

## Influences of Zeta Potential, Water Absorption and Surface Roughness of Porous Ceramics on Marine Bio-fouling

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### **Abstract**

*The red tide organisms occurring at seashores in Korea damage the marine fish-raising industry every summer. Several methods to prevent the occurrence of red tide organisms, therefore, have been tried; one of them is to filter out red tide organisms using a membrane filled with porous ceramic bodies, allowing only fresh seawater to pass into a fish farm. When this method is used for long period of time, however, the problem of marine bio-fouling can develop on the surfaces of the porous ceramic body, deteriorating the filtering function of the porous bodies. In this paper, the influences of the zeta potential, water absorption and surface roughness of porous ceramics on marine bio-fouling have been inspected. In order to control the above three factors, three kinds of ceramic powders, alumina, titania and zirconia, were coated on the porous bodies. As a result, the water absorption and the surface roughness of the porous ceramics were found to be equally important factors in preventing bio-fouling, while the zeta potential of the specimens did not show a prominent effect. In detail, the water absorption of specimens was an effective factor in the early stages of bio-fouling for about one month; on the other hand, the surface roughness of the specimen was a main factor that could be used to control the amount of bio-fouling after one month. Among the three ceramic powders used as coatings, alumina, by imparting lower water absorption and higher surface roughness to the specimens, proved to be the optimum one to prevent marine bio-fouling.*

**Keywords:** *Bio-fouling, Porous ceramic, Zeta-potential, Water absorption, Surface roughness*

### **1. Introduction**

The waste water discharged from various industrial sites and from domestic use has seriously contaminated rivers and the ocean in Korea. As a result, occurrences of green algae in rivers and red tide in the ocean have become very significant social problems. Especially, red tide in ocean has turned into an exorbitant source of damage to the marine fish-raising industry every summer [1-3]. Several methods that can be used to reduce occurrences of red tide, such as dusting the ocean with ocher, have been tried in Korea; however, no perfect and safe method has yet been established.

Recently, a method to filter out red tide organisms using a membrane filled with porous ceramic bodies, allowing only fresh seawater to pass into a fish farm, has become a subject of study. When this method is used for long period of time, however, the problem of marine bio-fouling can develop on the surfaces of the porous ceramic body, deteriorating their filtering function of the porous bodies [4, 5]. Bio-fouling is normally found to occur at the bottoms of ships, on turbines in power stations located on the seashore or on marine structures. In the early stages of bio-fouling, a lightweight and soft form of life such as micro-organisms usually attaches itself to the marine structures and, consequently, a variety of species come to be stuck on these structures to feed them, and

so the amount of bio-fouling gradually increases [6]. Finally, very big and heavy forms of life such as rock barnacles and sea acorns stick to the structure. The attachment of such forms of life can accelerate the increase of the weight of the vessel or marine structure and can cause a structural safety problem [7]. Anti-bio-fouling paints have been developed that contain a wide variety of materials such as organic tin compounds, which, even with a concentration of 1 ppt (part per trillion,  $10^{-12}$ ), can exert a fatal toxicity to marine organisms; as such the use of such materials is now prohibited around the world [8].

Environment-friendly methods for inhibiting bio-fouling of artificial structures or bodies in seawater, therefore, have been continuously studied. Most methods involve modifying the surface character of the body to impart a hydrophilic or hydrophobic character, a plus or minus charge, and large or small roughness. Cho et al. showed that an aluminum substrate surface, with a hydrophobic character, had an anti-bio-fouling effect in the initial stages of bio-fouling [9]. Bai and Jones changed the surface charge through surface modification of polymeric membranes to demonstrate a preventative effect against bio-fouling [10, 11]. Kim and Lovitt reported that bio-fouling can be controlled by changing the surface charge and surface roughness of the filtration membrane used in seawater [12, 13].

