

Article

Production of the Hydroxyl Radical and Removal of Formaldehyde by Calcined Green Tuff Powder and Tile

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Abstract: Waste green tuff powder produced by cutting Towada stone has been utilized to eliminate formaldehyde related to greenhouse gases. The green tuff contains TiO₂ on zeolite as observed by scanning electron microscope (SEM). The green tuff is a natural catalyst that can produce hydrogen peroxide with moisture and oxygen with light. The optimum temperature for calcination of the green tuff powder has been investigated in order to produce hydroxyl radicals from the decomposition of hydrogen peroxide using ultraviolet light (UV) and no light. The green tuff calcined at 800 °C showed a high decomposition rate of hydrogen peroxide with no UV light under high alkaline conditions when measured by using ESR. With UV light, the optimum temperature for calcination of green tuff powder in order to reduce the hydroxyl radical was also 800 °C. Next, the powder calcined at 800 °C was used to produce the tile by compression and heating, and then the formaldehyde adsorption rate was measured. The green tuff powder calcined at 800 °C showed a high adsorption rate, similar to that of the activated carbon. The tiles formed at 40 MPa and heated at 1100 °C were the strongest and also showed adsorption with respect to formaldehyde. The adsorbed formaldehyde on the green tuff tile and powder was possibly decomposed by the hydroxyl radical produced by photocatalysis.

Keywords: green tuff; towada stone; calcination; recycle; tile; hydrogen peroxide; radical; ESR; adsorption; formaldehyde; UV; photocatalysis

1. Introduction

For sustainable development, it is necessary to reduce greenhouse gases, not only CO₂ but also other related gases and to recycle waste materials. In this report, by utilizing rock (green tuff) cutting waste powders, the possibility of reducing formaldehyde [1,2], which is a volatile organic compound recognized by WHO, was investigated. Green tuff is a sedimentary rock formed in rivers and lakes from 20 million to 15 million years ago and is distributed widely along the coast of the Sea of Japan in the Japanese Archipelago [3]. Nowadays, Hinai Green tuff, a beautiful greenish color block (Towada Stone) found in Akita prefecture, Japan, is utilized in building walls and floors, and so on [4]. However,

when the tuff stone is quarried and ground, about 60% of all quarried stone becomes waste powders and about 4000 t of powder per year are discharged and wasted. It is important to utilize a large amount of produced green tuff powder. Several applications have been suggested to use cutting powder of green tuff, for example, utilization in food processing [5], activation of microorganisms [6], precipitation reagents for wastewater treatment [7], and adsorption of chemical substances [8]. Sugai et al. produced several boards of green tuff aggregate (1-3 mm and less than 1 mm in size) using a mixture with 40 wt% of white Portland cement at 20 °C for 10 days. They measured the adsorption capacity of toluene and formaldehyde in the air using these boards and reported that the adsorption was similar to the board used in diatomaceous earth [8]. LIXIL Co. produced the “ECOCARAT” tile to adsorb the toluene and acetaldehyde [9]. Both articles explained that the reason for volatile chemical substance removal in the air was adsorption onto porous materials. However, the adsorption amount was limited. On the other hand, if the chemical substances can be decomposed by a photocatalyst, it is more effective to remove the adsorbed chemical substances to prevent desorption. The metal oxides (such as TiO₂, WO₃, ZnO, Fe₂O₃, Ta₂O₅, and CuO) are heterojunction photocatalysts [10]. Davari et al. reported that synthesized ZnO/Fe₂O₃ and TiO₂/Fe₂O₃ on zeolite could decompose the organic substance [11]. As the calcined green tuff contains small amounts of similar components, the elemental distribution is measured and investigated, especially for TiO₂ existence on zeolite. If the natural photocatalyst exists, the synthetic photocatalyst production cost can be reduced. Photocatalytic production of hydrogen peroxide on semiconductors, such as TiO₂, has been reported using water and oxygen with UV; however, hydrogen peroxide can be produced by using visible light [12,13]. The produced hydrogen peroxide can be decomposed by higher alkaline [14], UV light irradiation and Fenton reaction with Fe²⁺ ions. As the produced hydroxyl radical can react to formaldehyde, the better hydrogen peroxide decomposition conditions are examined after the calcination of green tuff at various temperatures. Hoshiba et al. reported the generation of hydroxyl radicals from the calcined dolomite powders dispersed in H₂O₂ [15]. In this experiment, the hydroxyl radical existence is measured with ESR and spin trapping agent G-CYPMPO under no UV and UV irradiation. The adsorption and decomposition of formaldehyde on photocatalyst rutile are also reported by Liu et al. [16]. Next, a certain amount of formaldehyde in a closed room can be adsorbed onto green tuff powder and tile and compared with activated carbon. In the practical use to remove formaldehyde associated with sick building syndrome [1], the tile is more convenient. The strength of produced tiles was also investigated by changing pressing and calcination conditions. In case of the adsorption of formaldehyde, the materials reached the saturation concentration of formaldehyde. It is suggested that the photocatalyst can decompose the adsorbed formaldehyde, due to the presence of the hydroxyl radical on calcined green tuff or tile.

