Study of Biofouling on Fly ash – Bottom ash (FABA) Media Subtract

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Abstract. Biofouling is the process of attachment and growth of organisms on the surface of living and non-living objects. Biofouling is one of the biggest issues found on the surface of structures and unwanted organisms. The biofouling process starts from the information of microfouling *biofilm* (*colonization* of *bacteria* and microalgae) and the bacterial *biofilm* will facilitate the *colonization* of *micro* and macroorganisms such as *cyanobacteria, fungi, diatoms, barnacles, algae*, and *protozoa*. PLTU is the sector that uses the most coal and has utilized many coastal areas. The combustion results of coal emissions are in the form of fly ash and bottom ash. Fly ash has pozzolan properties containing silica or aluminium reacting with calcium hydroxide, while bottom ash has characteristics resembling sand so that it can be used as a substitute for aggregate and both ashes have the potential as a mixture of concrete substrates and artificial reefs. However, fly ash – bottom ash also contains radioactive pollutants and toxic barium elements that may interfere with the life of biota and the surrounding environment. As in the biota of *clams* (*Mytilus californianus*) at the larval level which will be disturbed in the formation of its *shell*. Marine organisms have a certain influence on the dose value of ash waste received by each biota. It was revealed that there was still accumulation of *tube worms* and *bryozoans* in the fly ash – bottom ash concrete substrate, but there was a decrease in diversity, and found eight types of macrofouling in twenty-two concrete feed media, namely *tube worms, barnacles, crabs, bryozoans, green algae, tunicates, hydroids, brown algae, sponges, and red algae.*

1 Introduction

Biofouling is a natural process in the marine environment that refers to the *colonization* of microorganisms and macroorganisms on the surface of living and non-living things [1]. Marine biota attachment has become one of the unwanted accumulations of living organisms on the surface of static and dynamic structures in seawater [2]. Biofouling is also called *fouling* organisms which pose significant problems to human activities in the marine environment [3]. Biofouling on submerged surfaces will form a conditioning layer, possibly dissolving materials from surrounding waters. Surface *colonization* of microorganisms

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constitutes a community of *plankton* and settlement of *larval* forms of higher organisms and *macroalgal spores* [4].

Biofouling is divided into two, including microfouling, which is the formation of *biofilms (colonization* of *bacterial* and *microalgae)* while macrofouling is the attachment of macroorganisms *(colonization* of *vertebrates* and *macroalgae)* which are destructive [5]. Submerged materials are quickly *colonized* by *marine bacteria* and form *bacteria* and from *bacterial biofilms* on the surface (microfouling). This *bacterial biofilm* facilitates the *colonization* of other *micro* and *macro*organisms such as *cyanobacteria, fungi, diatoms, barnacles, algae* and *protozoa* (macrofouling) [6]. The stages of *colonization* of cementitious in the marine environment are illustrated in figure 1. After immersion, organic and mineral *molecules* are rapidly absorbed on the surface. This absorption, known as *"conditioning film formation"* or *"surface conditioning",* changes the physical and chemical properties of the surface and makes it count for stable *bacterial adhesion*. One or more *bacterial* species will adhere to the surface and become enclosed in a matrix of *extracellular DNA* and *polysaccharides*. Days to months later, other *micro*-and *macro*-organisms such as *diatoms, algae*, and *larvae* attach to the surface, causing the formation of macrofouling. Therefore, biofouling in seawater is the process by which *fouling* organisms gather and grow on the surface, and its morphology is characterized by its thickness, *bioadhesive* strength, and weight.

