Article

Production of hydroxyl radical and removal of formaldehyde by calcined green tuff powder and tile

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Abstract: Wasted Green tuff powder produced by cutting Towada stone is recycled as environmental cleaning material. The optimum temperature for green tuff powder calcination to reduce the hydroxyl radical produced in hydrogen peroxide decomposition with ultraviolet light (UV) and no light. The green tuff calcined at 800°C shows the large decomposition rate of hydrogen peroxide with no UV light when measured by using ESR. With UV light, the optimum temperature for calcinating the green tuff powder in order to reduce hydroxyl radical is also 800°C. Next, the powder calcined at 800°C is 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 st 1100°C were the strongest and also adsorbed formaldehyde. The adsorbed formaldehyde on the green tuff tile and powder might have a possibility to decompose by photocatalytic.

Keywords: Green Tuff; Towada stone; Calcination; Recycle; Tile; Hydrogen peroxide; Radical; ESR; Adsorption; Formaldehyde, UV; Photocatalysis

1. Introduction

Environmental cleaning is one of the important topics of sustainability. Here the reaction of hydroxyl radical and removal of formaldehyde are discussed by using wasted rock powders (green tuff). Green Tuff is a sedimentary rock formed in rivers and lakes from 20 million to 15 million years ago, and distributed widely along the Sea of Japan coast of the Japanese Archipelago [1]. Nowadays, Hinai Green tuff in Akita prefecture, Japan is utilized in building wall and floor as a beautiful greenish color of block (Towada Stone), and so on. However, when the tuff stone is quarried and grinding, about 60% of all quarried stone becomes wastes powders. It is important to utilize 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 [2], activation of microorganisms [3], precipitation regents for wastewater treatment [4], and adsorption of chemical substances [5]. Especially, Sugai et al. produced several boards of green tuff aggregate (1-3 mm and

less than 1mm) mixture with 40 wt% of white Portland cement at 20°C for 10 days. They measured the adsorption qualities of toluene and acetaldehyde in the air using these boards and reported that the adsorption characteristics was similar to the board used in diatomaceous earth [5]. On the other hand, LIXIL Co. produced the "ECOCARAT" tile to adsorb the toluene and acetaldehyde [6]. Both articles explained that the reason of volatile chemical substances removal in the air was adsorption by porous materials. On the other hand, if the chemical substances can be decomposed by UV light and so on, it is more effective to remove the adsorbed chemical substances to prevent the desorption. The metal oxide semiconductors (TiO_2, WO_3, ZnO, Fe_3O_3, Ta_2O_5, and CuO) shows the characteristics of heterojunction photocatalysts [7]. Davari et al. reported that synthesized ZnO/Fe_2O_3 and TiO_2/Fe_2O_3 on zeolite could decompose the organic substance [8]. The calcined green tuff contains small amount of similar components. In this experiment, the decomposition of hydroxyl radical in H_2O_2 aqueous solution has been examined by using the calcined green tuff powder at various temperatures comparing with as-received green tuff powder as the basic study for decomposition possibility of organic substances with ultraviolet light (UV) or no UV. Hoshiba et al. reported the generation of hydroxyl radical in the calcined dolomite powders suspension with H_2O_2 [9]. Also in this experiment the tile using calcined green tuff powders are produced and the formaldehyde removal rate is measured by comparing to various powders.

2. Materials and Methods

2.1. Materials of green tuff powder

The green tuff powder is collected from "Towada stone" cutting place in the quarry to produce the architectural materials in Odate city of Akita prefecture, Japan [10]. The composition of as received green ruff is listed in Table 1. The composition was analyzed by means of a X-ray Fluorescence spectroscope (XRF). The iron oxide is mainly ferrous in as received powders. The main composition minerals are albite 35%, silica 25%, chlorite 7%, zeolite 5% and the average density is 2.1g/cm^3, specific surface area is 4.0m^2/g, the peak in pore size distribution is 51 nm and pore volume is 0.028 cm^3/g. [3]. The zero point of charge is about pH 2.5 [4].