2. Materials and Methods

2.1. Materials of Green Tuff Powder

The green tuff powder is a sedimentary rock that provides us with evidence about the formation process of the Japanese Archipelago [4] and is collected from the “Towada stone” cutting place in the quarry to produce architectural materials, such as walls and floor flat tiles in Odate city of Akita prefecture, Japan. The composition of the as-received green tuff is listed in Figure 1. As-received means original cutting waste green tuff powder less than -100 mesh in size. The composition was analyzed by means of an X-ray fluorescence spectroscope (XRF). The iron oxide is mainly ferrous in as-received powders. The main composition minerals are albite 35%, quartz 25%, chlorite 7%, zeolite 5%, stilbite 3% and laumontite 2% by XRD and the average density is 2.1g/cm³, the specific surface area is 4.0m²/g, the peak in pore size distribution is 51 nm and pore volume is 0.028 cm³/g. [6]. The zero point of charge is about pH 2.5 [7].

Composition	Content ,w/v %			
Na ₂ O	0.30	Minerals in Towada green tuff		
MgO	0.73			
Al ₂ O ₃	9.16			
SiO ₂	61.69		Albite (NaAlSi ₃ O ₈)	35%
P ₂ O ₅	0.21		Quartz (SiO ₂)	25%
SO ₃	0.17		Chlorite(Mg,Fe,Al) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈	7%
Cl	0.04			
K ₂ O	6.19		Zeolite	5%
CaO	4.07		Stilbite (CaAl ₂ Si ₇ O ₁₈ ·7H ₂ O)	(3%)
TiO ₂	0.71		Laumontite(Ca ₄ Al ₈ Si ₁₆ O ₄₈ ·18H ₂ O)	(2%)
MnO	0.49			
FeO or Fe ₂ O ₃	14.42~16.03			
Co ₂ O ₃	0.01		Residual	28%
ZnO	0.07			
Rb ₂ O	0.03			
SrO	0.08			
Total	98.37~99.98			

Figure 1. Chemical composition of as-received green tuff (Towada stone) powder and mineral composition [6].

Next, the green tuff powder was calcined at 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C, 1100 °C, and 1200 °C for 10 min, and the calcined powder was kept dry. As a result, all FeO changed to Fe₂O₃ by heating in an air atmosphere. The green tuff powder and the shape of the calcined powder were investigated by SEM, and the element distribution by EDS.

2.2. Hydroxyl Radical Measurement by ESR

The green tuff powder (1g) was mixed in a 50 mL tube with 0.1 w/v hydrogen peroxide, which was derived by diluting 35 w/v% hydrogen peroxide. To investigate the radical characteristics, ESR measurement using a spin trap reagent is necessary. After mixing, the tube was strongly shaken for 10 seconds. In this study, a novel radical trapper, {2-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)-3,4-dihydro-2-methyl-2H-pyrrole N-oxide, G-CYPMPO}, was used to trap free radicals [17]. The chemical structure of G-CYPMPO is shown in Figure 2a. G-CYPMPO®(100 mM, 25mg) was dissolved in 2 mL ultrapure water. PO₄ buffer 1mM flow is used. A JEOL JES-TE25X ESR spectrometer was used to record ESR spectra of spin adducts. Typical ESR measurement conditions were as follows: microwave power, 4 mW; microwave frequency, 9.2 GHz; magnetic field, 328.0 mT; field sweep with, ±7.5 mT; field modulation, 0.16 mT; sweep time, 1 min; 0.003663 mT/Point, 4096 points in total. ESR measurements were performed at room temperature.

The hydroxyl radical is generated by the decomposition of 0.1 w/t% hydrogen peroxide under 5s UV-irradiation with a UV-irradiator (SUPERCURE-203S UV LIGHTSOURCE, USHIO INC., Tokyo, Japan) and the observed ESR spectra are shown in Figure 2b.

ESR of G-CYPMPO toward the hydroxyl radical has been investigated by Oka et al. and shows eight peaks [18]. It is possible to compare any peaks of hydroxyl radicals; however, in this experiment, the central 4th peak (marked with inverted triangle) is used to compare ESR intensity for hydroxyl radicals in the absence and presence of green tuff powders. Also, Kohri et al. used the one central peak to compare the other data [19]. In the plot of $I_0/I - 1$, I_0 and I denote ESR intensity in the absence and presence of green tuff powder oxidant species, respectively. To investigate the effect on calcination temperature of green tuff powder for free radical generation, 0.5 g of green tuff powder, calcined at different temperature, was hydrated with 0.1 w/v hydrogen peroxide for 24 h before ESR measurement.