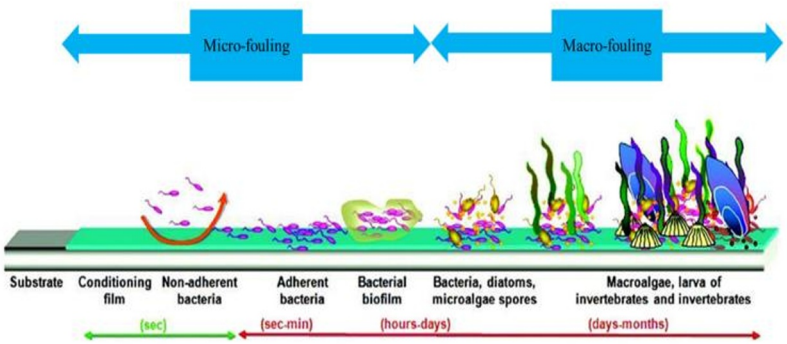

Figure. 1. Schematic representation of marine biofouling formation

Steam Power Plant (PLTU) is the sector that uses the most coal. PLTU has utilized many coastal areas, because in Indonesia almost all PLTU are located in coastal areas. PLTU produces coal waste in the form of 5% solid waste in the form of fly ash (fly ash and bottom ash), of which 10% to 20% bottom ash and around 80% to 90% fly ash from the total ash produced [7]. Fly ash and bottom ash in previous studies have been used to substitute raw materials for making products such as bricks, paving blocks, and artificial reef materials. This is due to the good results on the physical quality of the products produced and with the issuance of Government Regulation Number 22 of 2021 concerning the Implementation of Environmental Protection and Management, it is regulated that fly ash and bottom ash waste that meets several criteria can be categorized as non-B3 waste and can be utilized.

Fly ash is characterized by being heavier than air and has pozzolanic properties [8]. Pozzolan is a material containing silica or aluminium that reacts chemically with calcium hydroxide at certain temperatures to form binding compounds. Fly ash contains compounds of Silicon Dioxide (SiO_2), Titanium Dioxide (TiO_2), Aluminium Oxide (Al_2O_3), Iron (II) Okxide (FeO), Manganese (II) Oxide (MnO), Magnesium Oxide (MgO), Calcium Oxide (CaO), Sodium Oxide (Na_2O), Potassium Oxide (K_2O), Phosphorus Pentoxide (P_2O_5), Water (H_2O), Sulfur Trioxide (SO_3), Sulfur (S).

2 Fly ash – Bottom ash on the coast

Globally, coal is one of the most important energies, especially in the electricity generation sector which reaches 39%, contributing to the production of electricity called PLTU. In Indonesia, Presidential Regulation No. 71 of 2006 became the basis for the construction of coal-fired power plants known as the 10,000 MW Power Plant Acceleration Project. On of the Tanjung Awar – Awar PLTU, Tuban, East Java is a PLTU included in the 10,000 MW Energy Diversification Acceleration Program (EDAP) phase 1 with a capacity of 2 x 350 MW. The fuel used is low calorie coal from Bontang, Kalimantan, as much as 160 tons. The use of coal as a power plant fuel can produce emissions in the form of fly ash and bottom ash containing natural or radioactive radionuclides. Radioactive materials that occur (NORM) with certain activities. In the process of burning coal in PLTU, cracking will occur which causes the release of radionuclides into the atmosphere along with other emission gases through bottom ash and fly ash containing NORM 10 times the initial value. Are natural radioactive elements that are concentrated in processing to form a radioactive concentrate called TENORM [9].

The most dominant radioactive pollutants in coal samples are radioactive elements such as Lead, Polonium, Protactinium, Radium, Torium, Uranium, Carbon and Potassium [10]. These natural radioactive pollutants are included in the heavy metal group, when entering the human body will follow a level pathway that has a negative impact on health. The pathway is through the consumption of marine organisms. Various marine organisms can be accumulated by elemental polonium, which is the main contributor (90%) to the natural radiation dose from radionuclides.

Table 1. Radioactive Dominance.