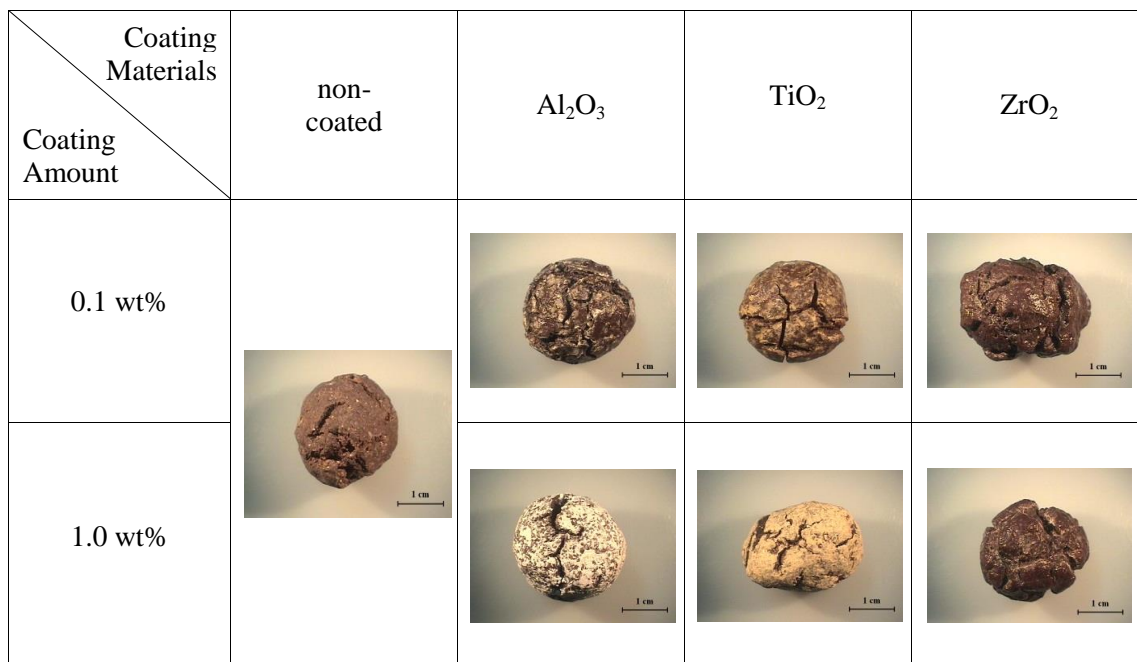
Previous studies, however, have focused mostly on the anti-bio-fouling effects of metals or polymers, and so the anti-fouling effects of porous ceramic materials have not been very frequently studied. In this study, an environmentally friendly method to achieve anti-bio-fouling on porous ceramic bodies without the use of toxic materials was examined. Especially, the influences of the zeta potential, water absorption and surface roughness of porous ceramics on marine bio-fouling have been studied. In order to control the above three factors, three kinds of ceramic powders, alumina, titania and zirconia, were coated on the porous bodies.

## 2. Experimental Procedure

Three kinds of oxides of alumina, titania, and zirconia were coated on porous ceramics whose main constituent is silica. The most porous ceramic specimens used were of spherical shape; the mean diameter was  $17.5 \pm 2$   $\mu\text{m}$ . Oxide powder reagents were used including  $\text{Al}_2\text{O}_3$  (High Purity Chemicals, Japan, 99.9%),  $\text{TiO}_2$  (High Purity Chemicals, Japan, 99.9%) and  $\text{ZrO}_2$  (Junsei Chemicals, Japan, 99.0%); the average particle size of the oxide powders was  $1.8 \pm 0.7$   $\mu\text{m}$ .

The oxide powders were coated on the surface of porous ceramic bodies by soaking the bodies for 10 seconds in 1.0 wt% PVA (polyvinyl alcohol) solution, giving them a sticky surface. Then, the sticky ceramic bodies were coated for 10 minutes with oxide powder in a rotating vessel with a rotation speed of 70 rpm. The amount of the oxide coating was varied from 0.1 to 1.0 wt%. The ceramic bodies were then dried for 24 hours at 105 °C, and heat-treated at 1200 °C for 10 minutes to completely bond the oxide powder to the surface of the ceramic bodies. The appearance of the porous ceramics, observed by optical microscopy, is shown in Fig. 1.