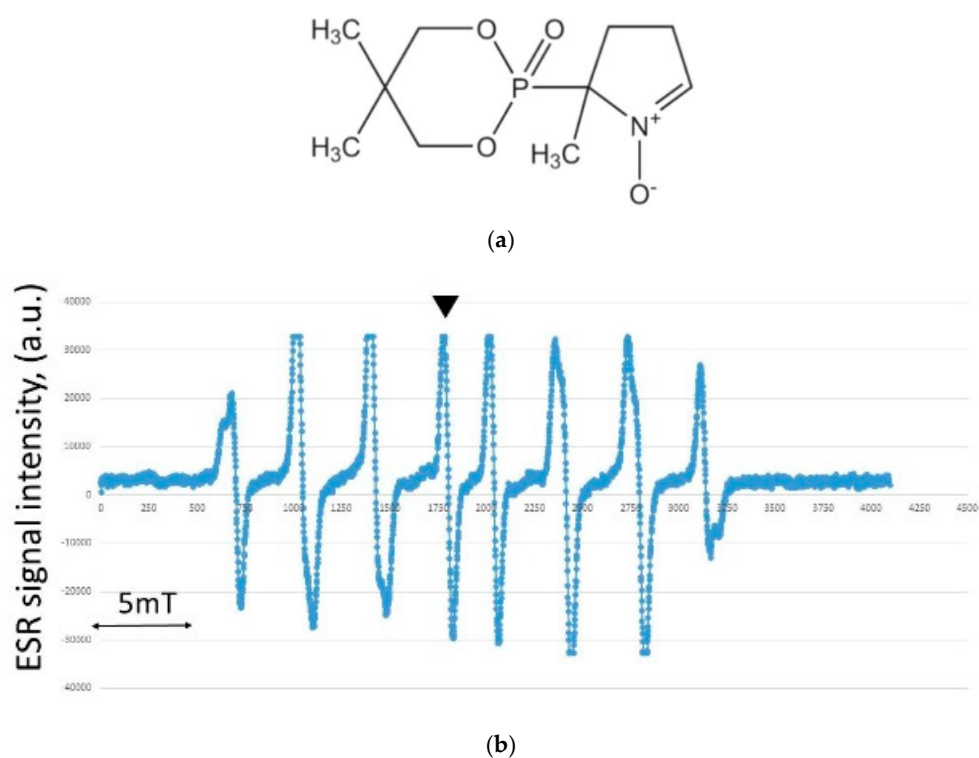


Figure 2. Chemical Structure of G-CYPMPO (a) and the ESR spectra of G-CYPMPO-trapped adduct in UV-illuminated hydrogen peroxide solution (0.1 w/v%) (b).

2.3. Production of Tile Using Calcined Green Tuff Powders

The calcined powders are used to produce the tile. The tile can be used as building materials (i.e. for wall and floor), since its quality is comparable to other conventional materials. In this experiment the small manually operated molding machine is used to produce the rectangular molded blocks as shown in Figure 3.

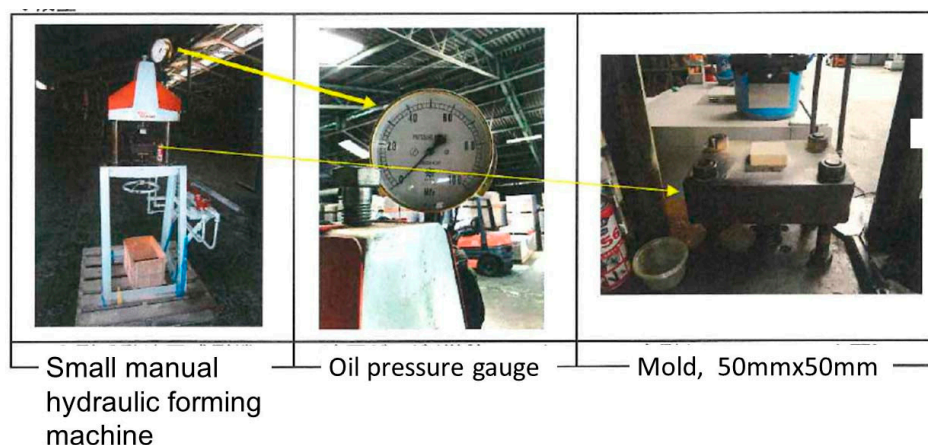


Figure 3. Photographs of oil pressure molding apparatus.