Table 1 Chemical composition of as received green tuff (Towada stone) powder

Composition	Content ,w/v %
Na_2O	0.30
MgO	0.73
Al_2O_3	9.16
SiO_2	61.69
P_2O_5	0.21
SO_3	0.17
Cl	0.04
K_2O	6.19
CaO	4.07
TiO_2	0.71
MnO	0.49
FeO or **Fe_2O_3**	14.42～16.03

Co_2O_3	0.01
ZnO	0.07
Rb_2O	0.03
SrO	0.08
Total	98.37～99.98

Next, The green tuff powder was calcined at 500 ℃, 600 ℃, 700 ℃, 800 ℃, 900 ℃, 1000 ℃, 1100 ℃, and 1200 ℃ for 10 minutes respectively. And the calcined powder was kept in dry condition. All FeO changes to Fe_2O_3 by heating in an air atmosphere.

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. After mixed, 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 radical. The chemical structures of G-CYPMPO is shown in Figure 1 (a). G-CYPMPO® (100 mM) 25mg was dissolved in 2 mL ultrapure water. PO_4 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 follow: 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.

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) and the observed ESR spectra is shown in the Figure 1 (b). Kohri's ESR Spin-trap Method is utilized to analyze the data [11]. The peak-to-peak intensity of the selected ESR line of the free radical adduct was monitored in the presence or absence of antioxidant.

In the presence of the spin trap (ST) and antioxidant (AO), the following free radical (R) trapping reaction should occur:

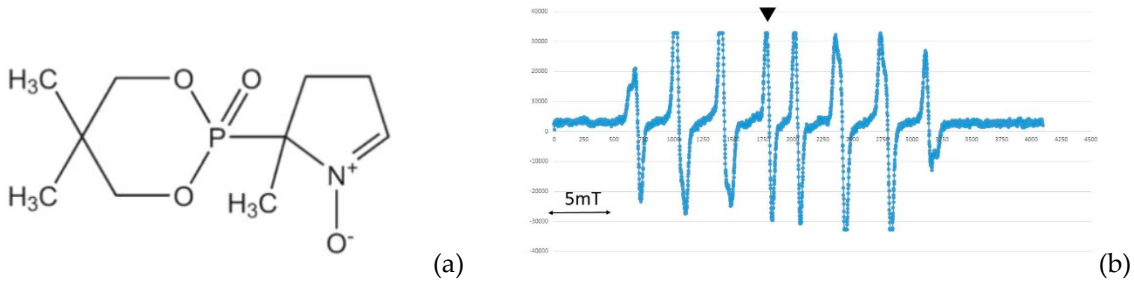
R + Spin Trap → R-adduct rate constant : tk_{st} (1)

R + Antioxidant → product rate constant : k_{AO} (2)

When I_0 and I are the ESR peak height in the presence of ST alone and ST+Antioxidant, respectively, the amount of the product in Eq.(2) is $I_0 - I$. Thus, I_0 / I -1 are calculated to quantify free radical scavenging capacity.

To quantify free radical generation capacity, oxidant species was mixed with free radical generation system few hours before the ESR measurement. When I_0 and I are the ESR peak height in the presence of ST alone and ST+oxidant, respectively, the amount of free radical generation system oxidized by oxidant species is $I_0 - I$. Thus, I_0 / I -1 are calculated to quantify free radical generation capacity. In this study, only on the forth peak near the center of spectra (marked with inverted triangle sign) is focused to quantify the amount of hydroxyl radical adduct.

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, were hydrated with 0.1 w/v hydrogen peroxide for 24 hours before ESR measurement.



(a) (b)

Figure 1. 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 title. 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 2.

A 55g of green tuff powders that was calcined at 800°C and then used to mold in each block. The two kinds pressure 20 and 40 MPa are utilized to form the blocks. Next the molded blocks are heated and kept at 800, 1000 and 1100°C for 15 minutes. The blocks are heated at those temperature and two kinds of pressure by using 800°C calcined green tuff powder and the several tiles are produced. The photograph of produced tiles are shown in Figure 3. The color of tile changed from yellow to black at 1100°C. The strength of tile produced at 1100°C and 40MPa is the largest.