The density and water absorption of the porous ceramic body was measured in accordance with the Korea Industrial Standard "KS F 2503: the test method for density and water absorption of coarse aggregates." In addition, the surface roughness was observed and measured using a confocal laser microscope (Confocal Laser Scanning Microscope, OLS3000-300 mm autostage, OLYMPUS).



**Figure 1. Appearance of Porous Ceramics Coated with Various Oxides**

Using an organic adhesive, porous ceramic bodies were attached onto acrylic plates that had dimensions of 15 cm in width and 21 cm in length. The specimens attached to the plates were put in seawater of 1 m in depth, located in Geoje-si, Gyeongsangnam-do, Korea, during the period from July to October in 2014. The amounts of bio-fouling generated were measured every month and were calculated using the following equation, Equation (1):

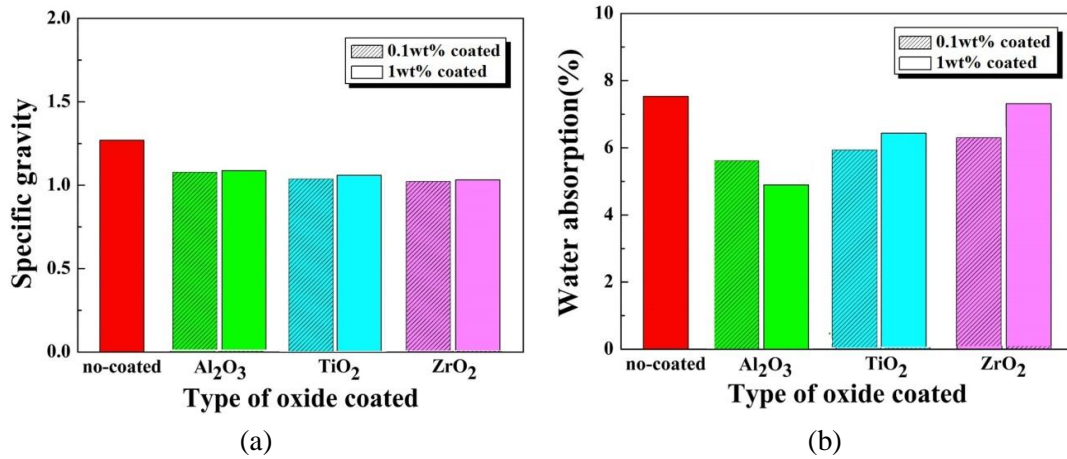
$$\text{Amount of biofouling(\%)} = \frac{(W_a - W_b)}{W_b} \times 100 \quad (1)$$

Where  $W_a$  is the weight of the specimen after one month and  $W_b$  is the weight of the specimen before its installation in seawater.