A 55 g sample of green tuff powders was first calcined at 800 °C and then used for molding in each block without additives. Two pressures, 20 and 40 MPa, are applied to form the blocks with no additives. Next, the molded blocks are heated and kept at 800, 1000 and 1100 °C for 15 min. The blocks are heated at those temperatures and pressures by using 800 °C calcined green tuff powder and several tiles are produced. The photograph of produced tiles is shown in Figure 4. The color of tile changed

from yellow to black at 1100 °C. The strength of tile produced at 1100 °C and 40 MPa is the highest. On the other hand, the tile heated at 800 °C is easily broken and forms a powder. Therefore, only tiles heated at 1000 °C and 1100 °C are used in this experiment.

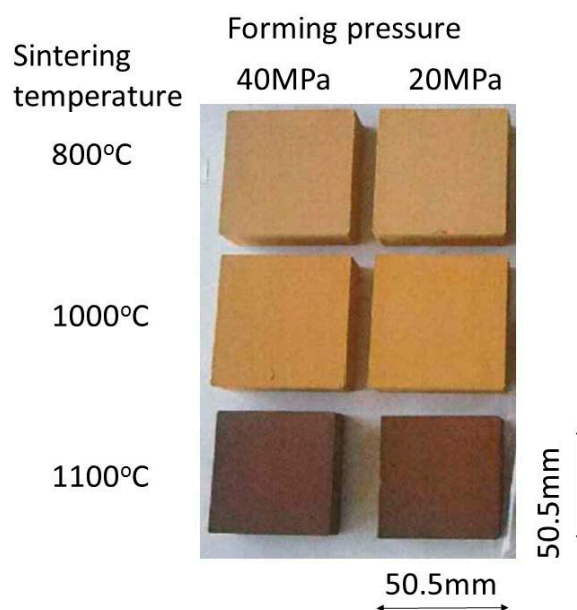


Figure 4. Photograph of tiles prepared by using compressed 800 °C green tuff powder. (Tile size is 50.5 × 50.5 mm, Thickness 14.5 mm at 40 MPa and 15.7 mm at 20 MPa).

2.4. Formaldehyde Adsorption Experimental Method

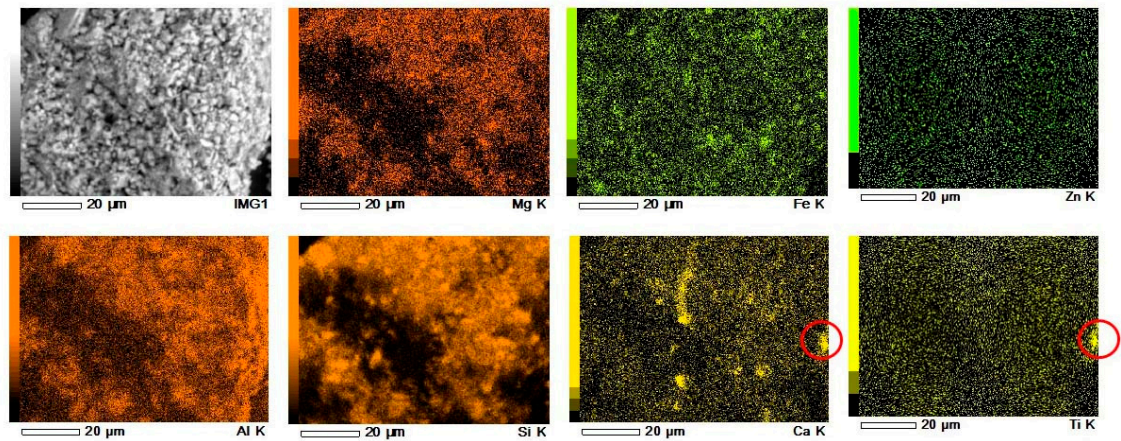
Formaldehyde at concentrations above 0.1 ppm in air can irritate the eyes and mucous membranes, resulting in watery eyes, causing the so-called sick building syndrome. The adsorption experiment of formaldehyde is studied using various green tuff powders and tile. The reagent grade formaldehyde (HCOH, Wako Pure Chemical Industries, Ltd, Osaka, Japan) is about 37% aqueous solution with methanol. A small amount of formaldehyde is vaporized in the 0.25 m³ of glove box. The initial concentration of formaldehyde in glove box is regulated at 0.6 ppm. Next, 55g of green tuff powder or tile is put on the floor in the glove box and the concentration of formaldehyde is measured as a function of time. The weight percent of green tuff in the room is 220 g/m³. The comparison of adsorption, the granular activated carbon (Wako Pure Chemical Industries, Ltd, Osaka, Japan) is used at the same weight. Formaldehyde concentration is measured by a formaldehyde detector (FP31, RIKEN KEIKI Co., Ltd, Tokyo, Japan).