Number	Pollutant	Symbol	Radiation	Radiation
1	Timbal-210	^{210}Pb	Beta	19,4 Year
2	Polonium-210	^{210}Po	Alpha	138 Days
3	Protactiniu m-231	^{231}Pa	Alpha	3,43 x 10^4 Year
4	Radium-226	^{226}Ra	Alpha	1620 Year
5	Thorium-232	^{232}Th	Alpha	1,39 x 10^{10} Year
6	Uranium-238	^{238}U	Alpha	4,5 x 10 Year
7	Karbon-14	^{14}C	Beta	5730 Year
8	Kalium-40	^{40}k	Alpha	1,28 x 10^9 Year

Fly ash has physical properties that are heavier than air. At certain times the ash will fall into the environment around the power plant, which is dominated by marine waters. So that it will slowly disturb the life of marine biota. Usually it will stick to the outside of the biota's

body and enter the biota's body through the respiratory tract, or absorption through the skin, which will cause death with a mortality rate of up to 50%. In addition, substances dissolved into seawater can change the pH and other parameters around it, which adversely affect marine life. For example, *microalgae* in the ocean play a major role in binding inorganic carbon and are an integral part of the marine food and nutrient chain.

3 The level of biofouling diversity of fly ash – bottom ash concrete substrates

3.1 Mortar block test experiment

Macrofouling unwanted fouling organisms settle or grow on underwater surfaces. Previous reports have shown that organically attached macrofouling can cause major damage and severe corrosion to steel structures. Like *amphibalanus amphitrite* or commonly known as *"barnacles"* are *invertebrate* organisms that inhabit the marine environment. Their life cycle consists of two stages, a *planktonic larval* stage and an adult stage attached to the substrate. *Barnacles* have a strong resistance to environmental fluctuations and will breed in carefully selected locations. The growth of biofouling on the mortar block was conducted to determine the nature of the substrate to marine organisms such as *molluscs, bryozoans, polychaeta, hdyrozoans, and others* [11]. Previous studies using coal bottom ash and fly ash used as marine structures were tested for chloride resistance and concrete deterioration from accumulated growth of marine organisms. Several materials have been found to disrupt and shift the balance of natural communities [12]. This is due to various factors including surface chemistry, smoothness, etc. The elemental contact of the waste ash used has a low calcium content of 6%, a combined Si + Al of 23% which is considered a low pozzolan in nature, The silicon content in the ash was about 16% and comparable to the OPC used (SiO_2 19%), while the calcium content was much lower for ash (Ca 6%) than cement (CaO 66%). Revealing the fact that there was still a stacking of *tube worms* and *macroalgae* during one month of immersion of the ash mortar and control which was progressively followed by *bryozoans* in the second and third months of immersion and increased every month until the sixth immersion. It was also revealed that there was a decrease in the diversity found in the ash mortar, although not too significant, which is assumed to contain the element barium where the concentration of barium is relevant to the environment which is known to be toxic, such as to Mytilus californianus larvae, which will be disrupted during *shell* formation and changes in pH and other parameter that will inhibit the attachment of macrofouling.

Marine organisms have a certain influence on the dosage value of wash received by each biota. An increased level of diversity in the mortar control was assumed from the study. The phenomenon of biofouling attachment is accumulated with nutrients from ordinary concrete surfaces, such as the increase of biofouling attachment on concrete surfaces, because concrete surfaces trigger food supply and attract organisms to attach [13].

3.2 Artificial reef test experiment

Artificial reefs (Ars) were originally used to increase fisheries production, but now their functions have been expanded to manage erosion in coastal areas, protect marine habitat, rehabilitate hard corals and ecological studies [14]. Artificial reef in Trenggalek water, 8 type of macrofouling were found during observations on 22 artificial reef media, such as *tubeworms, barnacles, hermit crab, bryozoans, green algae, tunicates, hydroids, brown algae, sponges, and red algae*. It's assumed that the fly ash – bottom ash concrete substrate

also depends on the parameters around it. As *tube worms* are affected by temperature and salinity [15].