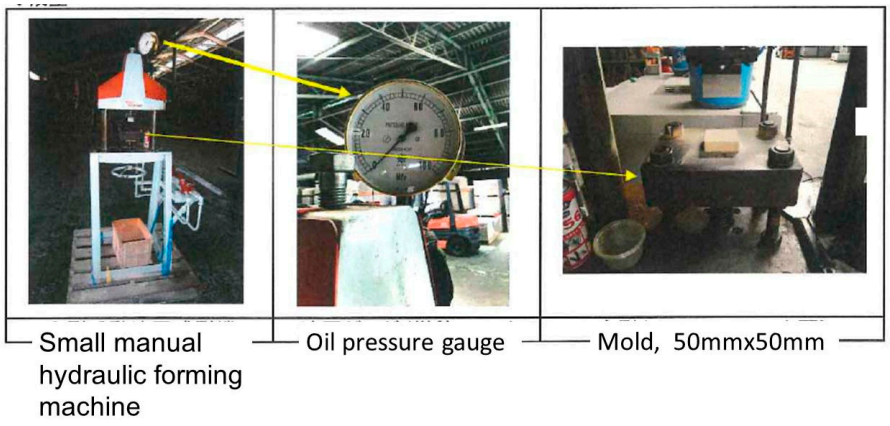


Figure 2. Photographs of oil pressure molding apparatus.

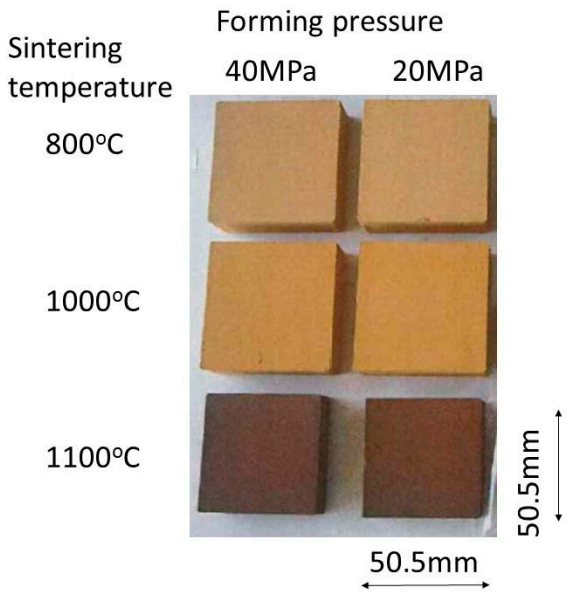


Figure 3. Photograph of tiles prepared by using compressed of 800°C green tuff powder. (Tile size is 50.5x50.5mm)

2.4 Formaldehyde adsorption experimental method

Formaldehyde causes the Sick House Syndrome [12] and at concentrations above 0.1 ppm in air formaldehyde can irritate the eyes and mucous membranes, resulting in watery eyes. The adsorption experiment of formaldehyde is studied using various green tuff powders and tile. The regent grade

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formaldehyde (HCOH, Wako Pure Chemical Industries, Ltd) is about 37% aqueous solution with methanol. The small amount of formaldehyde is vaporized in the 0.25m^3 of glove box. The initial concentration of formaldehyde in glove box is regulated at 0.6ppm. Next, a 55g of green tuff powder or tile is put on the floor in grove box and the concentration of formaldehyde is measured by passing the time. As the comparison of adsorption, the granular activated carbon (Wako Pure Chemical Industries, Ltd) is used as the same weight. Formaldehyde concentration is measured by formaldehyde detector (FP31, RIKEN KEIKI Co., Ltd.).

3. Results and discussion

3.1 pH change of calcined green tuff powder

The as-received green tuff powder and green tuff powder calcined at 800 ℃ is put into ion-exchange water and agitated by magnetic stirrer. The pH of passed agitation time is shown in Figure 4. The calcined green tuff powder shows strongly alkaline pH10.8, while the as-received green tuff is about pH9.7. This pH tendency is similar to the calcined dolomite [9]. The alkaline solution can decompose hydrogen peroxide [13].