3. Results and Discussion

3.1. Calcined Green Tuff Powder

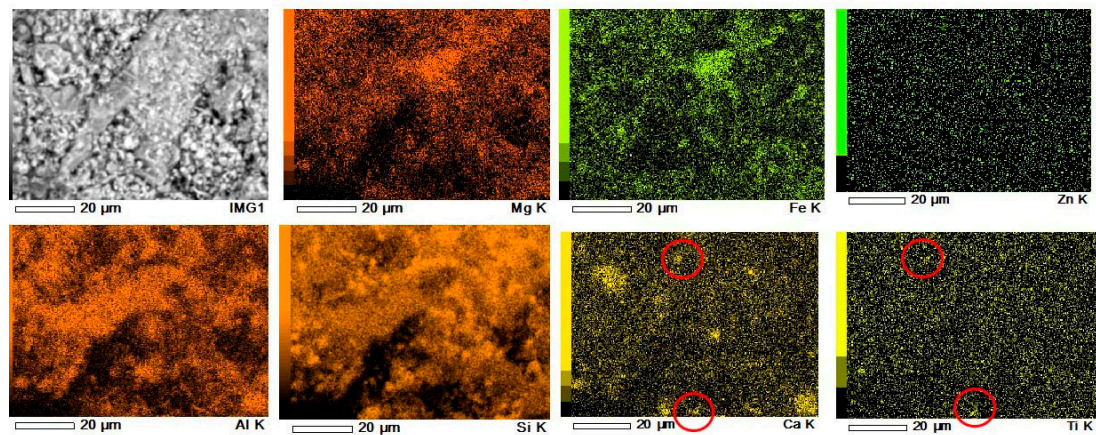
The surface structure has been observed by SEM, and Al, Mg, Si, Fe, Ca, Zn and Ti elemental maps are obtained. Figure 5 shows the SEM images of the fine particles, calcinated at 800 °C and compared with as-received particles. At 1100 °C, the small particles are coagulated and sintered to slightly larger particles, compared with particles calcinated at 800 °C; however, several pores are still observed. The elemental maps show that Si and Al, the main elements, have similar distributions except for quartz, considering the mineral composition shown in Figure 2. The corresponding particles of Mg and Fe map show mainly chlorite. The Ca map shows mainly zeolite in Figure 2. A concentrated Ti map corresponds to the Ca map and they are indicated in circles, which are observed in all as-received samples and those calcined at 800 °C and 1100 °C. On the other hand, the Zn map cannot be measured due to a small percentage. The fine grains of TiO₂ on zeolite may be a photocatalyst in any green tuff.

As-received green tuff powder



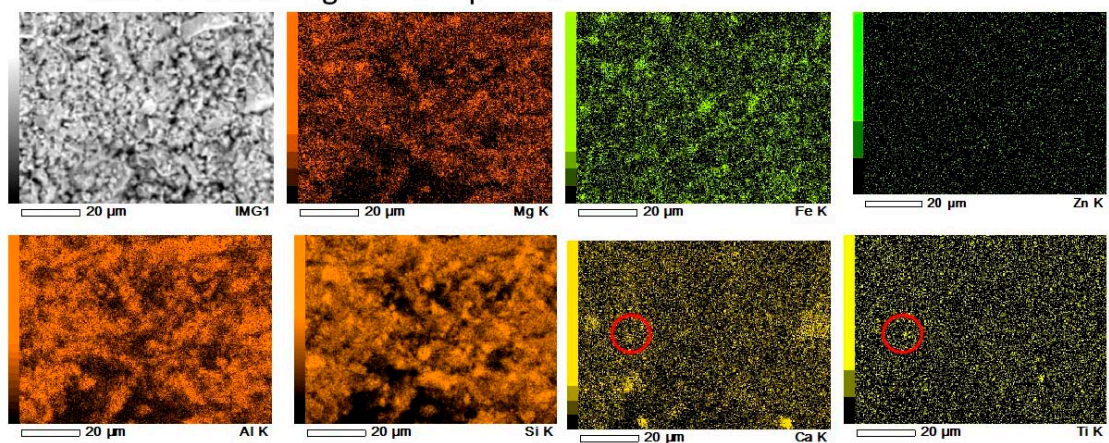
(a)

800°C calcined green tuff powder



(b)

1100°C calcined green tuff powder



(c)

Figure 5. SEM and EDS elemental maps of Mg, Fe, Al, Si, Ca, Ti and Zn for as-received (a), 800 °C calcined (b) and 1100 °C calcined (c) green tuff powder. Ti and Ca corresponding locations are shown in red circles.

If TiO_2 on zeolite in green tuff and calcined green tuff are photocatalyst, the hydrogen peroxide can be produced as indicated in the following equation as positive hole h^+ [12,19].