### 3. Result and Discussion

#### 3.1. Water Absorption and Specific Gravity

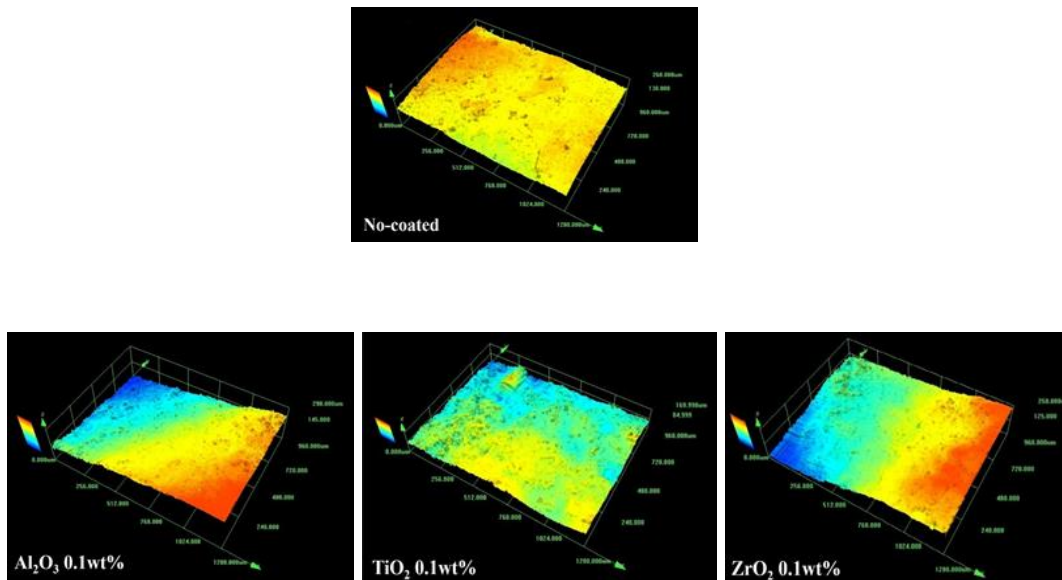
The specific gravity and the water absorption of the porous ceramic bodies used in this study are shown in Fig. 2. The specific gravity values of the specimens coated with oxide powders were higher than that of the specimen that was not coated. There is no significant difference in the specific gravity values of the specimens coated with different coating amounts. The specimen coated with oxide powder had a lower water absorption value than that of the specimen that was not coated. Comparing the water absorption values for the three types of specimen, the Al<sub>2</sub>O<sub>3</sub>-coated sample showed the lowest value and the ZrO<sub>2</sub>-coated sample had the highest value. In addition, increasing the amount of oxide coating from 0.1 wt% to 1.0 wt% was found to increase the water absorption of the specimen slightly, except for the Al<sub>2</sub>O<sub>3</sub> coating, which had no such effect. The lowered water absorption for the coated specimen is due to the filling-up by fine powders of open pores or cracks present on the specimen surface.



**Figure 2. Physical Properties of Porous Ceramics Coated with Various Oxide Powders: (a) Specific Gravity, and (b) Water Absorption**

### 3.2. Surface Roughness

Topographic images of the specimens coated with 3 different types of oxide powders, observed using a confocal laser scanning microscope, are presented in Fig. 3. The specimen that was not coated showed a relatively smooth surface, while the specimens coated with oxide powders had rough surfaces. Fig. 4 shows that an average roughness value determined using four points selected randomly from the confocal microscope images. The roughness of the specimens with no coatings showed a value of about 100  $\mu\text{m}$ , while the specimens coated with oxide powders showed increased roughness regardless of the type or the amount of coating.



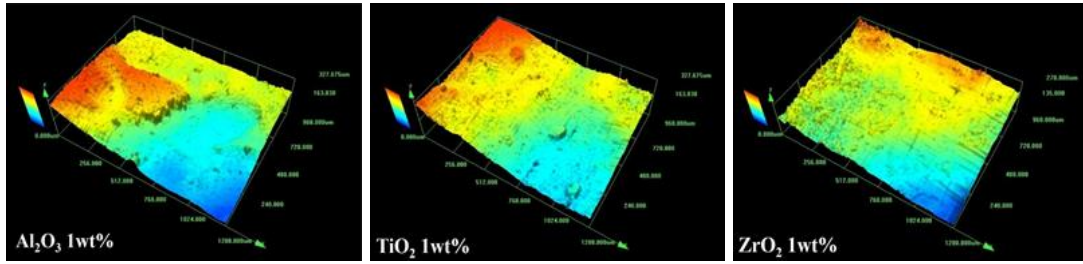


Figure 3. Image of Surface of Porous Ceramics Coated with Various Oxides, Obtained using Confocal Laser Scanning Microscope