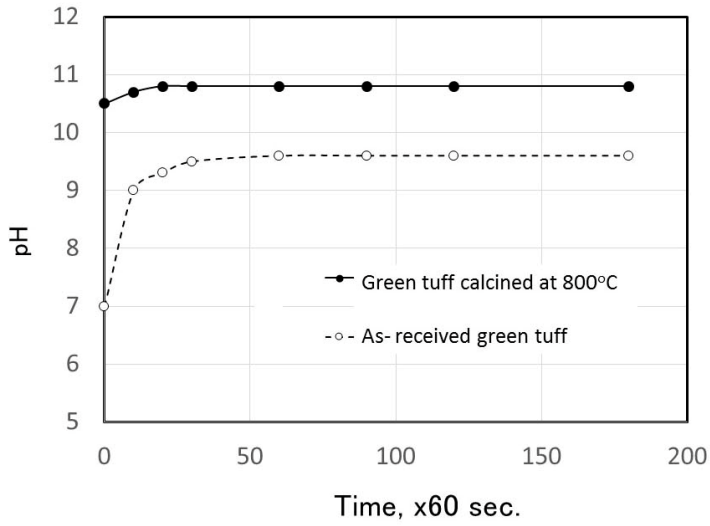

Figure 4. pH change depending on time for as-received green tuff and 800°C calcined green tuff.

3.2. Hydroxyl radical measurement results

The green tuff powder and calcined powder are put into 0.1wt% H_2O_2 solution. ESR spectrum measured after 24 hours passed without UV irradiation is shown in Figure 5. There is no spectrum for no powder added only 0.1wt% H_2O_2 solution and green tuff powder calcined at 1200°C. In the as-received green tuff powder few amount of ESR spectrum is observed. On the other hand, green tuff powder calcined at 800°C showed large ESR spectrum of hydroxyl radical even if the UV is not irradiated. It is considered that the H_2O_2 decomposed by 800°C calcined powder with a small amount of UV of the daylight for 24 hours and produced the hydroxyl radical.

When the strong UV light is applied to the all specimen, the large hydroxyl radical ESR peaks are observed. The ESR spectra of only 0.1% of H_2O_2 in water and calcined 800°C green tuff added 0.1% of H_2O_2 in water with UV is shown in Figure 6. The height on the forth 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 is shown in Figure 7. The green tuff calcined at 800°C can largely decrease the hydroxyl radical. More than 1200°C calcination it is impossible to decompose hydroxyl radical. By

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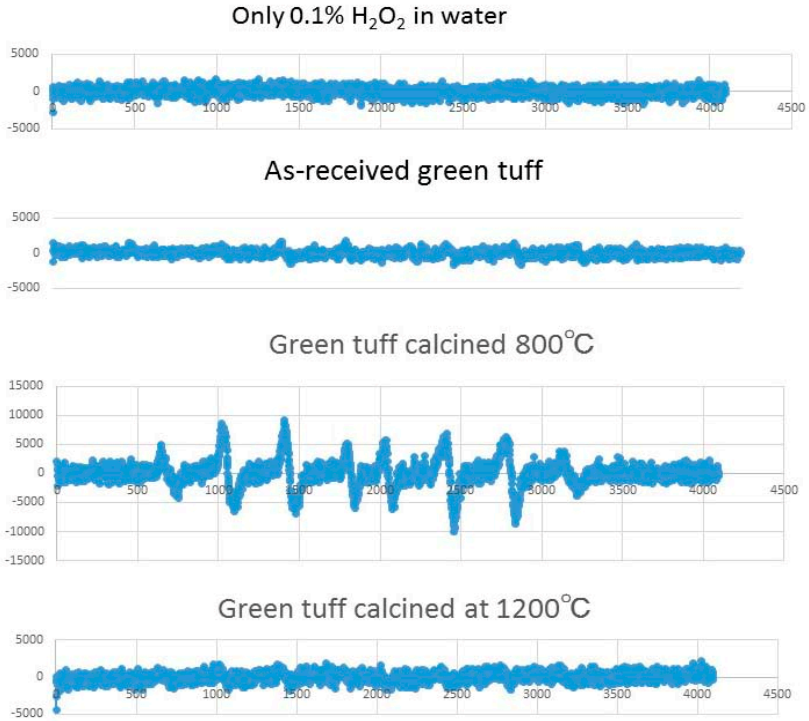
irradiating UV light, H_2O_2 produce hydroxyl radical (・OH) in the following equation. Here, h is Plank constant and ν is light frequency.

$H_2O_2 + h\nu = 2$ ・OH (1)

On the other hand, Fenton reaction shows the following equation, however, this spectra by ESR is indicated by Eq. (1) as the iron in calcined green tuff is Fe^{3+}.