3.2. pH Change of Calcined Green Tuff Powder

The produced hydrogen peroxide is unstable at higher pH [14] and is decomposed to hydroxyl radicals. The effect of pH in dispersed calcined green tuff and as-received green tuff have been investigated. The 1wt% of as-received green tuff powder and green tuff powder calcined at 500 °C, 800 °C, 1200 °C are put into ion-exchange water and agitated by a magnetic stirrer. The pH of the passed agitation time is shown in Figure 6. The green tuff powder calcined at 500 °C and 800 °C shows higher pH compared with as-received green tuff at 9.7, whereas the 1200 °C calcined tuff powder has a lower pH. The highest pH shows 800 °C calcined green tuff and reaches pH 10.7. This pH increase by calcination is similar to the calcined dolomite [15]. The alkaline solution can decompose hydrogen peroxide and it seems the 800 °C calcined green tuff has the greatest decomposition ability.

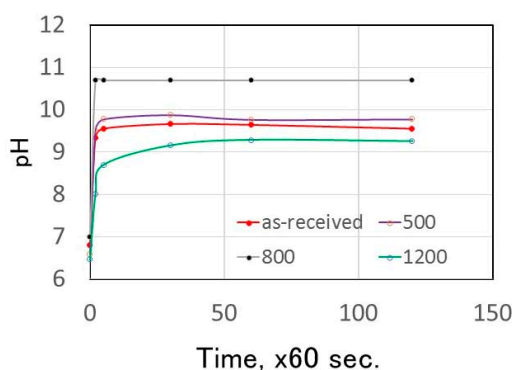


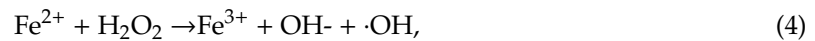
Figure 6. pH change depending on time for as-received green tuff and calcined green tuff at different temperatures.

3.3. Results of Hydroxyl Radical Measurement

The green tuff powder and calcined powder are put into 0.1wt% H_2O_2 solution. ESR spectrum measured after 24 h without UV irradiation is shown in Figure 7. There is no spectrum for powder added to only 0.1wt% H_2O_2 solution and green tuff powder calcined at 1200 °C. In the as-received green tuff powder, small peaks of ESR spectrum are observed. On the other hand, green tuff powder calcined at 800 °C shows a large ESR spectrum of hydroxyl radical even if it is not UV irradiated. It is considered that the H_2O_2 decomposed by powder calcined at 800 °C with higher pH as shown in Figure 6. When strong UV light is applied to the all specimens, large hydroxyl radical ESR peaks are observed. The ESR spectra of only 0.1% of H_2O_2 in water and green tuff calcined at 800 °C added to 0.1% of H_2O_2 in water with UV are shown in Figure 8. The height of the fourth peak is compared. The hydroxyl radical can decrease by the addition of calcined green tuff. The ESR peak ratio $I_0/I - 1$ depending on calcined temperature and pH is shown in Figure 9. The green tuff calcined at 800 °C decreases the hydroxyl radical at the highest pH. When the calcination temperature is higher than 1200 °C it is impossible to decompose the hydroxyl radical by decreasing the pH. At higher than pH 10, the decomposition of hydrogen peroxide occurs easily. By irradiating UV light, H_2O_2 produces the hydroxyl radical ($\cdot\text{OH}$) in the following equation [20]. Here, h is Planck's constant and ν is light frequency.



The Fenton reaction is shown by the following equation; however, this spectrum by ESR is indicated by Equation (3), as the iron in calcined green tuff is Fe^{3+} .



The green tuff calcined from 600 °C to 1100 °C reduces the hydroxyl radical faster and the one calcined at 800 °C is the largest reduction material of the hydroxyl radical.

