanoparticle reinforcement in the system of Ag/GIC increased the net setting time and the compressive strength over 30% larger than that of pure GIC. In terms of antibacterial performance, GIC reinforced Ag nanoparticle has significantly induced *Escherichia coli* and *Streptococcus mutans* growth inhibition zones due to the Ag⁺ ions diffusion [10]. In general, all samples perform different mechanical and antibacterial characteristics. Fig 6 reveals the VHN of pure GIC is near 80, similar with sample G and H. However, the pure GIC shows a severe antibacterial property, its inhibition zone diameter is below 2 mm, identical to sample H. Therefore, sample H is not recommended as a proper dental restorative material. On the other hand, sample B and C perform a relatively excellent inhibitive feature, but their VHNs are relatively low. Sample D and E have HVN values above 50 (below sample F), and the inhibition zone diameter is around 10 mm, slightly higher than that of sample F. Hence, the incorporation of alumina and impregnated activated zeolite enhance the GIC characteristic, particularly the mechanical and antibacterial properties.

4. Conclusion

To conclude, a dental restorative material from impregnated activated zeolite/alumina/GIC composites have been successfully prepared. The prepared composites comprise of crystalline phases of mordenite (Ca₂Al₂Si₄O₁₂(H₂O)₉), quartz (SiO₂), sanidine (K(AlSi₃)O₈), orthoferrofesilite (FeSiO₃) tolbachite (CuCl₂), and corundum-Al₂O₃; and amorphous phase of GIC polymer. The microstructural analysis reveals that the alumina and GIC lead to denser composite-particles. In addition, the mechanical (in terms of Vickers hardness) and antibacterial (in terms of inhibitive performance) characteristics of GIC after CuCl₂ impregnated activated zeolite and alumina addition are feasible to be applied as in dentistry.

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