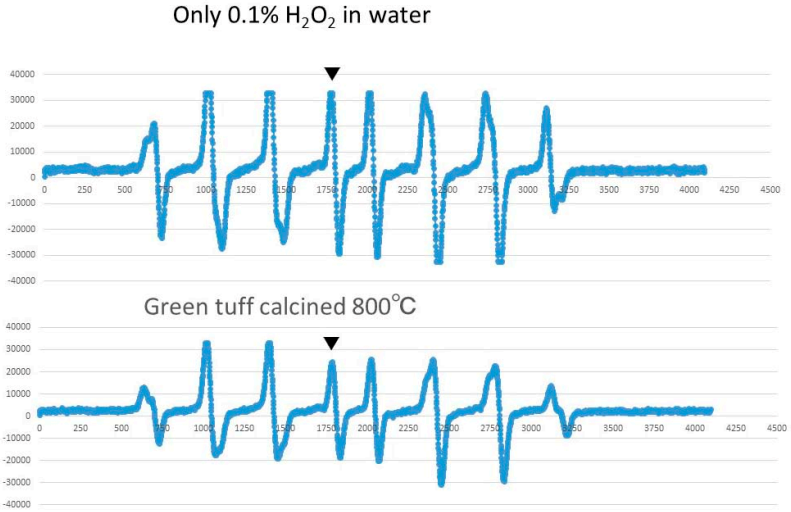
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- +$ ・OH (2)

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 materials of hydroxyl radical.



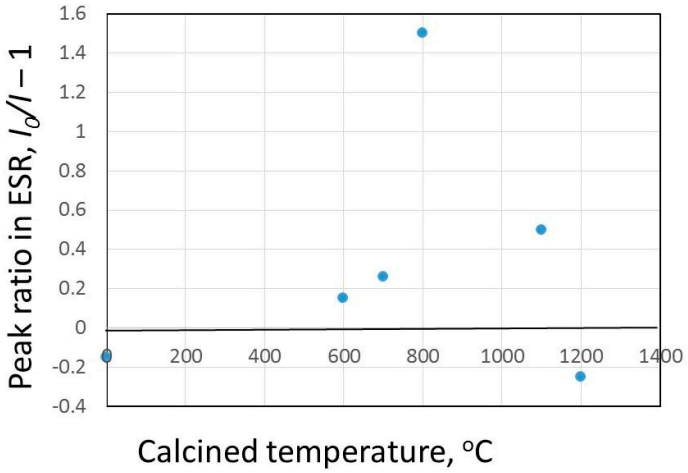
No UV light

Figure 5. 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 0.1% of H_2O_2 in water in without UV.



Applied UV light

177 Figure 6. ESR spectra of 0.1% of H_2O_2 in water and calcined 800°C green tuff added 0.1% of H_2O_2 in
178 water with UV.



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180 Figure 7 ESR peak ratio depending on calcined temperature.

181 **3.2 Formaldehyde adsorption result**

182 The fitting curves and measured point of formaldehyde concentration depending on time for two
183 kinds of tiles produced by using 800°C calcined green tuff powder, its powder and as-received
184 powder are shown in Figure 8. To compare the adsorption ability, the activated carbon is also
185 measured. The green tuff powder calcined at 800°C showed the larger formaldehyde adsorption and
186 near to the line using activated carbon powder. The tile heated at 1000°C and 1100°C showed almost
187 same adsorption behaviour. As the specific surface area of powder is larger than the same weight of
188 tile, the adsorption ability of powder is much higher. However, the tile is more convenient to use
189 practically in building material. Half value of period to decrease formaldehyde concentration in each
190 adsorbent is shown in Figure 9. The half value of period in green tuff powder calcined at 800°C is 5
191 hours, while the tiles heated at 1000 and 1100°C are 10 hours. The structure of calcined powder and
192 tile are porous as containing zeolite, therefore the adsorption rate is large. On the other hand, the
193 calcined green tuff contains 0.71% of TiO_2 and 0.07% of ZnO and 16% of Fe_2O_3. As the synthesized
194 ZnO/Fe_2O_3 and TiO_2/Fe_2O_3 on zeolite produced by Davari et al. could decompose the organic
195 substance as photocatalyst [8]. Though the mechanism for former reported tile and materials [5, 6] to
196 reduce the formaldehyde is only adsorption, the tile produced by calcined green tuff has a possibility
197 to decompose the adsorbed formaldehyde as following equation.