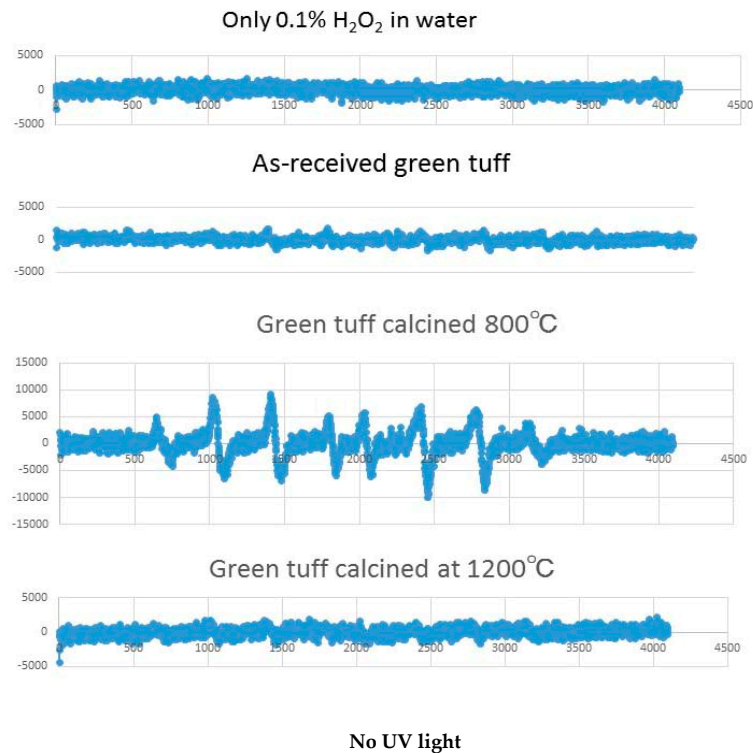


Figure 7. ESR spectra of 0.1% of H_2O_2 in water, as-received green tuff, calcined 800 °C green tuff and 1200 °C calcined green tuff added to 0.1% of H_2O_2 in water without UV.

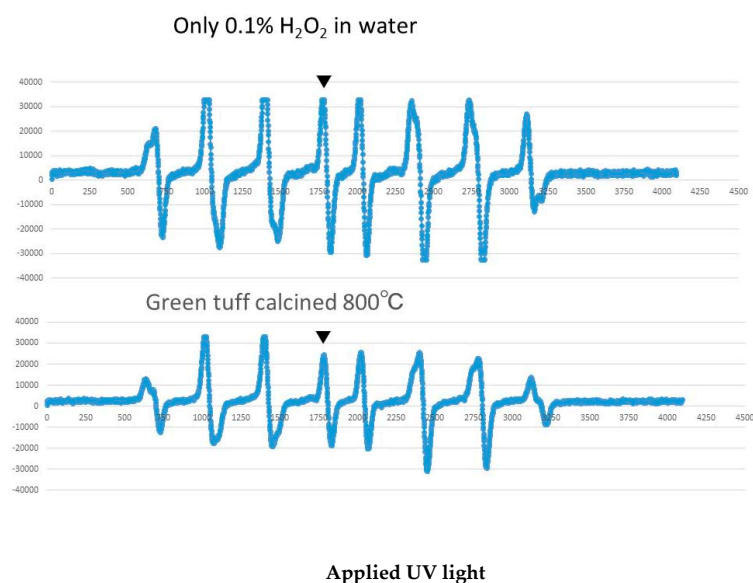


Figure 8. ESR spectra of 0.1% of H_2O_2 in water and calcined 800 °C green tuff added to 0.1% of H_2O_2 in water with UV.

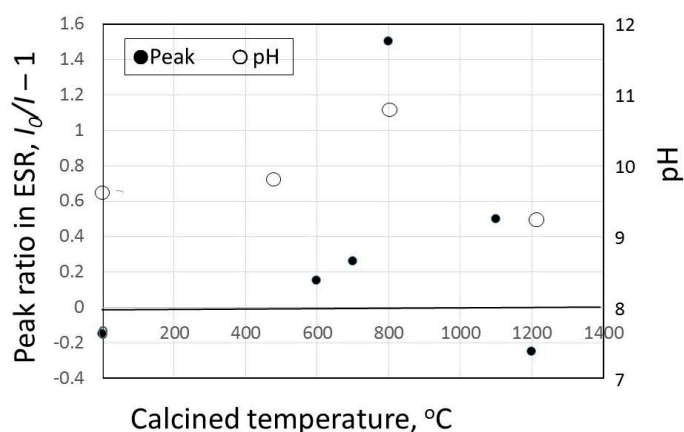


Figure 9. ESR peak ratio depending on calcined temperature.

3.4. Formaldehyde Adsorption Result

The fitting curves and measured point of formaldehyde concentration depending on time for two kinds of tiles produced by using 800 °C calcined green tuff powder, its powder and as-received powder are shown in Figure 10. To compare the adsorption ability, the activated carbon is also measured. The green tuff powder calcined at 800 °C shows the largest formaldehyde adsorption and near to the line using activated carbon powder. The tile heated at 800 °C shows the largest formaldehyde adsorption and near to the line using activated carbon powder. The tile heated at 1000 °C and 1100 °C shows almost the same adsorption behaviour. As the specific surface area of powder is larger than the same weight of tile, the adsorption ability of powder is much higher. However, the tile is more convenient to be used as building material. The 800 °C calcined powder is the most convenient to change hydrogen peroxide to the hydroxyl radical with no UV as shown in Figure 7, whereas the decomposed hydroxyl radical with UV is shown in Figure 9. However, it is difficult to produce the tile at 800 °C. Therefore, the tile produced at higher temperature has been heated for 15 min at 1000 °C and 1100 °C. The period to decrease to 50 % of formaldehyde concentration using different adsorbent is shown in Figure 11. The half value of period in green tuff powder calcined at 800 °C is 5 h, while the tiles heated at 1000 and 1100 °C are 10 h. The structure of calcined powder and tile is porous, containing zeolite; therefore, the adsorption rate is high. The calcined green tuff contains 0.71% of TiO_2 and 0.07% of ZnO and 16% of Fe_2O_3 . The synthesized $\text{ZnO/Fe}_2\text{O}_3$ and $\text{TiO}_2/\text{Fe}_2\text{O}_3$ on zeolite produced by Davari et al. could decompose the organic substance as photocatalyst [11]. Though the mechanism for former reported tile and materials [8,9] to reduce the formaldehyde is only adsorption, the tile produced by calcined green tuff has the potential to decompose the adsorbed formaldehyde as per the following equation by the photocatalyst.