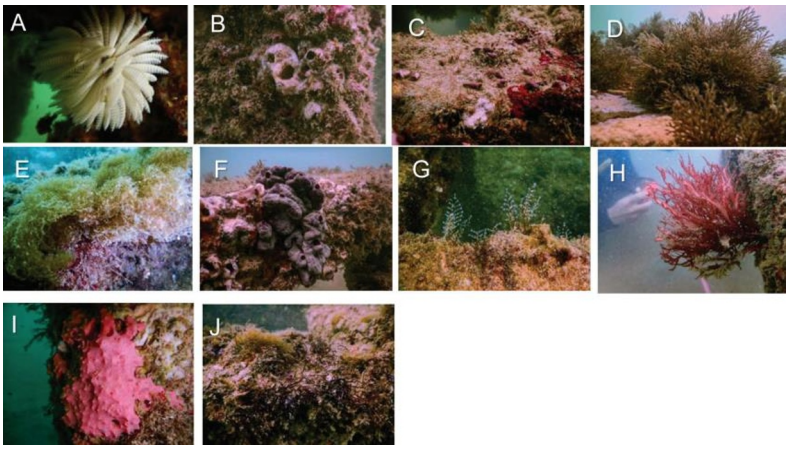

Figure. 2. Variates macrofouling, A : Tubeworm ; B : Barnacle ; C : Hermit ; D : Crab ; E : Green algae ; F : Ascidians ; G : Hydroids ; H : Brown algae ; I : sponge ; I : Red algae

Water depth, in addition to ambient water parameters, is also influential in knowing wave action currents can increase the spread of fouling organisms. Previous research suggested that the elemental composition of ash contained in artificial coral reef materials during immersion in seawater did not show any significant changes [16]. Only Pb concentration decreased significantly, this study also explained that the attachment of attached biota caused changes in pH and oxygen due to the dissolution of Calcium (Ca). There was a decrease in Zinc (Zn) and Timbal (Pb) levels of coal ash after 1,5 years at sea and also some enhancement of Mangan (Mn) levels in previous studies. Mn enrichment at the surface, caused by localized deposition of insoluble Mn due to changes in pH and oxygen in the microenvironment at the surface of artificial reefs, has also been found in previous studies. However, the occurrence of changes in the hydroid species *Aglaophenia pluma* decreased over time. The concentration decreased over time which is opposite to the expected trend if bioaccumulation has occurred. Because in this study the age of the biota sample was not estimated, and it was assumed that the observed compositional changes might be due to changes in physiological state.

Table 2. Average heavy metal concentration

% CFA	Hg	Cd	Cu	Zn (ppm)	Cr	Pb	Mn	Fe (wt%)	Al
100 m	0.29	0.64	83	83	172	138	311	3.21	14.9
cv	3	8	4	1	2	10	1	2	10
80 m	0.14	0.36	49	72	98	66 (45)	254 (291)	2.24	7.9
cv	26	39	8	25	19	34 (10)	9 (2)	8	13
60 m	0.12	0.36 (0.26)	41	63	82	51 (31)	237	1.94 (1.67)	7.2 (5.7)

cv	33	8 (23)	10	22	16	40 (13)	8	4 (8)	15 (12)
40 m	0.071	0.23	30	48	59	35 (24)	191	1.56 (1.11)	5.1 (3.5)
cv	37	40	18	35	4	10 (23)	7	15 (9)	30(5)
0 m	0.014	0.15	14	39	24	32 (6.0)	115 (134)	0.54	0.96
cv	46	91	29	51	21	35 (8)	12 (11)	28	18

4 Conclusion

Fly ash and bottom ash are power plant wastes that have potential as substrates in concrete and artificial reef applications, but face biofouling challenges. Biofouling is the attachment of microorganisms (microfouling) and macroorganisms (macrofouling), occurring on the surface of substrates in the marine environment. This process is influenced by the chemical content of the substrate, such as barium which is toxic, as well as environmental factors such as pH and nutrients. Fly ash contains compounds such as SiO_2, Al_2O_3, and CaO with pozzolanic properties which are beneficial in binding and strengthening materials, bottom ash, characterized by a coarser grain that resembles sand, contains similar elements but in different concentrations. However, both types of ash also contain naturally occurring radioactive elements (NORM) that will negatively impact marine ecosystems, affecting organisms such as molluscs and microalgae found in the marine food chain. It is necessary to maximize their potential use and minimize their impact, requiring wise management.

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