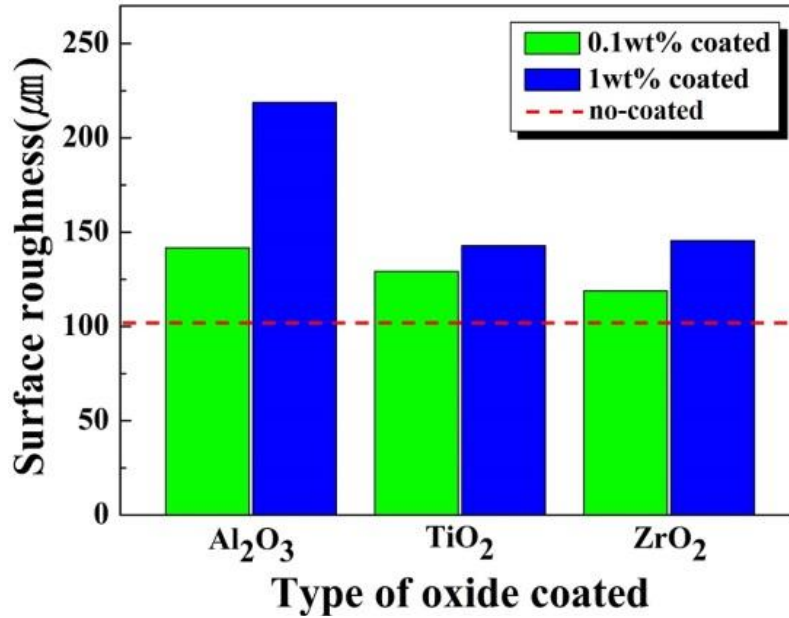
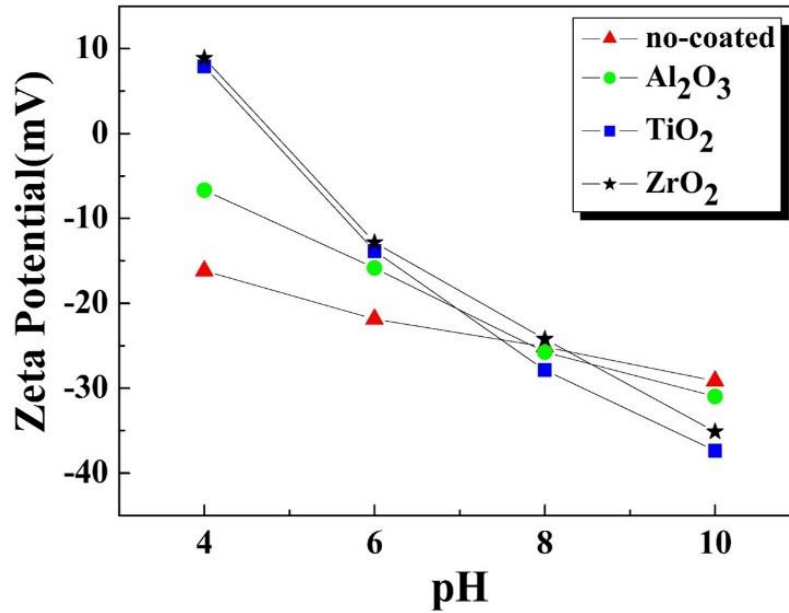


Figure 4. Surface Roughness of Porous Ceramics Coated with Various Oxides

Most specimens coated with oxide powders showed roughness values of 120~140  $\mu\text{m}$ , which are 20~40 % higher than the value of the non-coated specimen, except for the sample coated with 1 wt%  $\text{Al}_2\text{O}_3$ . In particular, the specimen coated with 1 wt%  $\text{Al}_2\text{O}_3$  had an approximate roughness of 220  $\mu\text{m}$ , which is an intensely high value compared to that of the non-coated specimen.

### 3.3. Zeta Potential

The zeta potential values for the specimens coated with the 3 oxide powders having different iso-electric points (denoted as IEP) are shown in Fig. 5. The zeta potential decreases with increasing pH of solution regardless of the kind of oxide used as coating.