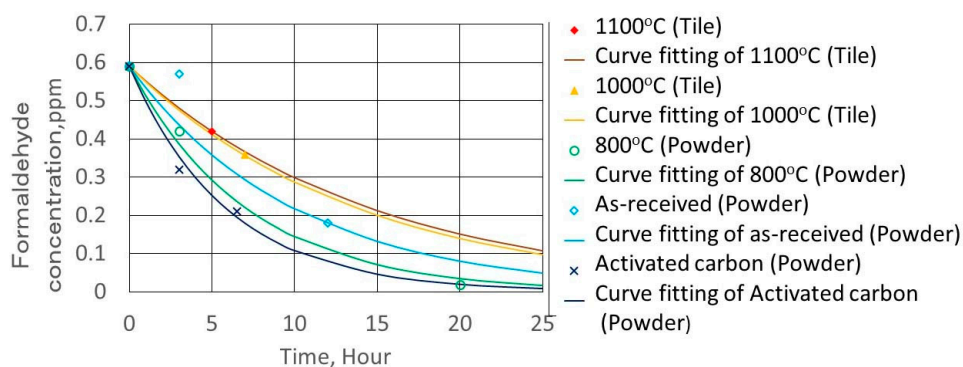


Figure 10. Formaldehyde concentration change depending on time for two tiles produced by using 800 °C calcined green tuff powder and 800 °C calcined green tuff powder and activated carbon.

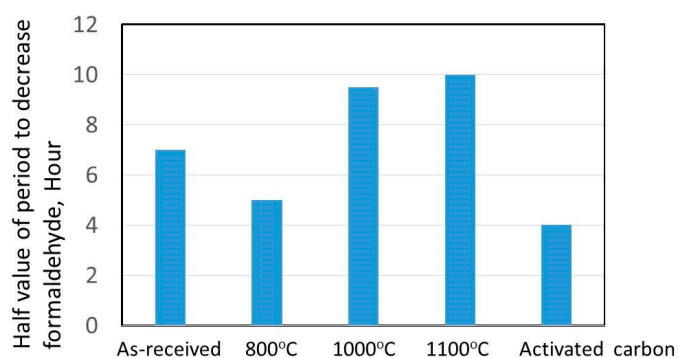


Figure 11. Half value of period to decrease formaldehyde concentration in each adsorbent.

4. Conclusions

In an attempt to contribute to sustainable development, waste green tuff powder produced by cutting Towada stone was utilized to eliminate formaldehyde, one of the many greenhouse gases, and the following results were obtained.

As the SEM and elemental map with EDS showed that fine TiO_2 exists on zeolite in green tuff powder, the green tuff powder and calcined powder were found to be natural photocatalysts.

The green tuff powder calcined at 800 °C showed the highest alkaline solution of pH 10.8 in water. At pH higher than 10, the decomposition of hydrogen peroxide to hydroxyl radicals without UV light occurs easily.

Under UV irradiation, the green tuff powder calcined at 800 °C most strongly decreased the amount of hydroxyl radicals in hydrogen peroxide aqueous solution. The as-received green tuff and that calcined at more than 1200 °C did not decrease the hydroxyl radical.

The tile was produced by pressing the 800 °C calcined green tuff powder with no additives. At 40 MPa and heating at 1100 °C for 15 min, the tile showed the largest strength, when compared with tiles produced by heating at 800 and 1000 °C.

Regarding the formaldehyde adsorption, the green tuff powder calcined at 800 °C showed that after 5 h, the formaldehyde concentration decreased to half of its initial concentration and a high adsorption rate similar to the activated carbon was observed. The tile heated at 1100 °C also adsorbed formaldehyde.

The adsorbed formaldehyde might be decomposed by hydroxyl radical produced for the presence of TiO_2 on zeolite in green tuff and tile as photocatalyst.

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