198 $HCHO + O_2 \rightarrow CO_2 + H_2O$ (3)

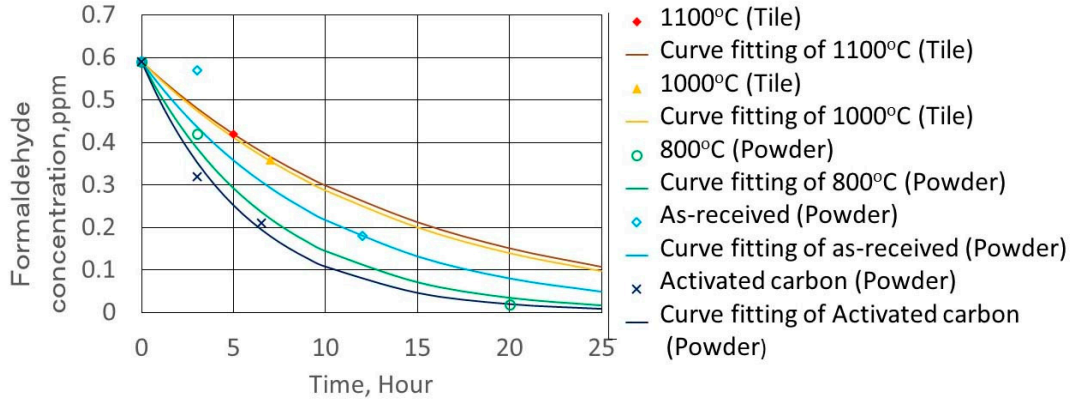

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Figure 8. Formaldehyde concentration change depending on time for tiles produced by using 800°C calcined green tuff powder and green tuff powder and activated carbon.

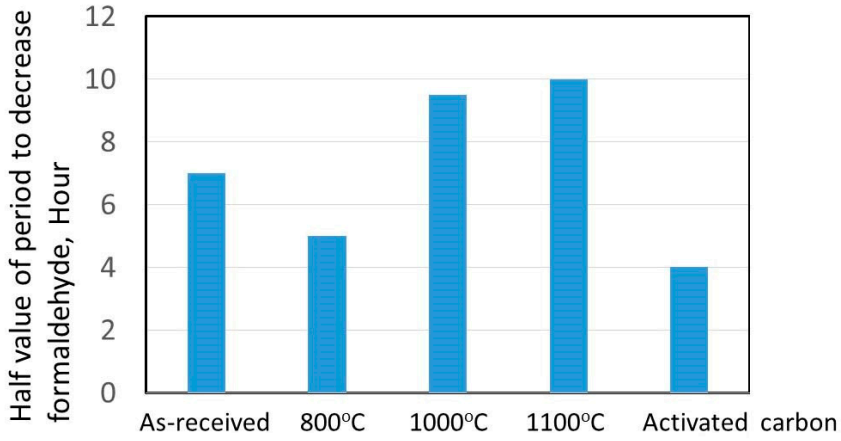

Figure 9. Half value of period to decrease formaldehyde concentration in each adsorbent.

4. Conclusions

The utilization of wasted green tuff powder produced by cutting Towada stone is investigated and its potential application as environmental cleaning material was considered. The following results are obtained.

The green tuff powder calcined at 800°C showed alkaline solution of pH 10.8 in the water and hydroxyl radicals were produced in the 0.1% of H_2O_2 aqueous solution without UV light.

In the irradiation of UV, the green tuff powder calcined at 800°C, the amount of hydroxyl radical in H_2O_2 aqueous solution decreased. The as received green tuff and calcined one at more than 1200°C did not decrease the hydroxyl radical, as indicated by ESR spectra measurement.

The tile produced by pressing at 40MPa and heating at 1100°C showed the greatest strength, when compared with tiles produced by heating at 800 or 1000°C.

In the formaldehyde adsorption the 800°C calcined green tuff powder showed that after 5 hours formaldehyde concentration decrease 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 on the green tuff tile and powder might have a possibility to decompose by photocatalytic for the composition of TiO_2 and ZnO with zeolite in green tuff.

Supplementary Materials: No supplementary material is available

Author Contributions: Conceptualization, T.F, L.Z; investigation, L.Z., H.K., H.M, S.Y. H.K.; writing-original draft preparation, T.F, L.Z.; writing-review and editing, G. D.; supervision, Y.W, J. A.

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Conflicts of Interest: The authors declare no conflict of interest.

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