**Figure 5. Zeta Potential of Porous Ceramics Coated with Various Oxides**

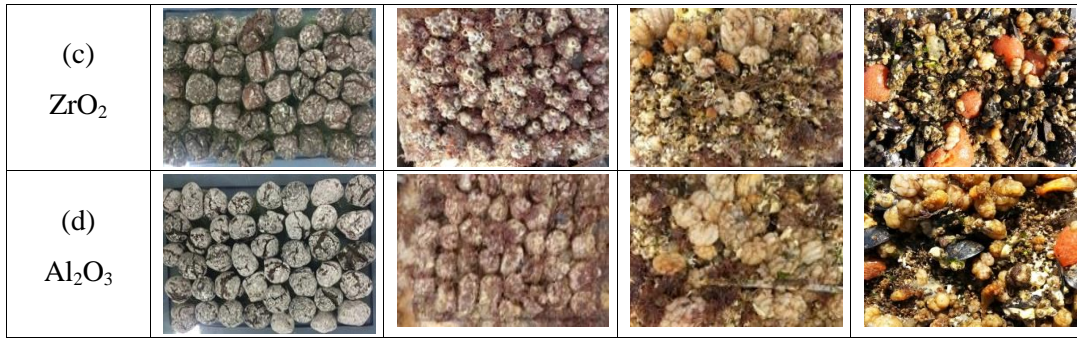
The IEP, in which the zeta potential is zero, is measured and found to be about 5 for the specimens coated with ZrO<sub>2</sub> or TiO<sub>2</sub>, while this value is below 3 for the specimens coated with Al<sub>2</sub>O<sub>3</sub>. The pH of the seawater at the site located in Geoje-si was measured and found to be in the range of 8.0~8.5. There is no significant difference between the 4 kinds of specimens in terms of the zeta potential in the pH range of 8.0~8.5.

### 3.4. Bio-fouling on Surface of Porous Ceramics

Pictures to show the appearance of the porous ceramic bodies bio-fouled as a function of submerged time in seawater are shown in Fig. 6. The specimens were first put in the marine environment at Geoje-si in July, 2014. All specimen surfaces can be seen to be light red in color, which means that red algae are weakly attached after one month. After one month, warty sea squirts seem to attach themselves to the surfaces. After three months, barnacles and shellfish such as mussels were found to be very firmly attached.

Time \ Specimen	As-installed	1 month	2 months	3 months
(a) Non-coated				
(b) TiO <sub>2</sub>				

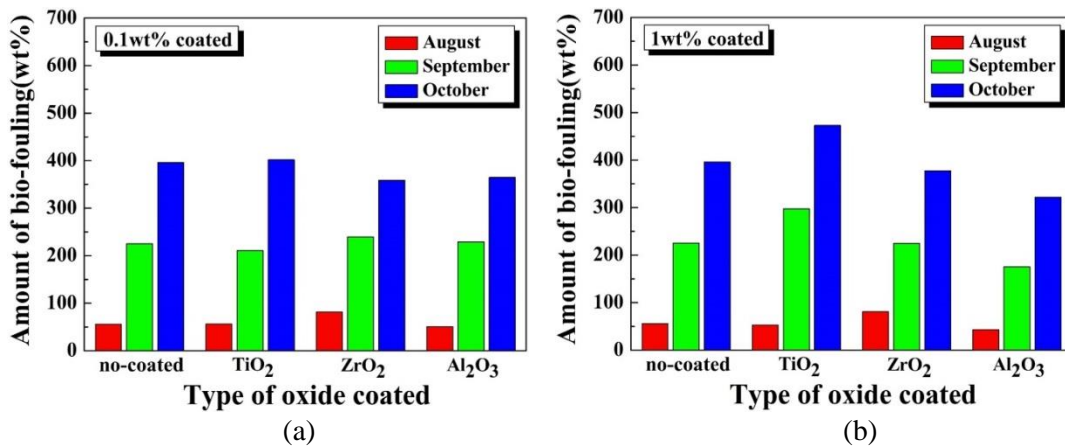




**Figure 6. Pictures to Show Appearance of Bio-fouling that Developed on Porous Ceramics Coated with Various Oxide, According to Submerged Time: (a) non-coated, (b) 1.0 wt% TiO<sub>2</sub>-coated, (c) 1.0 wt% ZrO<sub>2</sub>-coated, and (d) 1.0 wt% Al<sub>2</sub>O<sub>3</sub>-coated. The specimens were first put in the marine environment at Geoje-si, Gyeongsangnam-do Korea in July, 2014**

Fig. 7 shows the amount of bio-fouling measured every month during a period of three months. First, the amount of bio-fouling was not significantly large for any of the specimens during the first month. The amount of bio-fouling, however, showed a tendency to increase quickly with time after one month, regardless of the type of oxide coating on the specimens.

Microbial fouling organism films usually occur in the early stages, during approximately the first one month. However, the number of fouling organisms began to increase after one month and rapidly increased for all specimens after two months. The increased weight is due to large mussels or barnacles that attached themselves to the specimen after two months.



**Figure 7. Amount of Bio-fouling for Porous Ceramics Coated with Various Oxides: (a) 0.1 wt% coated and (b) 1 wt% coated. The specimens were first installed in the marine environment at Geoje-si, Gyeongsangnam-do in July, 2014**

When the amount of coating on a specimen was 0.1 wt%, the amount of bio-fouling according to the submerged time was similar to that of the specimen that was not coated, indicating that the effect of the oxide coating on preventing bio-fouling was not distinct when the amount of coating was only 0.1 wt%.

However, for the specimen coated with oxide powder to a level of 1.0 wt%, there is a meaningful effect of preventing bio-fouling. First, when analyzing the amount of bio-

fouling shown in Fig. 7 during the first month, and the water absorption of the specimens coated with  $\text{TiO}_2$  or  $\text{Al}_2\text{O}_3$ , as shown in Fig. 2, it can be seen that the amount of bio-fouling increased with water absorption. This means that coating of 1 wt% of  $\text{TiO}_2$  or  $\text{Al}_2\text{O}_3$  has an effect to suppress biological fouling for one month, during the early stage of fouling, due to the lower water absorption.

After 1 month, the amounts of bio-fouling for the specimens coated with 1 wt%  $\text{Al}_2\text{O}_3$  were lower than that of the non-coated specimen. When associating the amount of bio-fouling and the surface roughness of the specimen (Fig. 4), the larger surface roughness value was found to have a greater controlling effect on bio-fouling after one month, the period of long term exposure. Bio-fouling starts with the attachment of soft and light microorganisms; then, hard and large forms of life such as barnacles come to attach themselves to the specimens. The hard and large barnacles were proven to not grow easily on the specimen surfaces that had a larger roughness values.

The surfaces of most forms of marine life are known to be negatively charged, and so many studies so far have focused on making the surface of a sample negatively charged to induce a repulsive power between the marine life and the specimen. Although all specimens prepared in this study had a negative charge in the pH range of 8.0~8.5, which is the pH of the seawater at the site, the zeta potential values were very similar for all specimens, as can be seen in Fig. 5. So, the zeta potential value cannot be correlated with the amount of bio-fouling on a ceramic porous body. However, there have been many research results that have shown a prevention of bio-fouling by controlling the zeta potential on the surfaces of polymeric materials [10, 11]; so, a more exact conclusion about the effect of the zeta potential of a ceramic body will require additional experiments.

#### 4. Conclusion

In the early stages of fouling, for a period of about one month, bio-fouling was mostly caused by soft and light-weight organisms such as red algae or microbes. During the early stages, the amount of bio-fouling decreased with the water absorption of the specimens. After one month, however, the amount of bio-fouling decreased with increased surface roughness of the specimen because fouling in the later stages was found to be mostly due to larger and heavier organisms such as barnacles. It was shown that, among the three ceramic powders,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$  was the optimum coating material to prevent marine bio-fouling because this powder imparted lower water absorption and higher surface roughness to the specimens. Although all specimens prepared in this study had a negative charge in the pH range of 8.0~8.5, which is the pH of the seawater at the site, the zeta potential values are very similar. So, the zeta potential value cannot be correlated with the amount of bio-fouling on the ceramic porous body. It was confirmed that the amount of bio-fouling could be reduced by controlling the water absorption and the surface roughness of the porous ceramics through oxide coating. It is expected, therefore, that these results will be applied to future marine structures, allowing all parties involved to avoid the use of environmentally hazardous materials.

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